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Structure Reactivity Correlations of Azo Reactive Dyes Based on H-acid. III. Dye Degradation by Peroxide*

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ABSTRACT

In this paper we report on the influence of substituents on the degradation of azo reactive dyes based on H-acid caused by the action of hydrogen peroxide in aqueous solution and on cellulose. The results support the view that the perhydroxyl radical anion is the active agent in the dye degradation by hydrogen peroxide. We suggest that, predominantly, the dissociated form of the ortho-hydroxyazo dyes undergoes the degradation, and thus the pK_a *value of the dye is an important criterion for the fastness to peroxide. With this background, an expanded version of the Hammett correlation including the* pK_a *values of the dyes yields a linear free energy relationship. On cellulose, bifunctional reactive dyes seem to be more stable to peroxide bleaching liquor than monofunctional reactive dyes with comparable* pK_a *values.*

1 INTRODUCTION

The fading of dyed textiles caused by chlorine or hypochlorite, respectively, by peroxide- washing, and by combined action of perspiration and light is considered a challenging problem in the dyestuff industry, but current knowledge concerning the physical and chemical background is limited.[1] In

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this series of papers, we attempt to elaborate the structure reactivity correlations of closely related azo reactive dyes. We selected the H-acid monoazo chromophore, since many industrially important red reactive dyestuffs of this type are deficient with respect, to the above mentioned fastness requirements. In part I,[2] we reported on the selection and synthesis of the dyes and on their general characterization in terms of aggregation, pK_a values, and dyeing behaviour, etc. In part II[3] we covered the fastness to chlorinated water, and in part IV[4] we will discuss the light fastness in presence of water and perspiration. Here we report on structure reactivity correlations concerning the dye degradation caused by hydrogen peroxide.

Potential sources for peroxide are detergents and the bleaching processes used in the textile industry. Sodium peroxoborate is the standard bleaching compound in detergents. Its aqueous solution reacts like an alkaline solution of hydrogen peroxide. In order to depress the decomposition of hydrogen peroxide, e.g. by catalytic action of heavy metal ions, the bleaching liquor is stabilized with sodium silicate, chelating agents, and magnesium salts. Furthermore, derivatives of carboxylic acids, e.g. TAED[5] (tetraacetylethylenediamine) or TAGU[6] (tetraacetylglycolurile), are frequently used as activators. These compounds are acylating agents and react with H_2O_2, forming organic percarboxylic acids.

Generally, the peroxide anion $HO_2^{\ominus}$ is considered to be the active bleaching agent in peroxide containing alkaline bleaching liquor.[7] However, several other species are also conceivable as active bleaching agents, e.g. singlet-oxygen, and also some radical species, of which the hydroxyl radical $OH^{\odot}$ and the perhydroxyl radical anion $O_2^{\ominus\odot}$, being intermediately formed during the decomposition of peroxide in alkaline solution, have been proposed in the literature. Dannacher & Schlenker[8] concluded that bleaching with hydrogen peroxide is mainly due to the action of the perhydroxyl radical anion. Furthermore, it was reported that singlet-oxygen, which is generated from percarboxylic acids, is responsible for the bleaching effect of these agents.[9]

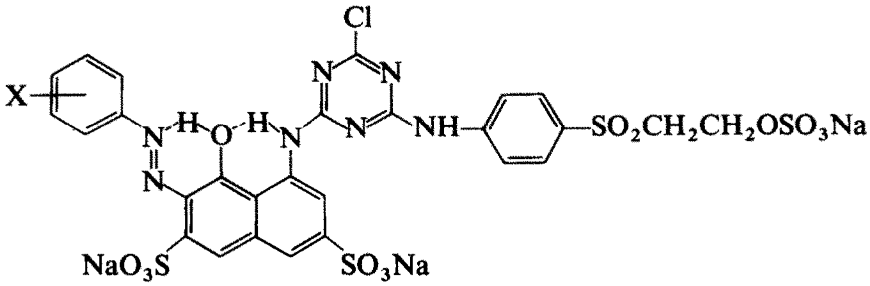
However, discussion concerning active bleaching agents covered the bleaching of cotton rather than the degradation of dyes by peroxide, and it is not known whether the same rules also hold true in the latter case.

