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Determination of the Lightfastness of Dyestuffs by Kinetic Characteristics

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ABSTRACT

The lightfastness of some azo dyestuffs has been evaluated using kinetic parameters. The rate of photodegradation of the dyestuffs has been determined in the presence of radicals generated from isopropanol in the liquid phase. Radical processes have also been produced with dyestuffs on cotton.

It has been found that the lightfastness of the dyestuff could be characterized using kinetic parameters which determine the radical-forming ability of the dyestuff and its reactivity towards radicals.

1 INTRODUCTION

It is well known that when coloured polymers are irradiated by light, free radicals are produced. These radicals are of high chemical activity and play an important role in the photodegradation of the dyestuffs which are present

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in the polymer matrix. The photodegradation processes can be described by the following scheme:

$$
\begin{array}{ll}
D + h\nu \longrightarrow D^{*} & \\
D^{*} + M_{P} \longrightarrow M_{P} + D & \text{Radical-producing reaction} \\
M_{P}\cdot + O_{2} \longrightarrow M_{PO_{2}} & \text{Chain reaction} \\
\left.\begin{array}{l} D^{*} + M_{P}\cdot \longrightarrow \\ D^{*} + M_{PO_{2}^{\cdot}} \longrightarrow \end{array}\right\} & \text{Decomposition of the dyestuff} \\
\left.\begin{array}{l} M_{P}\cdot + M_{P}\cdot \longrightarrow \\ M_{P}\cdot + M_{PO_{2}^{\cdot}} \longrightarrow \\ M_{PO_{2}^{\cdot}} + M_{PO_{2}^{\cdot}} \longrightarrow \end{array}\right\} & \text{Closing of the chain}
\end{array}
$$

where D is the dyestuff molecule, and D^{*} is its excited state;
P is the polymer macromolecule;
$P^{\cdot}$ is the radical developed from the polymer;
$PO_{2}^{\cdot}$ is the peroxide radical developed from the polymer.

It can be seen from this scheme that in case of a photodegradation mechanism, the lightfastness of the dyestuff is determined by the reaction between the dyestuff molecules and the polymer radicals developed under irradiation. The object of this investigation was to establish a correlation between the lightfastness of the dyestuff and its reactions with the free radicals present in the system.

2 EXPERIMENTAL: MATERIALS AND METHODS

2.1 Dyestuffs

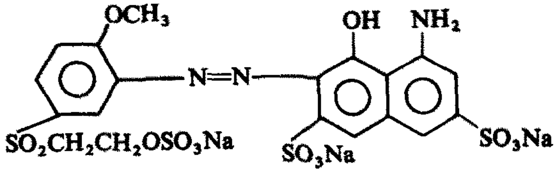
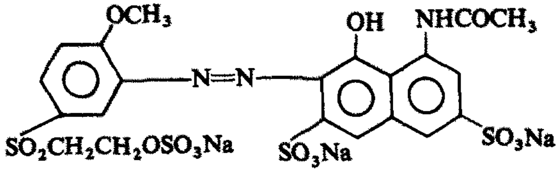
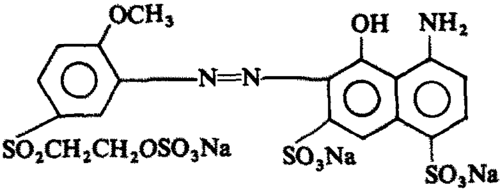
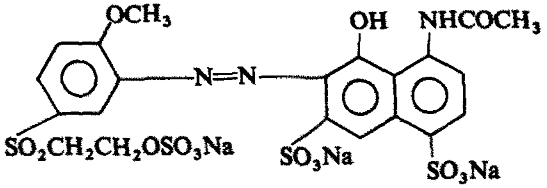
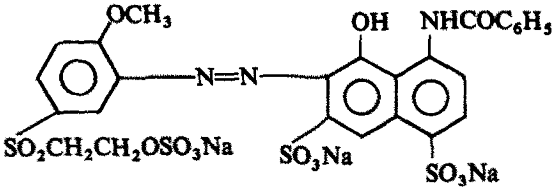
A series of chromatographically pure model reactive azo dyes, the structures of which are shown in Table 1, were synthesized.

