Polymerization of vinyl acetate using visible radiation and a dye-reducing agent sensitizer: 1. Pre-initiation and initiation reactions involving ethyl eosin and ascorbic acid*

D. R. Pemberton
Napier College, Colinton Road, Edinburgh EH10 5DT, UK

and A. F. Johnson
University of Bradford, Bradford, W. Yorkshire BD7 1DP, UK
(Received 11 October 1982; revised 17 June 1983)

The ethyl eosin/ascorbic acid photosensitized polymerization of vinyl acetate in aqueous methanol using visible radiation has been shown to occur by a mechanism in which polymerization occurs after an induction period during which the dye colour fades completely. During this period the dye is excited by incident radiation and reacts with the reducing agent to form free radical species. These react with dissolved oxygen to produce hydrogen peroxide. It is shown that the polymerization of vinyl acetate is initiated by products of the reaction between ascorbic acid and hydrogen peroxide.
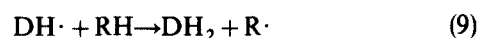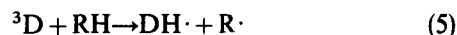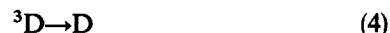
INTRODUCTION

Many different classes of photo-initiator have been described in the literature and the subject of photochemically initiated polymerization has been extensively reviewed[1,2].

The majority of the systems which have been reported use ultraviolet radiation to excite reaction. Some attempts have been made to find photosensitizer systems which will give rise to the polymerization of vinyl monomer using visible light. Such systems would have many advantages; they would allow the use of inexpensive light sources with glass rather than silica reaction vessels and, more particularly, would allow 'in depth' cure of aromatic monomers which themselves absorb near-ultraviolet radiation. From a practical point of view the advantages to be gained of using visible radiation to cure conventional styrene monomer bases polyester resins are obvious. Dye-reducing agent couples and visible light sources have found application in photography[3-5], in Holographic recording[6], for the preparation of gels for electrophoresis[7,8], for grafting acrylic polymers to fibres[9,10], and for cross-linking polyester resins[11].

Many fundamental investigations have been made into the reactions of dyes[12] induced by electromagnetic radiation and the following general reaction scheme is representative of the main reactions to be observed when xanthene dyes are irradiated in the presence of a reducing agent[13,14]:

$$D + h\nu \rightarrow {}^1D \qquad (1)$$

$$^1D \rightarrow {}^3D \qquad (2)$$

$$^1D \rightarrow {}^3D \qquad (3)$$

$$^3D \rightarrow D \qquad (4)$$

$$^3D + RH \rightarrow DH\cdot + R\cdot \qquad (5)$$

$$^3D + D \rightarrow 2D \qquad (6)$$

$$^3D + DH_2 \rightarrow D + DH_2 \qquad (7)$$

$$2DH\cdot \rightarrow DH_2 + D \qquad (8)$$

$$DH\cdot + RH \rightarrow DH_2 + R\cdot \qquad (9)$$

In this scheme D is the dye, ^1D the first excited singlet state, ^3D the triplet, $DH\cdot$ the semiquinone dye, DH_2 the leuco dye and RH the reducing agent. Similar schemes have been proposed for other classes of dye[15-17].

Despite the many investigations made into the reactions of irradiated dyes, and the many studies of polymerization sensitized by such systems, there is no agreement on the mechanism of initiation of polymerization. The importance, or otherwise of oxygen in the reaction mechanism is a key issue and has been the root of most disagreement in published work.

Yang and Oster[18] suggested that the initiation of vinyl monomer polymerization is by hydroxyl radicals produced by the reaction of leuco dye with dissolved oxygen whereas Delzenne et al.[19] proposed that initiation occurs through a redox system consisting of hydrogen peroxide and reducing agent, the peroxide being generated by re-oxidation of leuco and semiquinone dye by dissolved oxygen.

Takakura and Takayama[20], however, suggested initiation takes place by a photoredox process between photo-reduced dye and peroxidic compound produced during an induction period which preceeds

---

* Work carried out at: Norwich City College, Ipswich Road, Norwich, UK

polymerization. Many investigators consider oxygen to be unimportant in the initiation process[21-24].

Most reported work has been carried out in aqueous media. The few investigations carried out in bulk monomer or organic media have generally shown that the rates of polymerization are very slow and the yields of polymer are low[23,25].

Here, the reactions which lead to the eventual initiation of vinyl acetate polymerization are examined using ethyl eosin (1) and ascorbic acid (2) as the dye-reducing agent couple.
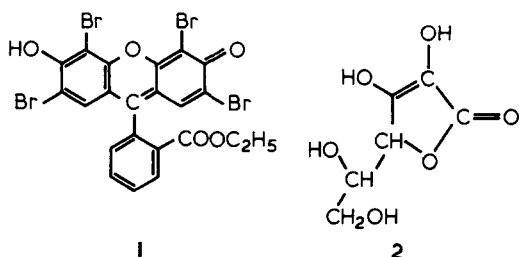
EXPERIMENTAL

Materials

Ascorbic acid (BDH Ltd., AR grade) was used as received. Ethyl Eosin (Hopkins and Williams Ltd., Revector Stain) was recrystallized twice from ethanol. Methanol (East Anglian Chemicals Ltd., AR grade) was dried over molecular sieve and fractionally distilled. Solutions of ascorbic acid in methanol were stored for no longer than 5 days at −5°C in the dark. Vinyl acetate (BDH Ltd.) was fractionally distilled twice under nitrogen. The purified monomer was stored over calcium hydride and sodium metabisulphite at −5°C in the dark. It was redistilled immediately prior to use.

