Dyes and Pigments **19** (1992) 235–247

The Role of Free Radical Transformation in the Photodegradation of Reactive Dyed Cellulosic Textiles

K. J. Sirbiladze,[a] I. Rusznák,[b,]* A. Víg,[b]
G. E. Krichevskiy,[c] O. M. Anysimova[c] & V. M. Anysimov[d]

[a]Technical University, Kutaisy, Georgia
[b]Department of Organic Chemical Technology, Technical University of Budapest,
H-1521 Budapest, PO Box 91, Hungary
[c]University for the Textile Industry, Moscow, Russia
[d]Institute of Physical Chemistry of the Academy of Sciences of the USSR, Moscow, Russia

(Received 14 January 1992; accepted 28 February 1992)

ABSTRACT

The role of radical reactions in the fading of reactive dyes and of reactive dyed cellulosics has been studied. Experimental evidence was obtained for radical formation, and for its role in the fading of reactive dyes. The proportional share of radical reactions in the total photodegradation was calculated. Stable free radicals could be detected in dyed cellulosic systems. An assumed mechanism of the combined radical process is also presented.

1 INTRODUCTION

It is known from numerous papers[1–6] that free radicals may be formed in the course of irradiation of dyed textiles within the range 250–500 nm. Free radicals may be generated from the fibre forming polymer and/or from small molecular compounds colouring, incrustating or soiling the fibre. Radical reactions may be initiated by these free radicals, leading to the destruction of the coloured system or dyestuff, respectively. Cellulosics irradiated by a mercury vapour lamp are the source of generation of free radicals having

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* To whom correspondence should be addressed.

Dyes and Pigments 0143-7208/92/$05.00

rather a long life time. The mechanism of this type of free radical generation has been explained by simultaneous splitting off of H-atoms from anhydroglucose units; C(V) atoms have been presumed to be the most probable sites of this process,[3] although other studies[4] assume that C(I), C(II), C(IV) and C(V) are equally possible sites. Japanese and Hungarian researchers have indicated that dyes might play the role of the radical initiator in the fibrous system.[5,6]

It has been demonstrated earlier[7] that the photodestruction of dyes in coloured textiles depends on two features, viz:

(a) the ability of the dyes to form free radicals, and
(b) the importance (proportion) of radical reactions in the complex process of photodestruction.

It can be concluded that free radical reactions play an important role in the photodecomposition of dye–polymer systems. No information is yet available as to the distribution of free radical reactions in the degradation processes. The object of this present study is to investigate this.

2 EXPERIMENTS IN LIQUID PHASE

2.1 Experimental

2.1.1 Theoretical considerations

Dyes were dissolved in a 10:1 mixture of isopropanol and water (Ip–W). The small amount of water improved the solubility of the dyes, while isopropanol did not form free radicals in the applied range of irradiation and also offered an easily split off hydrogen atom from the photoexcited dye molecule:

$$\left.\begin{array}{r} D + h\nu \rightarrow D^* \\ D^* + Ip\text{—}H \rightarrow Ip\cdot + DH\cdot \end{array}\right\}\text{initiation} \qquad \begin{array}{r}(1)\\(2)\end{array}$$

where D is the dye and D* is its excited form.

It has been previously demonstrated[8] in kinetic studies of fading that there is an initial slow first step, followed by a fast second one, if irradiation is carried out in the presence of dissolved oxygen in a sealed system. If, however, oxygen is not included in the solution, the initial fading is as fast as that in the second step of fading in the former system.

The next part of the radical process, including also an interaction between the free radicals formed and oxygen, is represented as follows:

$$\left.\begin{aligned} \mathrm{Ip}\cdot + \mathrm{O_2} &\rightarrow \mathrm{IpO_2^{\cdot}} && (3)\\ \mathrm{IpO_2^{\cdot}} + \mathrm{Ip{-}H} &\rightarrow \mathrm{Ip}\cdot + \mathrm{IpOOH} && (4) \end{aligned}\right\}\text{propagation}$$

$$\mathrm{D^*} + \mathrm{Ip}\cdot \rightarrow \text{decomposition of the dye} \qquad (5)$$

$$\left.\begin{aligned} \mathrm{Ip}\cdot + \mathrm{Ip}\cdot && (6)\\ \mathrm{IpO_2^{\cdot}} + \mathrm{IpO_2^{\cdot}} && (7)\\ \mathrm{Ip}\cdot + \mathrm{IpO_2^{\cdot}} && (8) \end{aligned}\right\} \rightarrow \text{termination}$$

Quadratic termination may be concluded from eqns (6)–(8).