2.2 Substrates

Experiments were carried out both in liquid- and in solid-phase systems. Cotton fabric dyed by the cold pad-batch process was used as substrate. In the liquid-phase experiments the dyes were dissolved in a 10:1 mixture of isopropanol and water.

Processes occurring on irradiation in solutions, either saturated with oxygen or free of oxygen, were investigated. Saturation with oxygen was

TABLE 1
The Structural Formulae of the Reactive Dyestuffs Used in the Investigation

Dye no.	*Structural formula*
1	
2	
3	
4	
5	

achieved by bubbling air through the dye solutions. To obtain oxygen-free solutions, subsequent to freezing them with liquid nitrogen (77 K) the air above their surface was pumped out (6·65 Pa). Due to subsequent heating, the adsorbed gases were released from the solution. This procedure (freezing, pumping, heating) was repeated five times. The concentration of oxygen in the solution was reduced in this way to less than 10^{-5} mol litre^{-1}.

2.3 Irradiation

Dyed cotton samples were irradiated in a Xenotest Model 450. Samples in the liquid phase were irradiated in a quartz cuvette, using a high-pressure mercury-vapour lamp (250 W). From the spectrum of light emitted by the lamp the component of 365 nm wavelength was selected using combined light filters (combination of SS-1 and UFS-6).[1]

2.4 Expression of fading

In order to follow the kinetics of the photodegradation, the absorption spectra of the solutions and the reflection spectra of the dyed fabrics were determined before and after irradiation. The visible absorption of the dyes did not change during irradiation. Consequently, either the change in optical density (liquid phase) or in reflexion (solid phase), both measured in the visible range of the spectra, were chosen for evaluation of the fading. The

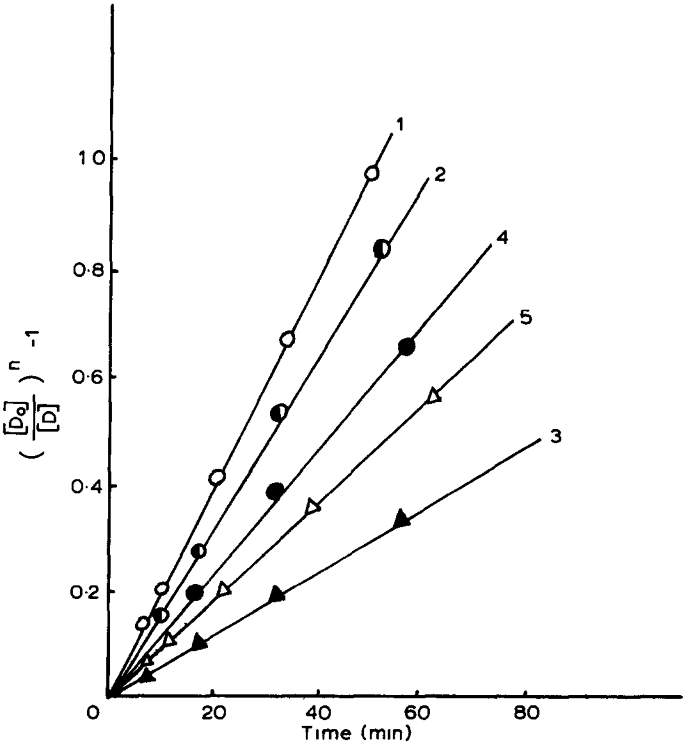


Fig. 1. The kinetics of the photodegradation of the dyestuffs, illustrated in the coordinate system $([D_0]/[D])^n - 1$ versus t, in oxygen-free solution, in the presence of AIBN. **1, 2, 3, 4, 5** are the serial numbers of the dyestuffs shown in Table 1.

concentration of the dyestuff was calculated either from the optical density (Lambert–Beer law) or from the reflection (Kubelka–Munk law).