Procedure

Polymerization rates were measured by dilatometry. The dilatomer was constructed of precision bore capillary of 2 mm i.d. attached to a cylindrical glass reaction vessel (diameter 5 cm, thickness 1 cm). The vessel was suspended in a thermostatically controlled water bath at 30(±0.01)°C, and irradiated using a collimated light beam from a 150 W (240 V) tungsten halogen lamp operated from a stabilized d.c. power supply. Infrared ($\bar{v} < 14\,000$ cm^{-1}) and ultraviolet ($\bar{v} > 25\,000$ cm^{-1}) radiation was removed from the radiation sources by filters. The same vessel was also used for other photochemical measurements.

Changes in dye concentration with time at different levels of incident light intensity were measured at 30°C by removing the cell from the water bath at intervals and observing the absorbance at 18900 cm^{-1} with a Unicam SP800 recording spectrophotometer. The Beer–Lambert Law was found to hold at this wavelength over the dye concentrations used in this work.

The incident light was varied by inserting blackened metal gauzes in the light beam and the intensity measured by ferrioxalate actinometry[26]. Solutions were deoxygenated by passing a stream of oxygen-free nitrogen through them for 20 min.

Polarograms were obtained using a Cambridge Recording Polarograph. In experiments where changes in hydrogen peroxide concentration with time were monitored, samples were removed from the reaction vessel under an atmosphere of nitrogen to avoid contamination of the reaction mixture with air.

E.s.r. spectra were obtained with a Varian E3 e.s.r. spectrophotometer using a 100 kHz field modulation and fitted with a sample temperature control unit.

Solutions were placed in a flat-faced quartz cell which was inserted into the cavity of the instrument and were irradiated using the light source described.

RESULTS

Vinyl acetate polymerization

Initially, attempts were made to polymerize vinyl acetate in dimethylformamide and methanol as solvents under aerobic conditions using ethyl eosin with ascorbic acid as initiator. No measurable polymerization occurred on irradiation, although the colour of the dye faded with time. However, when a small amount of water was added to the methanolic solution, a rapid polymerization reaction occurred when using similar incident light intensities to those used previously. The addition of water to the dimethylformamide solution gave only a very slow polymerization reaction. In both solvents, polymerization commenced after a marked induction period. During this period the colour of the dye faded completely and did not reappear if irradiation was discontinued. Once polymerization had started, irradiation had no effect on the reaction, i.e. it proceeded at similar rates in the dark to that observed if irradiation was continuous throughout polymerization. Examples of the monomer conversion with time for methanolic solutions are shown in Figure 1.

Spectrophotometric investigation of the photoinitiated reaction between ethyl eosin and ascorbic acid in methanol

Deoxygenated solutions. In the initial stages of the reaction the rate of fading of the dye was proportional to the quantity of light absorbed as shown by the
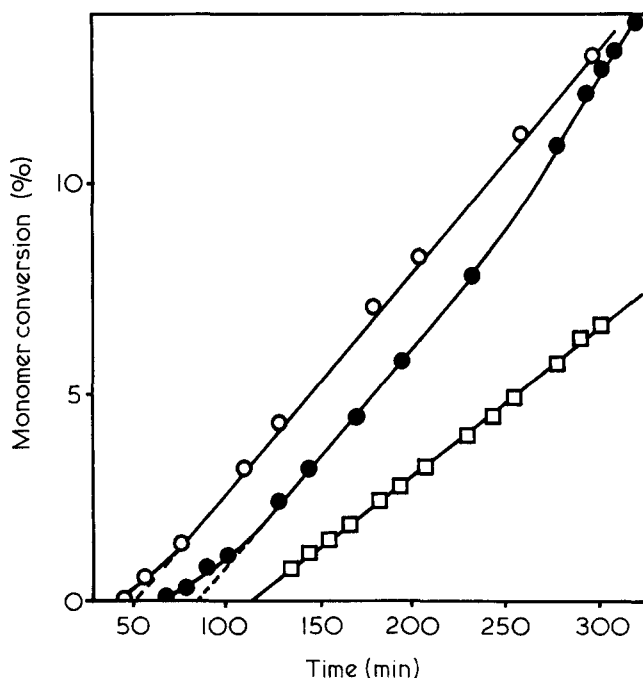

Figure 1 Monomer conversion – time curves for different ascorbic acid concentrations in the photo-polymerization of vinyl acetate in methanolic solution. [Ethyl eosin] = 2.27 × 10^{-5} mol dm^{-3}; [vinyl acetate] = 2.17 mol dm^{-3}; [water] = 4.44 mol dm^{-3}; ascorbic acid concentrations × 10³/mol dm^{-3}, □, 2.44; ●, 4.87; ○, 19.73

rectilinearity of plots of log $(e^{\alpha cd} - 1)$ against time *(Figure 2)*, where d is the path length of the system and c is the concentration of dye of molar Napierian absorptivity α. As the reaction proceeds, the plots deviate from rectilinearity for lower light intensities. For the initial part of the experiment though, a plot of rate of reaction against incident light intensity is rectilinear *(Figure 3)* within experimental error, confirming the applicability of first-order kinetics to the initial rate.

The rate of fading of the dye was also related to the concentration of ascorbic acid *(Figure 4)* for solutions in which the ascorbic acid concentration was less than 4×10^{-3} mol dm^{-3}. The addition of water or vinyl acetate had little effect on the rate of reaction. A solution of ethyl eosin in methanol containing no added reducing agent faded extremely slowly.