2.1.2 *Materials and methods*

The dyes and auxiliary chemicals used in the liquid phase experiment are shown in Table 1.

In measuring the optical density, a UV-VIS spectrophotometer was used to follow the fading of the dissolved dyestuff as a function of the time of irradiation. A mercury vapour lamp was used for irradiation of the dye solution sealed in a quartz cuvette. The complete spectrum of the mercury vapour lamp (180–400 nm), as well as the 365–400 nm part, was used for the irradiation.

To obtain experimental evidence for the changes represented by eqns (3)–(8), a compound which readily formed radicals was added to the dye solution prior to its irradiation, viz. azo-bis-isobutyronitrile (AIBN). The dye used was Rhodamine 6G and Ip–W (10:1) was the solvent. This dye, selected for the preliminary experiment, was not a reactive dye but one known for its high sensitivity to fading. The experimental procedure was elaborated for preparing oxygen-free dye solutions. The wavelength range of the irradiation was 365–400 nm and its intensity could be adjusted by means of appropriate bronze sieves of different mesh structures. The original 100% light intensity could thus be reduced to 26·3% and 8·8%, respectively.

Further experiments were made with solutions of the reactive dyes No. **3** (**RD-3**) and No. **4** (**RD-4**) (Table 1), in Ip–W (10:1). Solutions of the above dyes were prepared in the presence and absence of AIBN, respectively. Irradiation of the AIBN containing solutions was carried out in the 365–400 nm range emitted by the mercury vapour lamp (first procedure). Solutions prepared without addition of AIBN were irradiated with the full spectrum (180–400 nm) of the emitted light (second procedure). The dye solutions were in sealable quartz cuvettes, excluding air from the system.

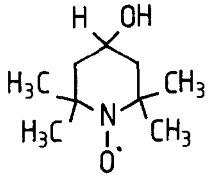
2.2 Results and discussion

When $-\ln D_t/D_0$ was plotted against t, a linear correlation was found for the various light intensities, with different slopes (D_0 was the initial optical

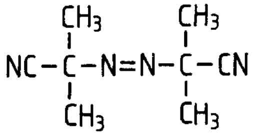
TABLE 1

Dyes and Chemicals Used in the Liquid Phase Experiments

1. 2,2,6,6-Tetramethyl-4-hydroxypiperidine-1-oxyl

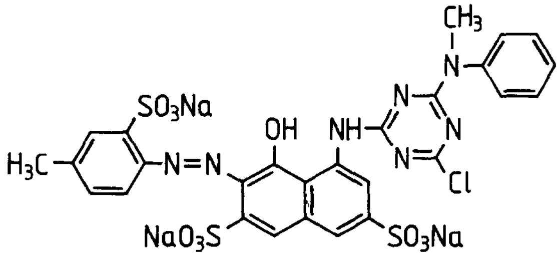


2. Azo-bis-isobutyronitrile (AIBN)

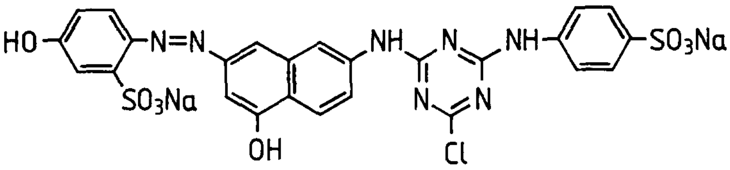


$$\mathrm{NC-\underset{CH_3}{\overset{CH_3}{C}}-N{=}N-\underset{CH_3}{\overset{CH_3}{C}}-CN}$$

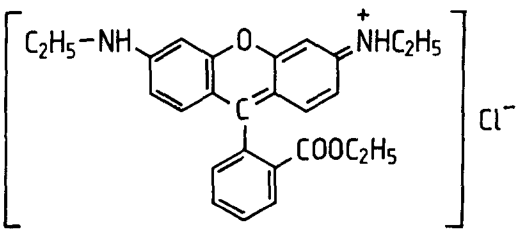
3. Reactive Brilliant Red 6B (Russian product)