The tendency for the dyed fabric sample to fade (lightfastness) was characterized by the duration of irradiation ($\tau_{10\%}$) needed for a 10% reduction in its original K/S value. The fading was characterized in the liquid phase by the reaction rate constant (K_d) of the dyestuff degradation.

The initial rate of fading of the dissolved dyestuff (W_0) as well as the time of irradiation (τ) needed for complete decomposition (i.e. lifetime) of 2,2′-azobisisobutyronitrile (AIBN) dissolved in the isopropanol/water mixture was determined for the calculation of K_d.

For the determination of W_0, the dyestuff concentration calculated from changes in optical density after different durations of irradiation were plotted in the $\{([D_0]/[D])^n - 1\}$ versus t coordinate systen (Figs 1 and 2). $[D_0]$ is the initial molar dyestuff concentration, $[D]$ is the actual dyestuff concentration in the solution at a given time of irradiation and n is an exponent, dependent on the given system and which has to be selected in such a manner that the initial section of the kinetic fading curve was a

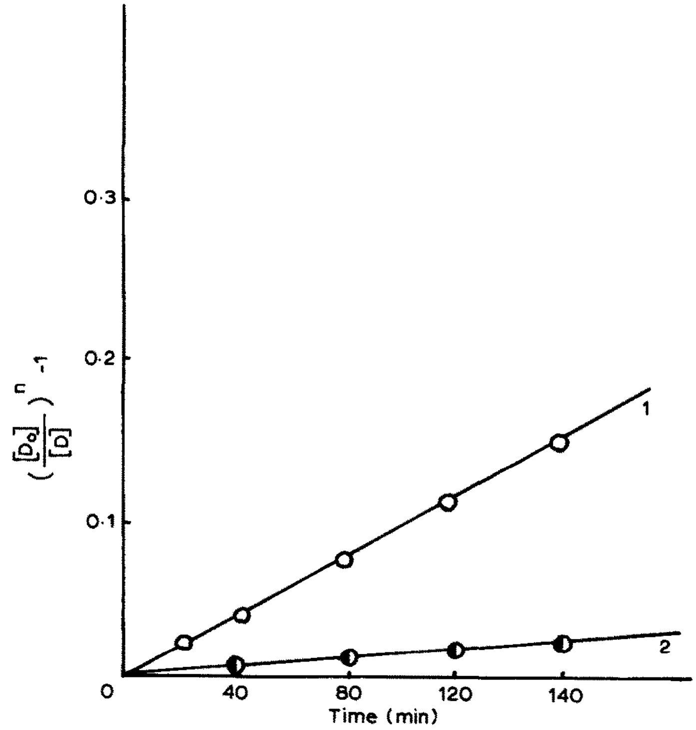


Fig. 2. The kinetics of the photodegradation of the dyestuffs, illustrated in the coordinate system $([D_0]/[D])^n - 1$ versus t, in oxygen-containing solutions, in the presence of AIBN, 1, 2 are the serial numbers of dyestuffs.