Air-saturated samples. A similar series of experiments to those described for deoxygenated solutions were carried out in which air was bubbled through the solutions for a short period before irradiation.
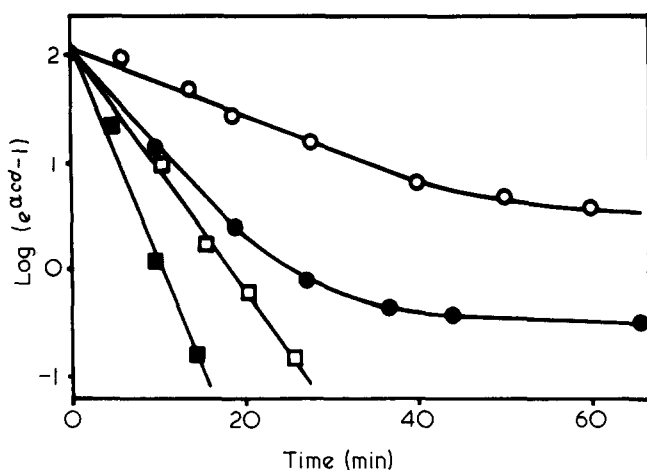

Figure 4 Photoreduction of ethyl eosin in methanolic solution at various ascorbic acid concentrations. [Ethyl eosin] = 2.27×10^{-5} mol dm^{-3}; [water] = 4.44 mol dm^{-3}; ascorbic acid concentrations $\times 10^4$/mol dm^{-3}: ●, 0.0; ○, 3.9; ■, 5.9; □, 9.8; ▲, 39.2; △, 196.0

Figure 2 Photoreduction of ethyl eosin in methanolic solution at various light intensities. [Ethyl eosin] = 2.27×10^{-5} mol dm^{-3}; [ascorbic acid] = 9.82×10^{-4} mol dm^{-3}; [water] = 4.44 mol dm^{-3}. Relative light intensities: ○, 0.12; ●, 0.26; □, 0.48; ■, 1.0

Figure 5 Photoreduction of ethyl eosin in air saturated methanolic solution at various water concentrations. [Ethyl eosin] = 2.27×10^{-5} mol dm^{-3}; [ascorbic acid] = 19.6×10^{-4} mol dm^{-3}; water concentration (mol dm^{-3}): ●, 4.4; □, 11.1; ■, 22.2; △, 44.4; ○, 0.0

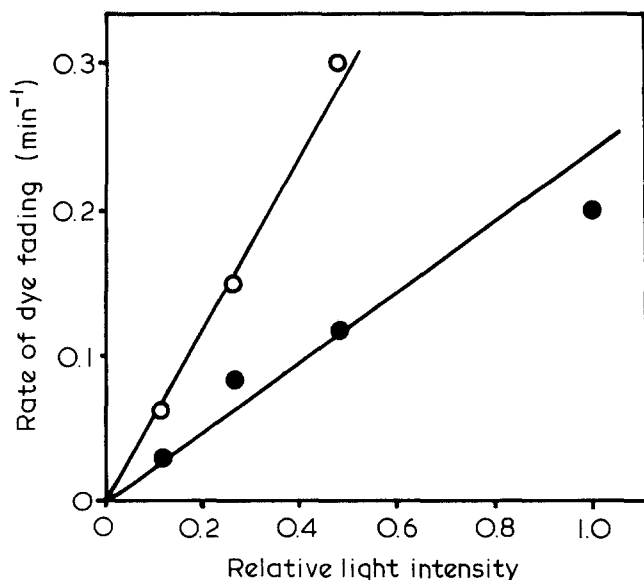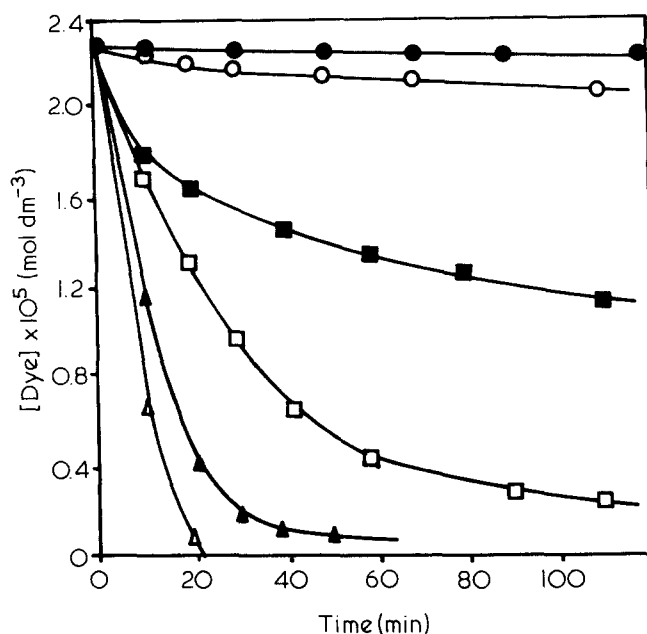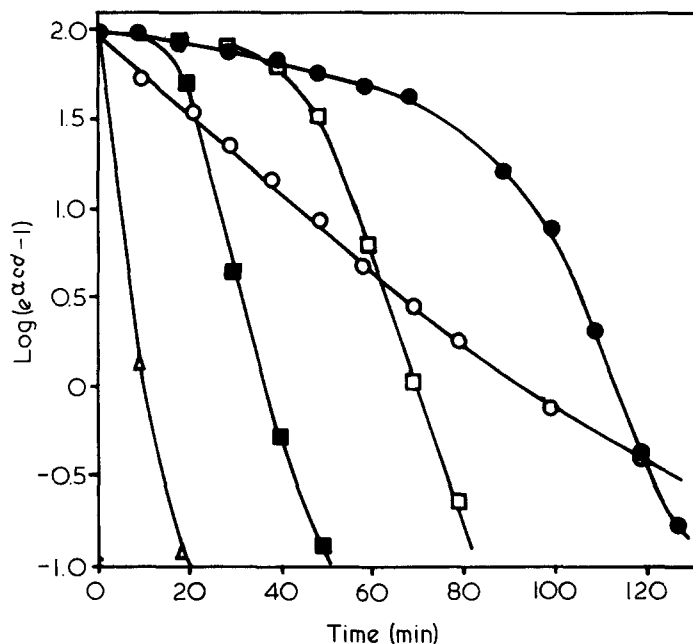**Figure 3** Effect of light intensity on rate of initial dye fading reaction. Ascorbic acid concentrations: ○, 39×10^{-4} mol dm^{-3}; ●, 9.8×10^{-4} mol dm^{-3}

Under these circumstances a solution containing no reducing agent showed no measurable fading after several hours irradiation. In solutions containing reducing agent and also some water there was a distinct induction period at low water concentrations during which the dye faded very slowly, followed by a rapid fading reaction the rate of which was relatively insensitive to the initial water concentration *(Figure 5)*. In solutions with a high ascorbic acid concentration, or containing a high proportion of water, this induction period was short or non-existent. At very low ascorbic acid concentrations the acceleration in

the reaction rate was non-existent or fading of the dye colour was incomplete (*Figure 6*). A decrease in the light intensity leads to a prolongation of the induction period (*Figure 7*).