4. Reactive Scarlet 2G (Russian product)



5. Rhodamine 6G



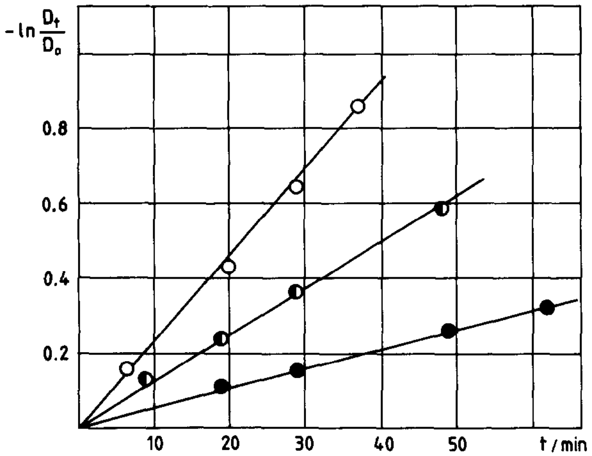


Fig. 1. Fading of Rhodamine 6G in oxygen-free 10^{-5} molar solution in Ip–W (10:1) in the presence of 3×10^{-2} mol litre^{-1} AIBN (first procedure). ○, 100% light intensity; ◐, 26·3% light intensity; ●, 8·8% light intensity.

density of the dye solution, whereas D_t was that after irradiation for t min) (Fig. 1).

The initial rate of fading (v) is represented by the slopes of the straight lines. A linear correlation between the square root of light intensity ($\sqrt{I}$) and the rate of fading is evidence for the quadratic termination of the radical process (Fig. 2).

Irradiation of dissolved **RD-3** and **RD-4**, using the first procedure, caused

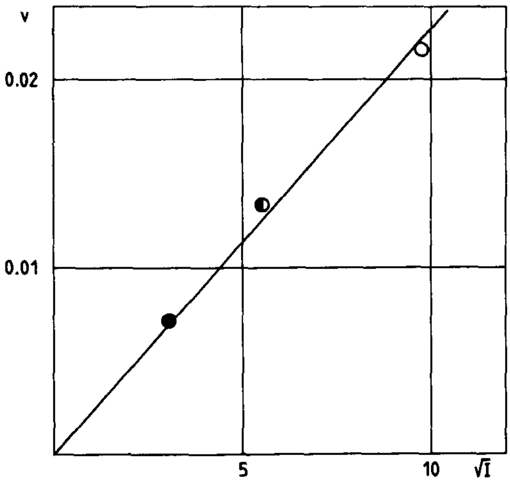


Fig. 2. Rate of fading as a function of the square root of the light intensity calculated from the data in Fig. 1. ○, 100% light intensity; ◐, 26·3% light intensity; ●, 8·8% light intensity.

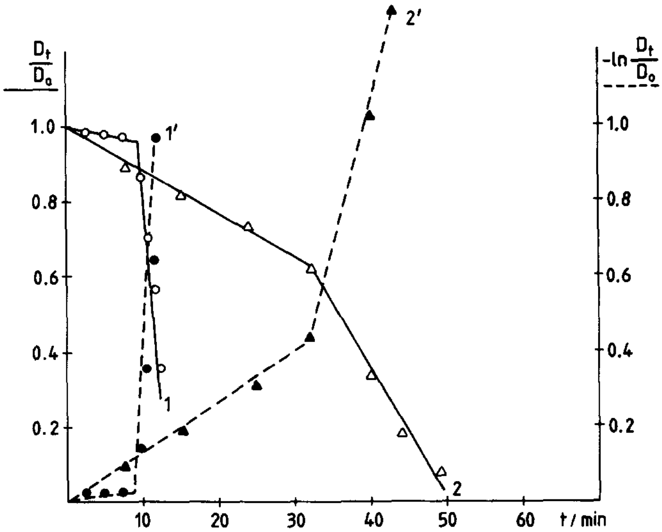


Fig. 3. Fading kinetics of Reactive Brilliant Red 6B (No. 3) in Ip–W (10:1). D_t/D_0 plotted against t (1, 2) and $-\ln D_t/D_0$ against t (1′, 2′). 1 and 1′ represent data from the first procedure, 2 and 2′ those from the second.

practically no photodegradation of the dissolved dyes in the absence of AIBN.

Because of this, and also taking into consideration the susceptibility of AIBN to photoinitiated radical formation, in the presence of AIBN the radical character of the dye degradation reaction could be concluded when the first type of fading procedure was used. The rate of radical initiation is determined by the rate of radical formation from AIBN in this case.