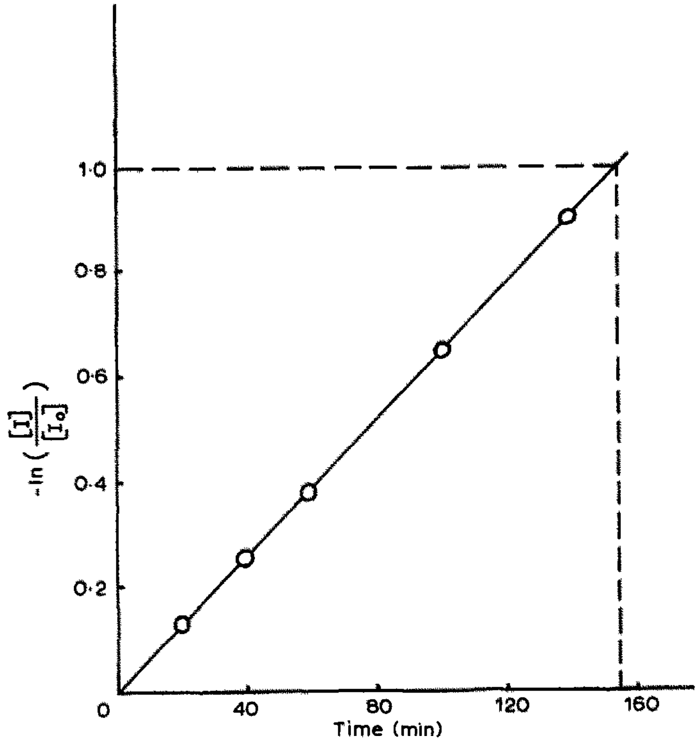


Fig. 3. Determination of the lifetime of AIBN in a solution containing 3 × 10^{-3} mol $litre^{-1}$ AIBN.

straight line in the coordinate system used (the determination of n is possible either graphically or by a computer program). The tangent of the directional angle of this straight line is equal to the initial rate of fading.[2]

$$W_0 = \frac{([D_0]/[D])^n - 1}{t} \qquad (1)$$

For the determination of τ, a solution of pure AIBN was irradiated and the kinetics of decomposition were plotted using the $-\ln[I]/[I_0]$ versus t coordinate system.[3] The time of irradiation corresponding to $-\ln[I]/[I_0] = 1$ is the required τ value (Fig. 3).

2.5 Registration of free radicals

The formation of free radicals was studied by ESR using an SE/x 2543 Radiopan. The ability of dyestuffs to generate radicals on cotton was characterized by the concentration of free radicals developed during irradiation.

2.6 A new method for following reactions between dyestuff and free radicals

Experiments were carried out in liquid phase both in the absence and in the presence of oxygen. Reactivity of the dyes was studied with alkyl radicals if oxygen was absent, and with peroxide radicals in the presence of oxygen. AIBN was used as an initiator in generating alkyl radicals. The irradiating light was of 365 nm wavelength. The dyestuffs investigated were practically insensitive to this radiation and therefore they do not fade in the absence of the initiator. Decomposition of AIBN occurs, however, during the irradiation, and radicals are formed simultaneously. Radicals generated in the course of the photodegradation of AIBN can directly bring about the decomposition of the dyes. Indirect degradation of the dyes, due to the action of alkyl radicals ($R^\cdot$) generated from propanol by AIBN-derived radicals, can also be assumed. Peroxide radical formation is very likely in the previous cases in the presence of oxygen. AIBN-derived peroxide radicals or alkyl peroxide radicals ($RO_2^\cdot$) can equally bring about decomposition of dyes but at a much slower rate than $R^\cdot$ radicals.

The reactivity of the dyestuff with the radicals can be characterized by the rate constant of their decomposition. Dye decomposition brought about by alkyl radicals in an oxygen-free system can be characterized by the rate constant $K_{d'}^{R^\cdot}$ and that caused by alkyl peroxide radicals in the presence of oxygen, by $K_d^{RO_2^\cdot}$.

The determination of $K_{d'}^{R^\cdot}$ was based upon the following theoretical considerations:

$$I \xrightarrow{h\nu} A^\cdot \xrightarrow{R} R^\cdot \qquad (2)$$

$$R^\cdot + D \xrightarrow{K_{d'}^{R^\cdot}} \text{decomposition} \qquad (3)$$

$$R^\cdot + R^\cdot \xrightarrow{K_t} \text{termination} \qquad (4)$$

where

$A^\cdot$ is the radical formed at the photoinitiated decomposition of the initiator (I);

$K_{d'}^{R^\cdot}$ is the rate constant of the dyestuff decomposition;

K_t is the rate constant of the termination reaction.