During irradiation of the deoxygenated sample it was noted that whilst the peak at 18900 cm^{-1} decreased in the early part of the experiment a weak band appeared at $\approx$ 25000 cm^{-1} (*Figure 8*). On prolonged irradiation that absorption also decreased. With air saturated solutions, the change in the weak absorption at 25000 cm^{-1} was not as marked, but an increase in adsorption in this region
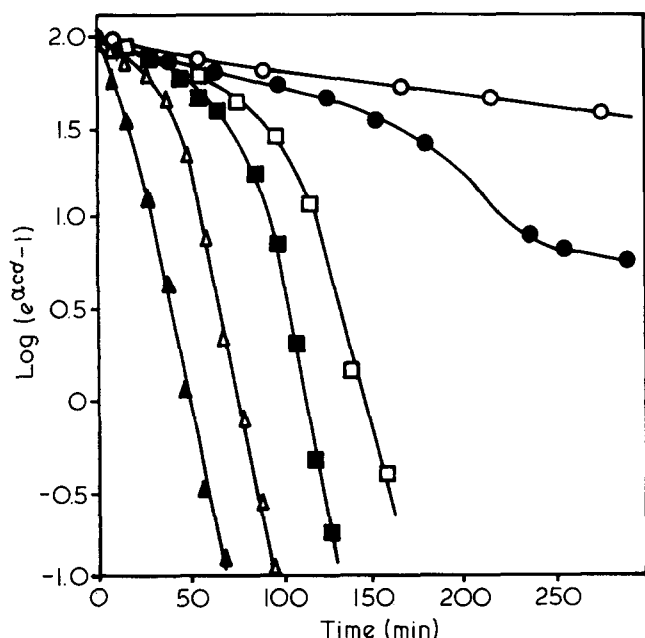

Figure 8 Changes in the spectrum of ethyl eosin in methanolic solution on irradiation in the presence of ascorbic acid. [Ethyl eosin] = 2.27 × 10^{-5} mol dm^{-3}; [ascorbic acid] = 19.6 × 10^{-4} mol dm^{-3}; [water] = 4.44 mol dm^{-3}. (——) Before irradiation; (———) irradiated for 8 min; (·····) after standing in the dark 40 min following 8 min irradiation

Figure 6 Photoreduction of ethyl eosin in air-saturated methanolic solution at various ascorbic acid concentrations. [Ethyl eosin] = 2.27 × 10^{-5} mol dm^{-3}; [water] = 4.44 mol dm^{-3}; ascorbic acid concentrations × 10^4 mol dm^{-3}: ●, 9.8; ○, 13.7; □, 15.7; ■, 19.6; △, 39.3; ▲, 196.0

Figure 9 (a) Polarogram of hydrogen peroxide (10^{-3} mol dm^{-3}) in aqueous methanol. (b) Polarogram given by irradiated reaction mixture. [Ethyl eosin] = 2.17 × 10^{-5} mol dm^{-3}; [ascorbic acid] = 1.96 × 10^{-3} mol dm^{-3}. Base electrolyte in both cases is 50% methanol, 50% water (vol/vol); potassium chloride (0.25 mol dm^{-3})
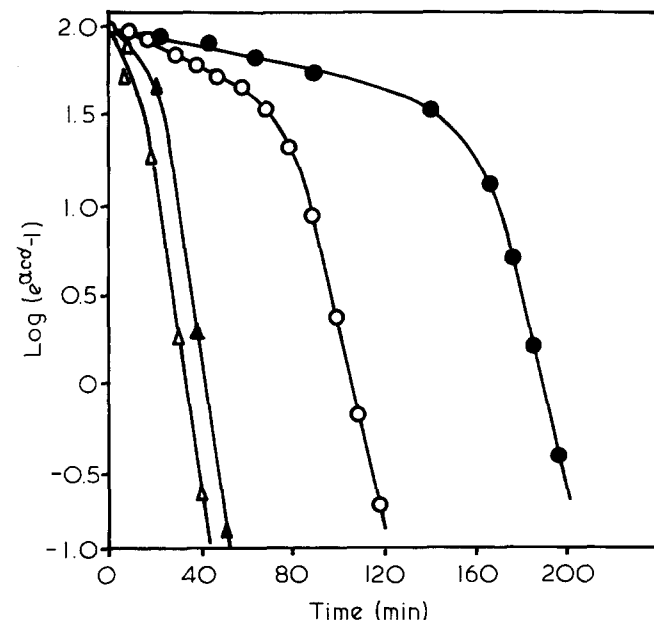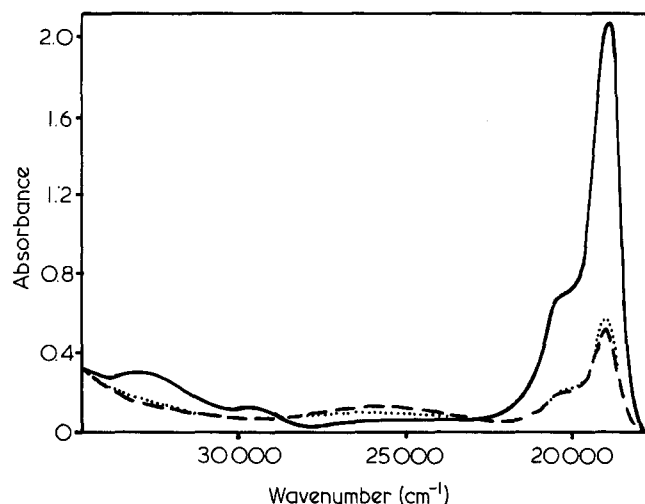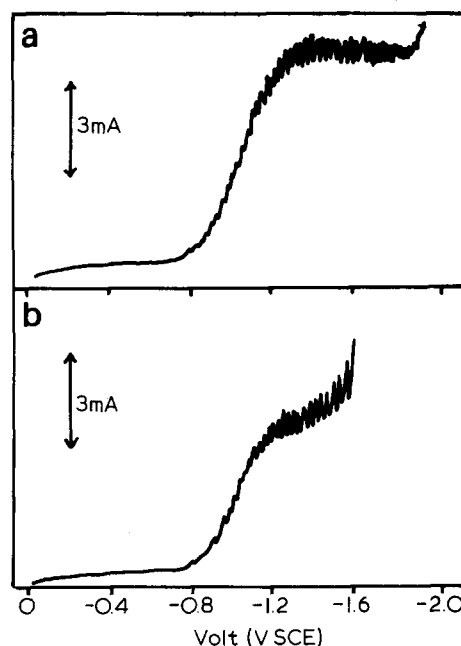
Figure 7 Photoreduction of ethyl eosin in air-saturated methanolic solution at various light intensities. [Ethyl eosin] = 2.27 × 10^{-5} mol dm^{-3}; [ascorbic acid] = 19.6 × 10^{-4} mol dm^{-3}; [water] = 4.44 mol dm^{-3}; relative light intensities: ●, 0.12; ○, 0.26; ■, 0.48; △, 1.0