Photodegradation of the dyes occurred when using the second fading procedure, and this might be due to both radical and photolytic reactions.

If the slopes of the straight lines, representing the second fast step of fading, were the same in the cases of both the first and second fading procedures, then the radical character of the photodegradation could be concluded in both systems. Experimentally, however, the second step of fading proved to be faster in the case of the second procedure than in the first, and consequently photodegradation of the dye in the second procedure is due to both radical and other photolytic reactions.

If v_1 (mol litre^{-1} s^{-1}) is the rate of the second step of fading in the first procedure, v_2 (mol litre^{-1} s^{-1}) is that in the second one, and $v_2 > v_1$, then the proportion of radical reactions in the total photodegradative processes bringing about fading in the second procedure can be represented by eqn (9):

$$x = \frac{v_1}{v_2} \cdot 100\% \tag{9}$$

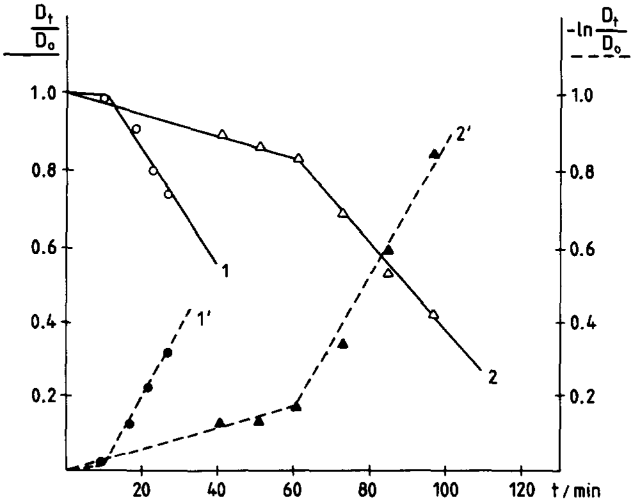


Fig. 4. Fading kinetics of Reactive Scarlet 2G (No. 4) in Ip–W (10:1). D_t/D_0 plotted against t(1, 2) and $-\ln D_t/D_0$ against t(1′, 2′). 1 and 1′ represent data from the first procedure, 2 and 2′ those from the second.

The validity of this last statement depends on the rates of radical initiation (first steps of fading) in both of the procedures. The determined correlation between v_1 and v_2 can only be considered valid if the rates of radical formation in the first steps of fading of both procedures are equal to one another. (The role of dissolved oxygen in the first step of fading has been previously demonstrated[8] and will be discussed later (Figs 6 and 7).)

Difference in the rates of radical initiation between the two procedures is demonstrated in Figs 3 and 4. The correlation (9) has to be modified in the following way:

$$x = \frac{v_1}{v_2}\sqrt{\frac{v_2^i}{v_1^i}} \cdot 100\% \tag{10}$$

where v_1^i is the rate of radical initiation in the first step of the first procedure, while v_2^i is that for the second procedure. According to the assumption the rate of radical initiation is equal to the drop in oxygen concentration in the time unit:

$$v_1^i = \frac{[O_2]_1}{t_1} \tag{11}$$

$$v_2^i = \frac{[O_2]_2}{t_2} \tag{12}$$

However, $[O_2]_1 = [O_2]_2$, and consequently

$$\frac{v_2^i}{v_1^i} = \frac{t_1}{t_2} \tag{13}$$

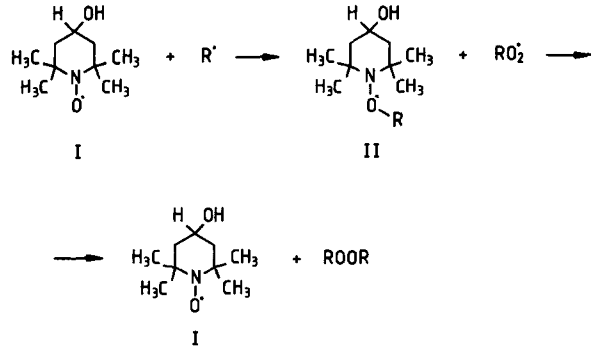


Fig. 5. Mechanism of inhibition of radical reactions (SNR).