According to the above scheme the photo-initiated dyestuff decomposition is a first-order reaction, represented by the following equation:

$$\frac{d[D]}{dt} = -K_{d'}^{R^\cdot}[D][R^\cdot] \qquad (5)$$

By integrating eqn (5) and assuming that both $K_{d'}^{R^{\cdot}}$ and $R^{\cdot}$ are constant, the following relationship is obtained:

$$K_{d'}^{R^{\cdot}} = \frac{-\ln([D]/[D_0])}{t/[R^{\cdot}]} \tag{6}$$

The $-\ln([D]/[D_0])/t$ expression represents the initial rate (W_0) of the photoinitiated dyestuff decomposition (fading) and hence eqn (6) can be written in a more simplified form, viz.

$$K_{d'}^{R^{\cdot}} = \frac{W_0}{[R^{\cdot}]} \tag{7}$$

Thus, for calculating $K_{d'}^{R^{\cdot}}$, the initial rate of the photoinitiated dyestuff decomposition and the concentration of the radicals in the system need to be determined.

The radical-generating ability of the initiator, as well as the probability of radicals entering into the system, are necessary factors required for the determination of the total concentration of radicals in the system.

The rate of initiation can be described as follows:

$$w_i = \alpha K_i [I_0] \tag{8}$$

where $[I_0]$ is the initial molar concentration of the initiator in the solution;

α is considered as a probability parameter expressing the proportion of radicals photogenerated from one molecule of the initiator which retains its reactivity;

K_i is the rate constant for the decomposition of the initiator.

Since the initiator concentration in the system varies according to an exponential function, the following equation can be written:

$$\frac{d[I]}{dt} = K_i [I_0] \tag{9}$$

By integration

$$[I] = [I_0]\,e^{-K_i t} \tag{10}$$

or

$$[I] = [I_0]\,e^{-t/\tau} \tag{11}$$

where $\tau = 1/K_i$ is the lifetime of the initiator in the solution.

Generally, the rate of the recombination of radicals is high, and therefore, in the case of a constant rate of initiation, a dynamic equilibrium is rapidly attained in the system, and subsequently the concentration of the different components will become quasi-stationary. According to the quasi-stationary principle, and considering the experimentally established fact[4] that a quadratic termination takes place, the following equation can be written:

$$W_i = K_t[R^\cdot]^2 \tag{12}$$

or

$$[R^\cdot] = \sqrt{\frac{W_i}{K_t}} \tag{13}$$

Considering eqns (7), (8) and (13), the rate constant of the dyestuff decomposition can then be expressed as follows:

$$K_{d'}^{R^\cdot} = \frac{W_0}{\sqrt{\frac{\alpha[I_0]/\tau}{K_t}}} \tag{14}$$

Some of the parameters in eqn (14) are known from the literature, i.e. $\alpha = 0{\cdot}38$,[3] $K_t = 1{\cdot}15 \times 10^9$ litre mol^{-1} s^{-1} for alkyl radicals and $1{\cdot}1 \times 10^9$ litre mol^{-1} s^{-1} for peroxide radicals,[5] and $[I_0] = 3 \times 10^{-2}$ mol litre^{-1}.

The values of W_0 and τ have to be determined experimentally, according to the methods described in Section 2.4. The radiation of 365 nm wavelength is absorbed not only by AIBN, but also partly by the dyestuff present in the system. Consequently the rate of radical formation from the AIBN is reduced. This effect varies with different dyestuffs and it was considered by using the following correcting equation:

$$K_d^{R^\cdot} = \frac{K_{d'}^{R^\cdot}}{\beta} \tag{15}$$

where

$$\beta = \frac{D_I(1 - 10^{-D_\Sigma})}{D_\Sigma(1 - 10^{-D_I})} \tag{16}$$

where β is the constant of shadowing;
$K_D^{R^\cdot}$ is the corrected rate constant of the dyestuff decomposition;
D_I is the optical density of the AIBN at 365 nm;
D_Σ is the joint optical density of AIBN and the dyestuff at 365 nm.