was observed during the second fast decay phase of the reaction. The species responsible for this absorbance has not been identified but is probably an unstable reduction product of the dye, which readily decomposes on irradiation.

One reaction product which was clearly identified in all the experiments involving air saturated solutions was hydrogen peroxide. The main evidence for its presence is that: titanium (IV) sulphate gave a characteristic yellow colour on mixing with the reaction mixture; acidified potassium dichromate gave a blue ethereal layer when shaken with the reaction mixture; a characteristic polarogram was obtained (*Figure 9*).

Investigation of the dye/reducing agent/oxygen reaction by polarography

A quantitative investigation was carried out on the formation and subsequent reactions of the hydrogen peroxide by polarography. It was readily observed that irradiation of air-saturated methanolic solutions of dye and reducing agent produced a large, broad polarographic wave which was completely absent in the polarogram of the unirradiated mixture.

During the early part of the dye/reducing agent reaction in air-saturated solutions, hydrogen peroxide was produced at a steady rate, attaining a maximum concentration towards the end of the photo induced reaction, when the fast dye fading reaction occurs. A series of experiments was carried out in which the hydrogen peroxide concentration was measured at the point in the reaction sequence when the dye fading was almost complete, giving a measure of the maximum hydrogen peroxide concentration produced. Where low ascorbic acid concentrations were used, the dye colour was never completely discharged, and irradiation was continued for 400 min to ensure that no further reaction was occurring. The results show that the final hydrogen peroxide concentration is related to the ascorbic acid concentration present in the original mixture with approximately 0.5 mol of hydrogen peroxide being produced for every mol of ascorbic acid consumed (*Figure*
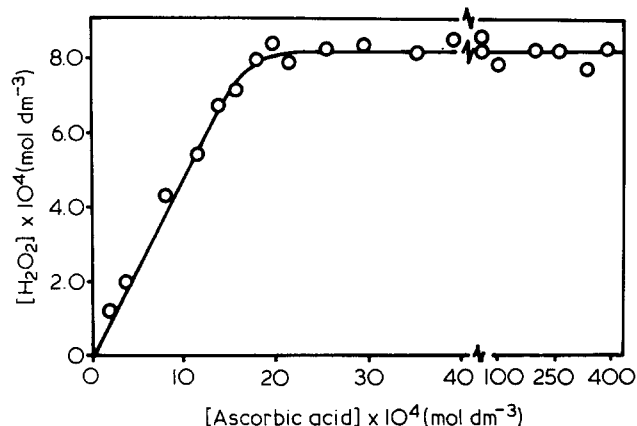
Figure 10 Hydrogen peroxide concentrations obtained in methanolic solution by irradiation of reaction mixtures containing different ascorbic acid concentrations. [ethyl eosin] $=2.27 \times 10^{-5}$ mol dm^{-3}; [water] $=4.44$ mol dm^{-3}

Table 1 Effect of ascorbic acid concentration on the rate of loss of hydrogen peroxide from irradiated reaction mixtures on standing in the dark. All solutions contained ethyl eosin 2.27×10^{-5} mol dm^{-3} and water, 4.44 mol dm^{-3} except where indicated

Initial ascorbic acid conc. $\times 10^4$ (mol dm^{-3})	Ascorbic acid conc. at end of photoinit. reaction $\times 10^4$ (mol dm^{-3}) (A)	Rate of hydrogen peroxide decomposition $\times 10^6$ (mol dm^{-3} min^{-1}) (R)	$\dfrac{A^{1/2}}{R} \times 10^6$
392.8	376.8	1.65	8.5
294.6	278.6	1.41	8.4
196.4	180.4	0.94	7.0
98.2	82.2	0.94	10.3
39.3	23.3	0.48	8.7
11.76	0	b	—
196.4	180.4[a]	b	—
58.2	43.9[a]	c	—