Some work on the effect of peroxide on dyed textiles has been reported by Schmid *et al.*[10,11] who conducted a screening of commercial dyes. Investigations of Rattee *et al.*[12,13] covered the dye–fibre bond cleavage of difluorochloropyrimidine reactive dyes by the concomitant action of light and peroxide. Davies & Jones[14] reported on dye degradation by peroxide involving radicals. Flick & Schollmeyer[15] found a retarded fading of acid dyes in the alkaline peroxide bleaching in the presence of tenside micelles compared to the tenside free solution.

2 EXPERIMENTAL

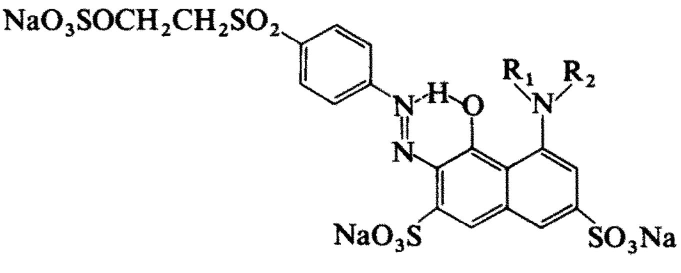
2.1 Dyes and dyeings

The reactive dyes used for our investigations were monoazo dyes based on H-acids whose structures are shown below:



X = *p*-OCH_3 (**1**), *p*-CH_3 (**2**), H (**3**), *p*-Cl (**4**), *p*-NO_2 (**5**),
o-OCH_3 (**6**), *o*-CH_3 (**7**), *o*-Cl (**8**), *o*-NO_2 (**9**),
o-SO_3H (**10**), *o*-sec-C_4H_9 (**11**), *o*-COOH (**12**)

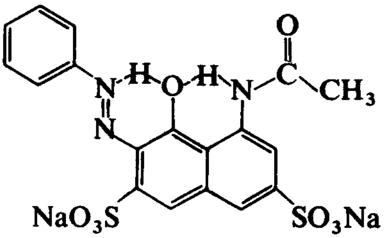
Dyes **1**–**12** contain bifunctional reactive groups, namely a vinylsulphonyl and a monochlorotriazinyl anchor, both attached on the side of the coupling component in a conjugated manner. The preparation, purification and characterization of the dyestuffs **1**–**12** as well as their dyeing behaviour were described in part I[2] in this series of papers.



NR_1R_2 = NH_2 (**13**), $NHCH_3$ (**14**), $N(CH_3)_2$ (**15**),
$NHCOCH_3$ (**16**), NCH_3COCH_3 (**17**)

The dyes **13**–**17** are monofunctional vinylsulphonyl reactive dyes with the anchor located on the side of the diazo component, while the substituents on the N-atom of the H-acid moiety are modified. The synthesis and characterization of the dyes **13**–**17** are described in Ref. 17.

In addition to the reactive dyes, C.I. Acid Red 1 (**18**) was used for investigations into the mechanism of peroxide fading.



(18)

The dyeing procedure (exhaust process, approximately 1% o.w.f. dyestuff on cellulose) on cellulose film (®Cellophane) and cotton fabric was described in part II.[3]

2.2 Peroxide degradation in aqueous solution

A solution of 100 ml of water containing 10^{-4} mol/litre of chromatographically purified dye (see part I[2]), 5 g/litre of sodium carbonate, 10 vol.% of dimethylacetamide (DMA), 0·15 g/litre of magnesium chloride, and 1·2 g/litre of sodium silicate ('wasserglas') was held at a constant temperature of 60°C in a thermostatable Erlenmeyer flask for 1 h under stirring. The application of $MgCl_2$ and 'wasserglas' was helpful in depressing the decay of the peroxide liquor and in obtaining reproducible degradation curves. To this solution was then added, with a syringe, a discrete amount of hydrogen peroxide, equivalent to 0·02 mol/litre H_2O_2 into the reaction vessel. The pH was 10·5 after the addition of H_2O_2. After defined reaction times, the solution was pumped in a flow cell connected with a Perkin Elmer (Überlingen, Germany) Lambda 2 UV-VIS spectrometer in order to monitor the progress of the degradation reaction.