3 RESULTS AND DISCUSSION

$K_d^{R^\cdot}$ and $K_d^{RO_2^\cdot}$ values characteristic for the reactivity of the investigated dyes with radicals are given in Table 2. The results prove that the reactivity of the dyestuffs studied is significantly higher with alkyl radicals than with peroxide radicals. Therefore possible correlations between $K_d^{R^\cdot}$ values and

TABLE 2
The Rate Constants Characterizing the Reactivity of the Dyestuffs with Alkyl ($K_d^{R^{\cdot}}$) and with Peroxide Radicals ($K_d^{RO^{\cdot}}$) in the Liquid Phase, and the Time of Irradiation Needed for 10% Fading ($\tau_{10\%}$) of the Dyed Cotton Fabric in the Xenotest 450

Dye number	$K_d^{R^{\cdot}} \times 10^{-3}$ (*litre mol*$^{-1}$ *s*$^{-1}$)	$K^{RO_2^{\cdot}} \times 10^{-3}$ (*litre mol*$^{-1}$ *s*$^{-1}$)	$\tau_{10\%}$ ($\times 10^3$ *s*)
1	10·1	0·9	7
2	8·9	0·1	12
3	3·4	<0·1	22
4	6·3	<0·1	38
5	4·1	<0·1	56

the corresponding lightfastness data of the dyestuffs were investigated. The lightfastness data of the dyestuffs in the liquid phase (represented by serial numbers in Table 2), estimated from the corresponding $K_d^{R^{\cdot}}$ values, decrease in the following order: **3** > **5** > **4** > **2** > **1**.

The order of lightfastness of the same dyestuffs on cotton fabric estimated from the corresponding $\tau_{10\%}$ values (Fig. 4 and Table 2) is as follows: **5** > **4** > **3** > **2** > **1**. A similar relative order of lightfastness could be estimated for the dyestuffs **5**, **2** and **1**, both in the liquid and in the solid phase. Thus, for dyestuff **3** a small $K_d^{R^{\cdot}}$ value and relatively rapid fading on fabric, and for dyestuff **4**, a relatively high $K_d^{R^{\cdot}}$ value and slow fading on fabric, are characteristic.

It may consequently be concluded that the lightfastness of the cotton fabrics dyed with these dyes cannot be characterized only by the corresponding $K_d^{R^{\cdot}}$ values. The fading of the dyestuffs is influenced, under the conditions of the investigation, by two processes; radical generation and the interaction of the dyestuffs with the radicals formed. Experimental conditions chosen for the liquid phase enabled the formation of radicals in a very great number. Thus a quasi-stationary concentration of alkyl radicals could be ensured in the system. Therefore presumably the fading of the dyes is dominantly controlled by the interaction of the dyestuff with the radicals present in the system.

Another kinetic characteristic, the rate of radical generation, plays a main role in fading of dyed cotton fabrics.

Due to the absence of AIBN initiator in the dyestuff–cotton fabric system, the interaction between the dyestuff and the AIBN-derived radicals has to be excluded from the explanation of fading. Lightfastness therefore might presumably be dependent on the rate of self-generation of dyestuff-derived radicals. To affirm the validity of the former assumptions, the radical-