[a] No water
[b] No measurable reaction after 8 hours
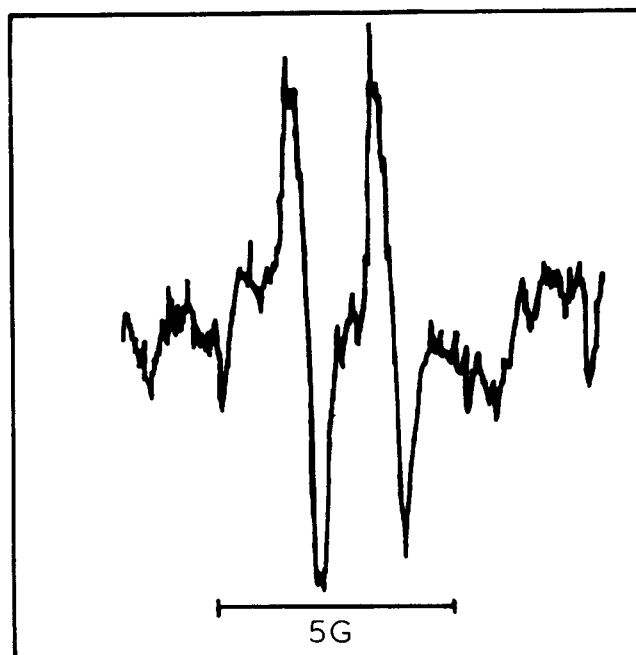[c] Too slow a reaction for accurate measurement

Figure 11 E.s.r. spectrum of methanolic solution of ethyl eosin after 10 min irradiation; 2.3×10^{-5} mol dm^{-3}; ascorbic acid, 9×10^{-4} mol dm^{-3}

10). At higher ascorbic acid concentrations the final peroxide concentration is independent of ascorbic acid.

When the reaction mixture was allowed to stand in the dark, the hydrogen peroxide concentration slowly decreased except in those cases where the initial ascorbic acid concentration had been so low that the colour of the dye was either not fully discharged or was only discharged by prolonged irradiation (*Table 1*).

E.s.r. spectroscopy

A brief e.s.r. spectroscopic analysis was attempted on the reaction mixture to detect and, if possible, identify any free radical species involved in the dye fading reactions.

A methanolic solution containing ethyl eosin $(2.3 \times 10^{-5}$ mol dm$^{-3})$, and ascorbic acid $(9 \times 10^{-4}$ mol dm$^{-3})$ was placed in the spectrometer cell at room temperature and irradiated for 10 min after which the e.s.r. spectrum scanned. A weak doublet $(a = 1.6$ G) appeared during radiation (*Figure 11*) but the signal collapsed immediately irradiation was stopped. The experiment was repeated using a more concentrated solution (ethyl eosin; 6×10^{-4} mol dm^{-3}: ascorbic acid; 1.8×10^{-3} mol dm^{-3}) under anaerobic conditions at $-35°C$. After 40 min irradiation, the spectrum consisted of a 1:2:1 triplet $(a = 3.3$ G) with each of the lines further split into triplets (*Figure 12*). A similar, but weaker spectrum was obtained with similar concentration solutions at room temperature but the signal collapsed immediately irradiation was stopped.

The weak doublet observed in the first experiment (*Figure 11*) can probably be attributed to the semi-oxidized form of ascorbic acid (**3**).
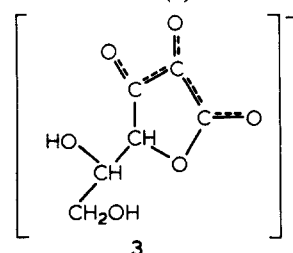
which has been reported previously and is known to produce a doublet ($a = 1.7$ G) similar to that observed in this work[27,28]. The triplet appearing after longer periods of irradiation is similar to that obtained by Leaver[29] in the reduction of eosin by indoleactic acid in methanolic solutions. Leaver attributes the spectrum to the semiquinone dye (4).

4
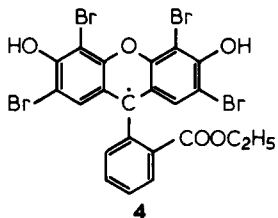
The appearance of the doublet in the early part of the reaction, which is later covered by the stronger triplet signal suggests that the semiquinone dye reacts rapidly with oxygen, its concentration only increasing when oxygen has completely reacted or is removed from the system. As the signals from both 3 and 4 collapsed as soon as irradiation was discontinued, it is unlikely that either species is responsible for the initiation of the polymerization reaction, for polymerization continued for long periods after irradiation at rates similar to those when the system was irradiated.

DISCUSSION

Dye/reducing agent/oxygen reaction

The results of the experiments under anaerobic conditions are similar to those obtained by other investigators for reactions of xanthene dyes with reducing agents in aqueous solutions[12,13,29]. The reaction scheme given earlier (equations (1)–(9)) leads to an expression for the initial rate of the dye fading reaction of the form:

$$\text{Rate } (R) = \frac{I_{ab}[RH]}{\gamma + \beta[RH]}$$

where I_{ab} is the intensity of the light absorbed, γ and β are constants. The expression predicts that a plot of $1/R$ against $1/[RH]$ should be rectilinear if the initial rate is taken so that I_{ab} is kept constant. This was found to hold for low concentrations of ascorbic acid (*Figure 13*)
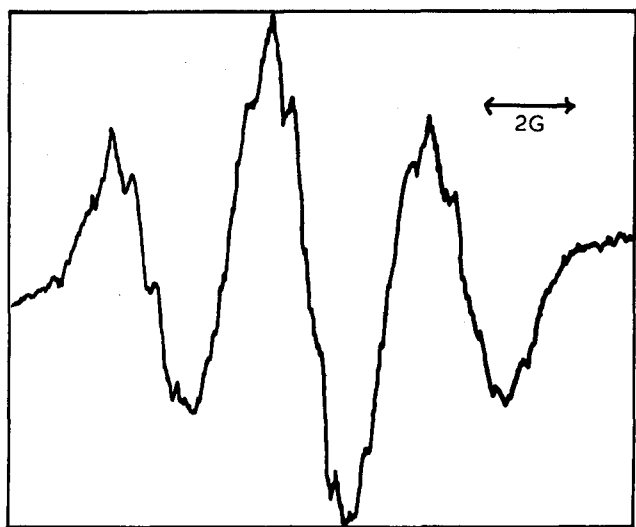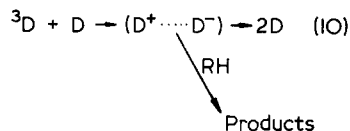
although the plot is curved for higher ascorbic acid concentrations. This is similar to the findings of Oster and Adelman[13].