During the bleaching reactions of the reactive dyes **1**–**17**, at pH 10·5 and 60°C, a concurring hydrolysis of the reactive groups occurs which, however, can be ignored. We conclude this from experiments with some hydroxyethylsulphonyl (HES)/MCT dyes (**1**–**5**) which gave analogous results concerning the substituent effects on the degradation.

The buffer solutions for measuring the pH dependence of the fading reaction were as described in part II.[3]

2.3 Peroxide degradation on cellulose film

Samples of dyed cellulose film (one sample per dye, approximately 1 × 3 cm each) were placed into 100 ml of water containing 5 g/litre of sodium carbonate, 0·15 g/litre of magnesium chloride, 1·2 g/litre of sodium silicate ('wasserglas'), and 0·06 mol/litre hydrogen peroxide. This solution was held at a constant 60°C in a shaking thermostat for 3 h. The samples were then rinsed with water and dried. The dye content was finally measured by means of a Perkin Elmer (Überlingen, Germany) Lambda 2 UV-VIS spectrometer.

3 RESULTS AND DISCUSSION

3.1 Investigations into the mechanism of peroxide fading

Investigations into the mechanism of dye degradation by peroxide were carried out with the model dye **18** (C.I. Acid Red 1) in aqueous solution. As in the case of hypochlorite degradation,[3] a significant influence of dyestuff aggregation on the fading kinetics was observed. This could be demonstrated by the increase in reaction rate upon the addition of solvents (such as ethanol and dimethylacetamide) having a disaggregating effect.[17]

According to the procedure which we applied in our investigations into hypochlorite degradation (part II[3]), we used the pH dependence of the bleaching curve of dye **18** (Fig. 1) as a helpful tool in order to understand the mechanism of the fading reaction. As can be seen in Fig. 1, there is a strong increase in the reaction rate, beginning at pH 9·5, and increasing with pH value, finally reaching a discrete maximum at approximately pH 10·5, and, at higher pH values, the degradation rate is then reduced again. This result is

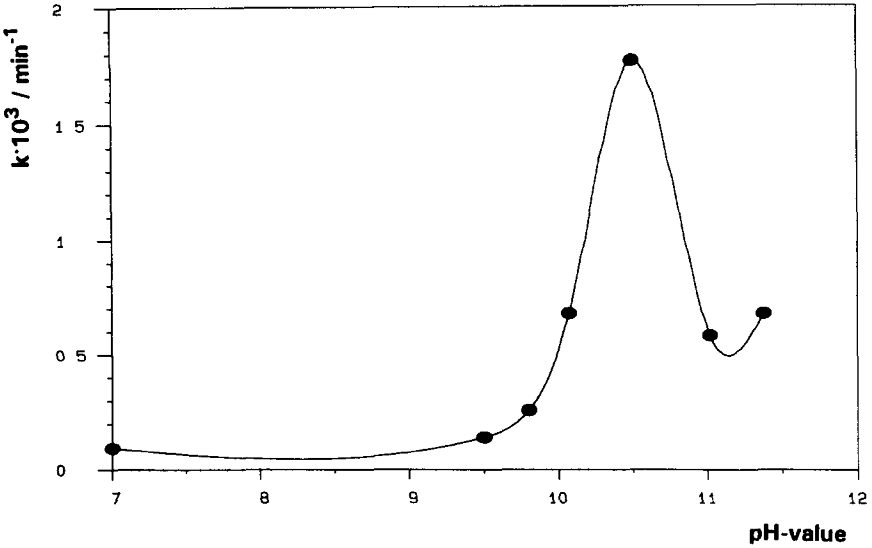


Fig. 1. Influence of the pH value on the peroxide degradation of C.I. Acid Red 1 in water. $[H_2O_2] = 0{\cdot}03$ mol/litre, $[Dye] = 5 \times 10^{-5}$ mol/litre; 60°C.