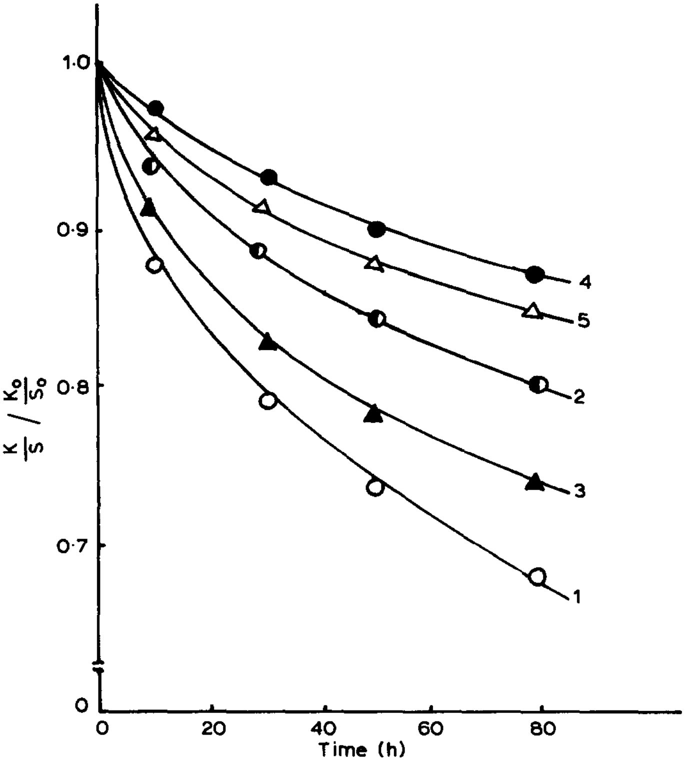


Fig. 4. The kinetics of the Xenotest 450 induced photodegradation of the dyestuffs on dyed cotton fabrics.

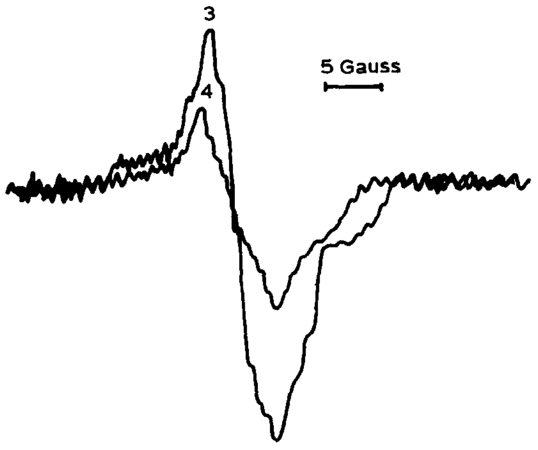


Fig. 5. The ESR spectra of radicals registered on cotton fabrics dyed with dyestuffs 3 and 4, after irradiation in the Xenotest 450 for 15 h 3, 4 are the serial numbers of dyestuffs.

generating ability of dyestuffs **3** and **4** were studied. ESR spectra were recorded after Xenotest 450 irradiation for 15 h on cotton fabric samples dyed with these dyestuffs. It was found that the concentration of free radicals generated from the dyed system **3** was 8×10^{17} spin. g^{-1}, whereas that from the dyed system **4** was 4×10^{17} spin. g^{-1} (Fig. 5). Consequently, the radical-generating ability of the dyed system **3** is about twice as high as that of the dyed system **4**. Comparing these data with the values characteristic of the lightfastness of the two systems, it can be seen that the relative ratio (1·8) is nearly identical to that of their radical-generating abilities.

4 CONCLUSIONS

Kinetic parameters have been found to be suitable for the characterization of the lightfastness of dyes. In the liquid phase, the interaction of dyestuffs with photo- or initiator-generated radicals plays an important role in the photodecomposition of both dyes and dye-containing systems.

The lightfastness of a dyestuff is determined by the rates of two reactions running simultaneously, viz. the formation of radicals and their interaction with the dyestuff. In the liquid phase, a quasi-stationary concentration of alkyl radicals has been ensured in the system by the presence of an initiator. Under these conditions the lightfastness of the dissolved dyestuff was dependent only on the interaction of the dyestuff with the alkyl radicals. In case of irradiated dyed cotton fabrics the dyestuffs in the dyed system may be regarded as radical-generating substances.

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