Because of this

$$x = \frac{v_1}{v_2}\sqrt{\frac{t_1}{t_2}} \cdot 100\% \qquad (14)$$

For reactive dye No. 3: $v_1 = 4{\cdot}2 \times 10^{-3}$ mol litre^{-1} s^{-1}; $v_2 = 3 \times 10^{-3}$ mol litre^{-1} s^{-1}; $t_1 = 9{\cdot}5$ min; $t_2 = 32{\cdot}0$ min; and consequently $x = 76{\cdot}8\%$. For reactive dye No. 4: $v_1 = 9{\cdot}0 \times 10^{-4}$ mol litre^{-1} s^{-1}; $v_2 = 6{\cdot}7 \times 10^{-4}$ mol litre^{-1} s^{-1}; $t_1 = 12{\cdot}0$ min; $t_2 = 61{\cdot}0$ min and consequently $x = 58{\cdot}9\%$.

The simultaneous occurrence of a direct photolytic degradation in addition to the radical degradation has to be assumed also in the first step of

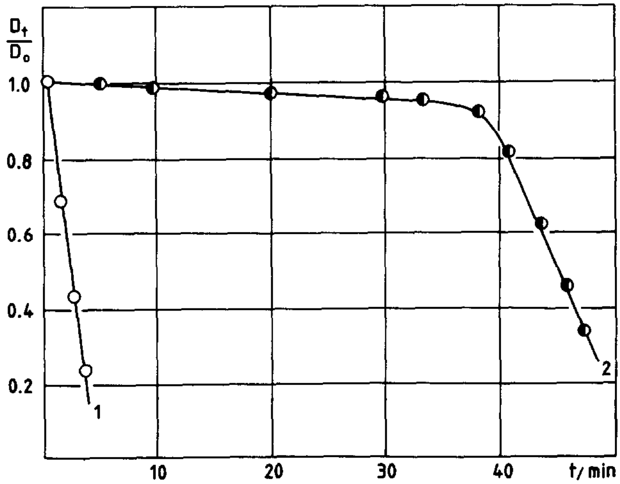


Fig. 6. Fading kinetics of Reactive Brilliant Red 6B (No. 3) dissolved in oxygen-free Ip–W (10:1) in the absence and presence of SNR (second procedure). ○, Without SNR; ◐, with 10^{-2} mol litre^{-1} SNR.

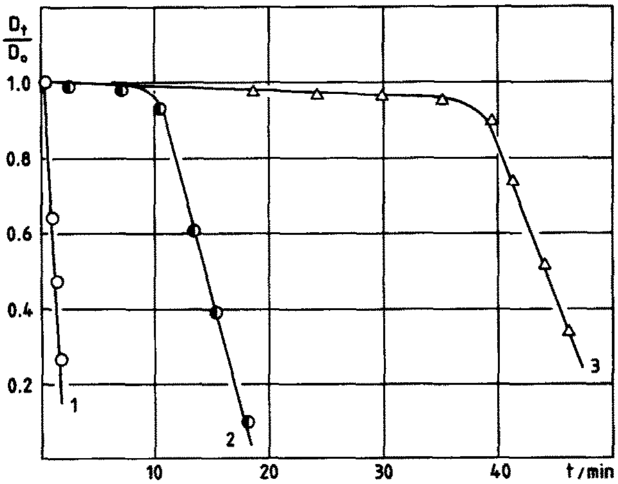


Fig. 7. Fading kinetics of Reactive Scarlet 2G (No. 4) dissolved in oxygen-free Ip–W (10:1) in the absence and presence of SNR (second procedure). ○, Without SNR; ◐, with 5×10^{-3} mol litre^{-1} SNR; △, with 10^{-2} mol litre^{-1} SNR.

the second procedure, on the basis of the data of Figs 3 and 4. Improved photostability of the reactive dyes could be expected by inhibiting radical reactions in the system.

Compounds susceptible to stable radical formation may be used for this purpose. 2,2,6,6-Tetramethyl-4-hydroxypiperidine-1-oxyl (Fig. 5) was selected as a stable radical (SNR) for the experiments. This radical can combine with a radical from the initiated ones, forming the addition product (**II**); (**II**) then reacts with a peroxide radical included in the system, leading to the regeneration of SNR (**I**).

To exclude the previously mentioned effect of dissolved oxygen, oxygen was eliminated by evacuation of the sealed cuvette filled with a solution of the reactive dyes No. 3 and No. 4, respectively, and (**I**) in Ip–W (10:1). It can be concluded from Figs 6 and 7 that:

(a) in the absence of dissolved oxygen, no first step occurred in the fading process, and
(b) the higher the concentration of (**I**) in the system, the longer the new first step of inhibition in the fading process.