completely inconsistent with the assumption of the peroxide anion $HO_2^{\ominus}$ as the active bleaching agent, according to

$$H_2O_2 \rightleftharpoons HO_2^{\ominus} + H^{\oplus}$$
$$pK_a = 11{\cdot}6\ (25°C)$$

since the fading rate significantly decreases at strongly alkaline pH values, while the $HO_2^{\ominus}$ concentration does not. The effectiveness of dye degradation is even reduced before H_2O_2 is half dissociated.

The pH dependence of the degradation of dye **18** is in accord with the pH-dependent peroxide bleaching curve of cotton[16] and tea-soiled cotton fabric.[8] In order to check for a potential radical mechanism we applied hydroquinone as a radical scavenger; this proved to depress the fading rate very efficiently, while, on the other hand, singlet oxygen scavengers did not.[17] Thus, the assumption of a radical involving a degradation pathway is clearly supported by our results. There is also a striking concurrence with the peroxide bleaching curve published by Dannacher & Schlenker,[8] who favoured the perhydroxyl radical anion species as active agent, since the formation of the latter species has an identical pH dependence as the observed bleaching curve.

3.2 Substituent effects on the dye degradation by peroxide in aqueous solution

Table 1 shows the rate constants for the degradation of dyes **1**–**17** by hydrogen peroxide in aqueous solution, containing 10% DMA (for disaggregation), according to pseudo-first order kinetic evaluation. The reaction order proved to be clearly pseudo-first order, with good reproducibility in solutions containing 10% DMA, but, surprisingly, a complex reaction order with poor reproducibility was sometimes found in water (the reaction order was determined from the slope of the $\log \Delta E/\Delta t$ versus $\log E$ plot as described in part II[3]).

If one looks at the data in Table 1, it is clear that the type and position of the substituents in the chromophore molecule have a significant impact on the rate of degradation. Electron donating substituents located in the para position of the diazo component seem to favour the degradation (**1**), while electron withdrawing ones seem to retard it (**5**), as one can conclude from the series **1**–**5**. But, the Hammett plot (Fig. 2), shows that there is no systematic influence of the para substituents on the degradation rate according to this correlation.

Furthermore, ortho substituents in the diazo component greatly decrease the degradation reaction of the dyestuffs (**6**–**12**) with *o*-SO_3H (**10**) and *o*-COOH (**12**) being by far the most effective (Table 1).

The observed substitution pattern on the peroxide degradation is very

TABLE 1

Degradation of **1–17** by Hydrogen Peroxide in Aqueous Solution. Pseudo-First Order Rate Constants k and pK_a Values of the Dyes. $[H_2O_2] = 0{\cdot}02$ mol/litre, [Dye] = 10^{-4} mol/litre, pH 10·5, 60°C, in 10% DMA, 0·15 g/litre $MgCl_2$, 1·2 g/litre Sodium Silicate

Dye	$k \times 10^3$ (min^{-1})	pK_a
1	62	10·96
2	40	11·22
3	38	11·15
4	42	10·72
5	24	10·53
6	4·0	11·03
7	6·0	11·94
8	5·3	11·53
9	2·4	12·26
10	0·9	11·74
11	5·2	11·64
12	0·7	12·93
13	4·9	12·90
14	8·1	12·50
15	9·4	≈12·5
16	22	10·50
17	37	11·00