Deviations from rectilinearity of plots of $\log (e^{xcd} - 1)$ against time at lower light intensities and also at lower ascorbic acid concentrations were ascribed by Ohno *et al.*[30] to the effect of the second-order reaction:

$$^{3}D + D \longrightarrow (D^{+}\cdots D^{-}) \longrightarrow 2D \quad (10)$$
$$\searrow_{RH}$$
$$\downarrow$$
$$\text{Products}$$

although this does not fully explain the effects observed in this work.

Under aerobic conditions, the dye fading reaction is retarded. Imamura and Koizumi[14] in a study of the photobleaching of ethanolic eosin in the presence of oxygen concluded that oxygen reacts with the semiquinone dye, a reaction that leads to the reformation of the dye:

$$DH\cdot + O_2 \rightarrow D + HO_2\cdot \quad (11)$$

On the assumption that the rate of reaction (11) is much faster than the other reactions involving the semiquinone dye (8 and 9), then the reaction scheme leads to an expression for the initial rate of dye fading of the form:

$$\text{Rate } (R) = \frac{I_{ab}[RH]}{[O_2](\gamma^1 + \beta^1[RH])}$$

where γ^1 and β^1 are constants. Hence, the initial reaction rate should be inversely proportional to the oxygen concentration and again, a plot of $1/R$ against $1/[RH]$ should be rectilinear (*Figure 13*). No simple relation was found between the initial ascorbic acid concentration or the light intensity and the length of the induction period before the onset of the fast dye fading reaction.

In solutions containing low initial ascorbic acid concentrations, all the ascorbic acid is used up in reacting with oxygen, and the final fast dye fading reaction is non-existent or incomplete (*Figure 6*).

The $HO_2\cdot$ radicals produced as shown in equation (11) react further to produce hydrogen peroxide by one or

Figure 12 E.s.r. spectrum of methanolic solution of ethyl eosin (sodium salt) after 40 min irradiation at $-35°C$: 6×10^{-4} mol dm^{-3}; ascorbic acid, 1.8×10^{-3} mol dm^{-3}
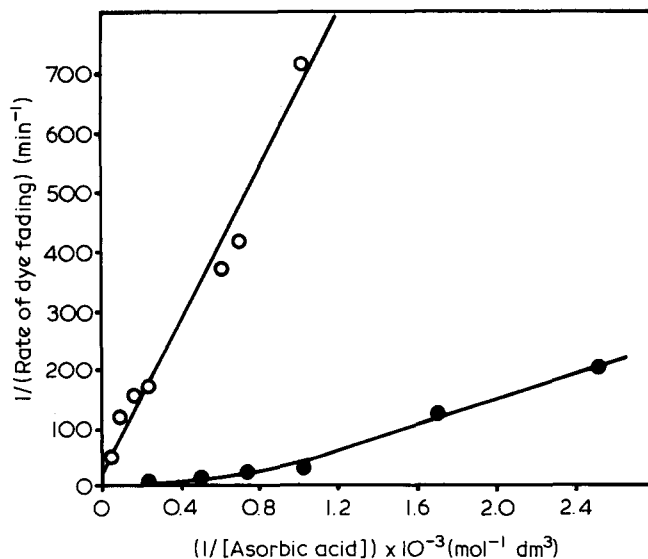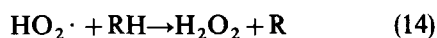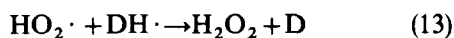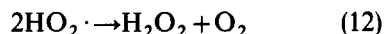
Figure 13 Plot of reciprocal of rate of initial dye fading reaction against reciprocal of ascorbic acid concentration. $\bigcirc$, aerobic solutions; $\bullet$, anaerobic solutions

more or several routes (equations (12)–(14)):

$$2HO_2 \cdot \rightarrow H_2O_2 + O_2 \qquad (12)$$

$$HO_2 \cdot + DH \cdot \rightarrow H_2O_2 + D \qquad (13)$$

$$HO_2 \cdot + RH \rightarrow H_2O_2 + R \qquad (14)$$

In methanolic solutions containing no water the course of the reaction must be different (*Figure 5*). Hydrogen peroxide was formed when water was not present but in lower concentrations, and the processes are clearly similar. The results suggest that in the absence of water reaction (equation (11)) is occurring at a slower rate.

Because the hydrogen peroxide concentration decreases on standing in these solutions in which excess ascorbic acid is present, it can be inferred that a redox reaction is occurring between the hydrogen peroxide and ascorbic acid remaining after the initial photo-induced reaction. Assuming that approximately 0.5 mol of hydrogen peroxide are produced for every mol of ascorbic acid used in the initial reaction it is estimated that the amount of ascorbic acid used up in this reaction is approximately 1.7×10^{-3} mol dm^{-3}. Subtracting this amount from the initial ascorbic acid concentrations given in *Table 1* gives an estimate of the ascorbic acid concentration at the start of the decline in peroxide concentration, and it appears that the initial rate of disappearance of hydrogen peroxide is approximately proportional to the square root of the ascorbic acid concentration.

The oxidation of ascorbic acid by hydrogen peroxide has been the subject of numerous studies[31–33], and many species have been shown to catalyse the reaction, but few studies have been made on the uncatalysed reaction, although it has been reported that hydrogen peroxide and ascorbic acid will react together slowly in the absence of a catalyst[31,32]. The reaction has been shown to involve a free radical mechanism, with the semi-reduced form of ascorbic acid being produced as an intermediate. It has also been established that the species which undergoes oxidation to this radical is the mono-ion of ascorbic acid, so that the first stage of the reaction mechanism must be ionization of the ascorbic acid molecule[31]:
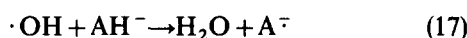
$$AH_2 + H_2O \rightleftharpoons AH^- + H_3O^+ \qquad (15)$$
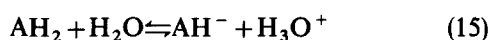
where AH_2 represents the ascorbic acid.