Consequently, the role of dissolved oxygen, as well as the importance of the formation and concentration of free radicals in the fading process, could be simultaneously demonstrated experimentally.

Similar experiments were made with other reactive dyes and the role of the radical reactions in the fading of these dyes was found to be similar.

3 EXPERIMENTS IN SOLID (FIBROUS) PHASE

3.1 Materials and methods

To demonstrate the similar role of radical reactions in the fading of reactive dyed cellulosics, further experiments were carried out on cotton (Co) and viscose rayon (Vi) fabrics as well as on cellophane films (Ce) dyed with the reactive dyes shown in Table 2. A Xenotest-450 was used for the irradiation of the dyed samples. Undyed cotton was used as a control blank sample in the irradiation experiments. The amount of free radicals generated in the course of the irradiation was measured by means of ESR (JEOL PE-1x, Japan).

3.2 Results and discussion

From Figs 8–10, it can be concluded that:

(a) blank cellulose did not form a significant amount of stable free radicals under the experimental conditions,
(b) no difference was evident between the dyed Co, Vi, Ce systems, as far as free radical formation from the reactive dyes is concerned, and
(c) the higher the dye pick-up in the coloured system, the more free radicals were formed under similar conditions of irradiation.

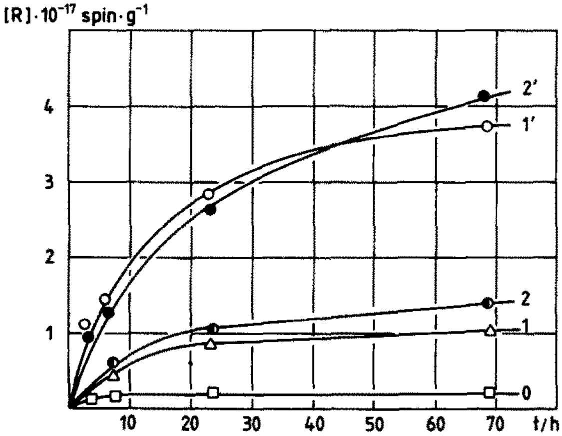


Fig. 8. Kinetics of stable free radical formation of Xenotest-450 irradiated blank and reactive dyed cotton fabric samples. ○, Blank cotton fabric; cotton fabrics dyed with Reactive Scarlet 2G: 1, 2×10^{-2} mol kg^{-1}; 1', 5×10^{-2} mol kg^{-1}; cotton fabrics dyed with Reactive Brilliant Red 6B: 2, 2×10^{-2} mol kg^{-1}; 2', 5×10^{-2} mol kg^{-1}.

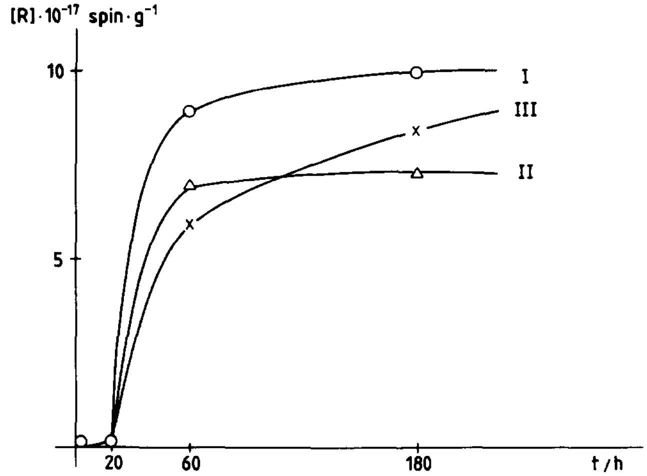


Fig. 9. Kinetics of stable free radical formation on Xenotest-450 irradiated Co, Vi and Ce samples dyed with 5×10^{-2} mol kg^{-1} C.I. Reactive Red 2. I. Cotton (Co); II. Viscose rayon (Vi); III. Cellophane film (Ce).

All the detectable free radicals proved to be stable for at least two weeks. Some of these free radicals were even stable to washing.