In the absence of a catalyst the most likely oxidation step will be direct reaction with hydrogen peroxide:

$$AH^- + H_2O_2 \rightarrow A^{\overline{\cdot}} + H_2O + \cdot OH \qquad (16)$$
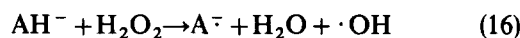
where $\cdot A^-$ is the semi-reduced form of ascorbic acid. The $\cdot OH$ radicals produced will then react with ascorbate ions:

$$\cdot OH + AH^- \rightarrow H_2O + A^{\overline{\cdot}} \qquad (17)$$

The hydroxyl radicals are more reactive than the semi-reduced ascorbate radicals and will be removed quickly by reaction (17) so that the most likely termination reaction is:

$$2A^{\overline{\cdot}} \rightarrow A + A^{2-} \qquad (18)$$

Where A represents a dehydroscorbic acid.

Assuming a reaction mechanism consisting of steps (15)–(18) and applying the steady-state approximation, and assuming that the only acid present in the system is ascorbic acid, it can be shown that the rate of reaction is given by:

$$\frac{-d[H_2O_2]}{dt} = k_{16} K_A [H_2O_2][AH_2]^{0.5}[H_2O]^{0.5}$$

where K_A is the first acid dissociation constant for ascorbic acid, and k_{16} is the rate constant for reaction (16). This equation is in agreement with the observed dependence of the rate of loss of peroxide on ascorbic acid concentration and it also shows the importance of water in the reaction.

The occurrence of the hydrogen peroxide/ascorbic acid redox reaction following the photo-initiated reaction sequence explains the continuation of the polymerization reaction after the termination of irradiation. The hydrogen peroxide/ascorbic acid system has been shown to initiate the polymerization of vinyl acetate[34].

REFERENCES

1 Oster, G. and Yang, N. L. *Chem. Rev.* 1968, **68**, 125
2 Ledwith, A. *Pure Appl. Chem.* 1977, **69**, 431
3 Oster, G. *Photographic Sci. Eng.* 1960, **4**, 237
4 Brault, R. G., Jenney, J. A., Margerum, J. D., Miller, L. J. and Rust, J. A. *Image Technology*, 1971, April/May, 13
5 Rust, J. B., Miller, L. J. and Margerum, J. D. *Polym. Eng. Sci.* 1969, **9**, 40
6 Sugawara, S. *Rev. Elect. Commun. Lab.* 1976, **301**, 24
7 Davis, B. J. *Ann. New York Acad. Sci.* 1964, **121**, 404
8 Needles, H. L. 'Symp. Photochem. Macromol. 129', (Ed. Reinisch), Plenum, New York, 1969
9 Needles, H. L. and Sarsfield, L. J. *Appl. Polym. Symp.* 1971, **18**, 569
10 Nagabhushanan, T. and Santappa, M. *J. Polym. Sci. Part A-1* 1972, **10**, 1511
11 Takimota, Y., Hamada, K., Ayabu, G. and Nogochi, M. *Chem. Abstr.* 1967, **67**, 91356
12 Koizumi, M. and Usui, Y. *Mol. Photochem.* 1972, **57**, 4
13 Oster, G. and Adelman, A. H. *J. Am. Chem. Soc.* 1956, **78**, 913
14 Imamura, M. and Koizumi, M. *Bull. Chem. Soc. Jpn.* 1957, **29**, 899
15 Oster, G. and Wotherspoon, B. *J. Am. Chem. Soc.* 1957, **79**, 4836
16 Millich, F. and Oster, G. *J. Am. Chem. Soc.* 1959, **81**, 1357
17 Hardwick, R., *J. Phys. Chem.* 1962, **66**, 349
18 Yang, N. L. and Oster, G. *J. Phys. Chem.* 1970, **74**, 856
19 Delzenne, G., Dewinter, W., Toppet, S. and Smets, G. *J. Polym. Sci. Part A* 1964, **2**, 1069
20 Takakura, K. and Takayama, G. *Bull. Chem. Soc. Jpn.* 1965, **38**, 328
21 Watanabe, A. and Koizumi, M. *Bull. Chem. Soc. Jpn.* 1961, **34**, 1086
22 Sherriff, A. I. M. and Santappa, M. *J. Polym. Sci. Part A*, 1965, **3**, 3131
23 Maiti, S., Saha, M. K. and Palit, S. R. *Makromol. Chem.* 1969, **127**, 224
24 Chaberek, S. and Allen, R. J. *J. Phys. Chem.* 1965, **69**, 647
25 Simionescu, S. and Ungureanu, C. *Rev. Roumaine Chim.* 1968, **13**, 347
26 Hatchard, C. J. and Parker, C. H. *Proc. Roy. Soc. London Ser. A* 1956, **235**, 518
27 McAlpine, R. D. and Cocivera, M. *Can. J. Chem.* 1973, **51**, 1682
28 Steenken, S. and Olbrich, G. *Photochem. Photobiol.* 1973, **18**, 43
29 Leaver, I. H. *Aust. J. Chem.* 1971, **24**, 753
30 Ohno, T., Usui, Y. and Koizumi, M. *Bull. Chem. Soc. Jpn.* 1965, **38**, 1022
31 Grinstead, P. R. *J. Am. Chem. Soc.* 1960, **82**, 3464
32 Kremer, M. L. *Trans. Faraday Soc.* 1967, **63**, 1098
33 Pekkarinen, L. *Finn. Chem. Lett.* 1974, 233
34 Hashimota, K. and Sakuguci, Y. *Kobunshi Kagaku* 1963, **20**, 312