This work was a continuation of studies to rationalise the quantitative correlations between radical formation and the rate of fading of reactive dyed cellulosic systems. Future demonstration of the similar role of radical reactions in the fading of reactive dyed cellulosics, as shown in the

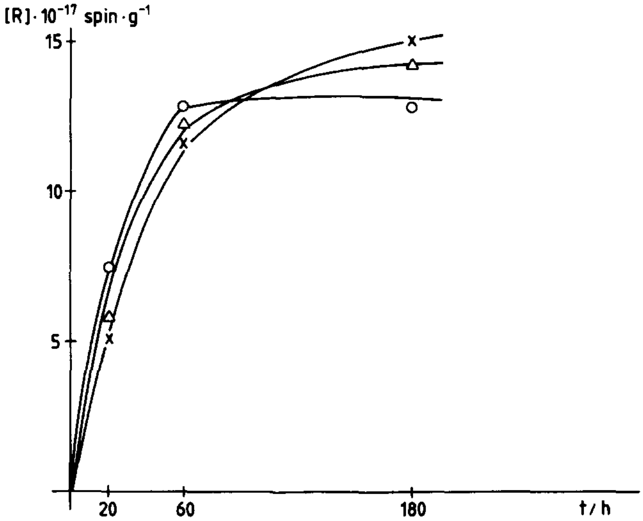
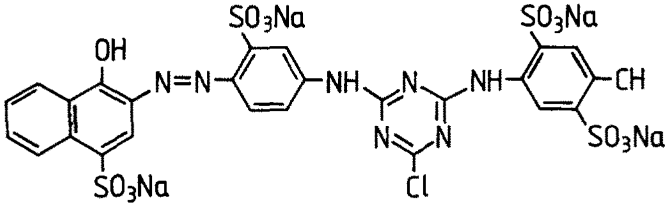


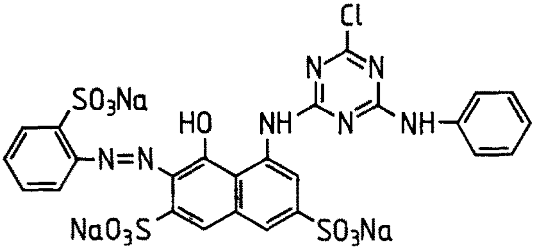
Fig. 10. Kinetics of stable free radical formation on Xenotest-450 irradiated Co, Vi and Ce samples dyed with 5×10 mol kg^{-1} C.I. Reactive Black 5. ○, Cotton; △, viscose; ×, cellophane.

TABLE 2
Reactive Dyes Used in the Solid (Fibrous) Phase Experiments

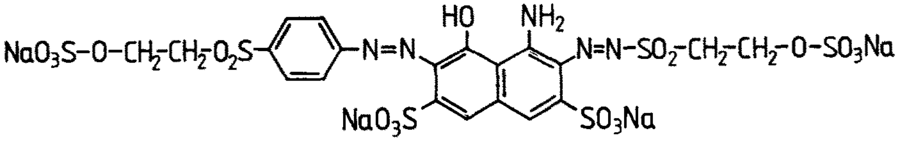
6. Reactive Orange 5R (Russian product)



7. C.I. Reactive Red 2



8. C.I. Reactive Black 5



photodegradation of dissolved reactive dyes, could verify the mechanism postulated in the authors' previous study.[7]

4 CONCLUSIONS

4.1 Liquid phase

The fading of selected reactive dyes dissolved in an Ip–W (10:1) mixture can be described with reference to a series of reactions. Free radical formation, and reactions based thereupon, can be demonstrated. The addition of an easily free radical forming compound (AIBN) to the dye solution generated faster initiation in the chain reaction. Quadratic termination of the radical process could also be demonstrated. No autoinitiation of free radical formation occurred if the dissolved dye was irradiated in the first procedure. In the absence of a photoinitiator, both radical and photolytic reactions simultaneously occur in the second procedure. The proportion of radical reactions in that system could be calculated. Different rates of radical initiation were observed in the studied procedures. The rate of radical initiation was equal to the decrease in dissolved oxygen in the time unit. No first step occurred in the fading process in the absence of dissolved oxygen. Improved photostability of dissolved reactive dye was brought about by the inhibitor SNR.

4.2 Solid phase

Negligible amounts of free radicals were formed from cellulosic fibres. The amount of free radicals formed from reactive dyed cellulosic fibres depends on the dye pick-up but does not depend on the type of cellulosic fibre. The free radicals formed were stable, sometimes even to washing.

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