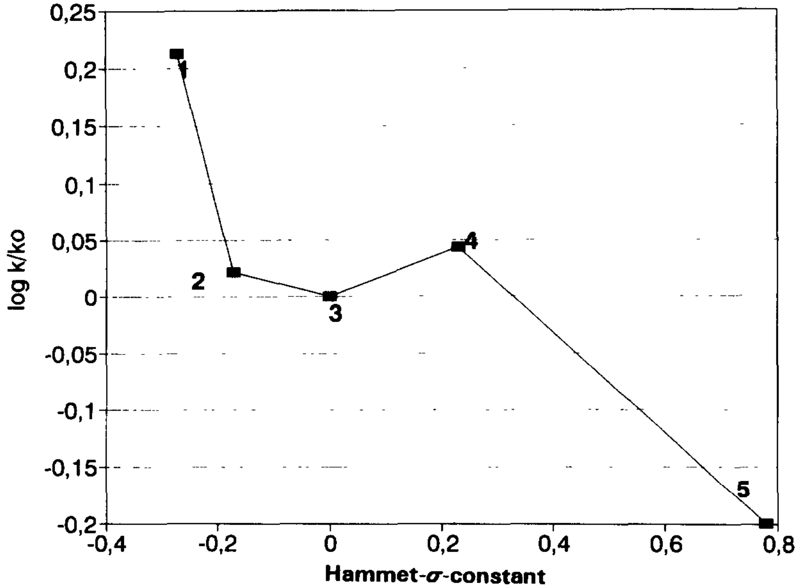


Fig. 2. Hammett plot for the peroxide fading of the dyes **1–5** in aqueous solution (10% DMA). $[H_2O_2] = 0{\cdot}02$ mol/litre, [Dye] = 10^{-4} mol/litre; 60°C, pH 10·5; k_o reaction rate of dye **3** (H).

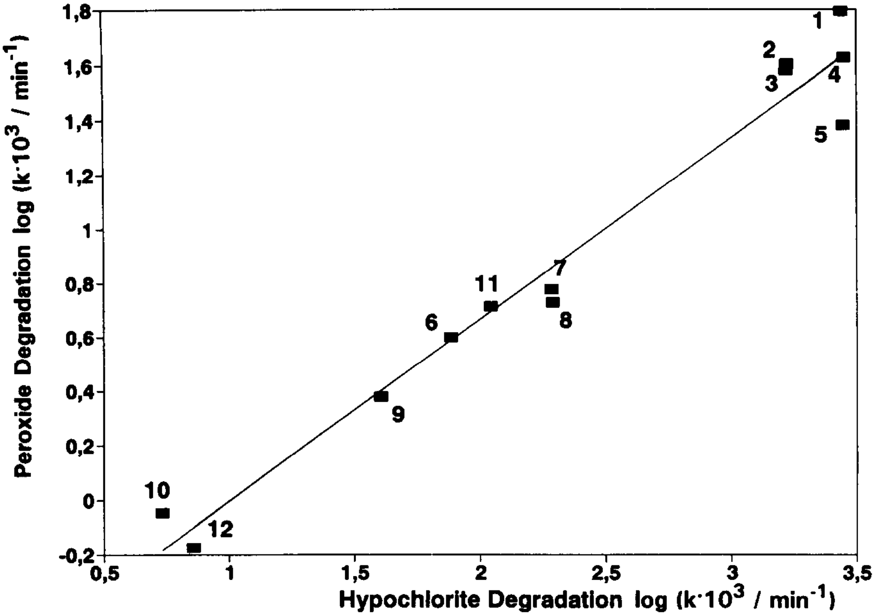


Fig. 3. Correlation of the rate constants of degradation for dyes **1–12** by hypochlorite[3] and peroxide (Table 1). Hypochlorite degradation: $[HOCl] = 5 \times 10^{-4}$ mol/litre; $[Dye] = 5 \times 10^{-5}$ mol/litre; 0–2°C, pH 7. Peroxide degradation: $[H_2O_2] = 0{\cdot}02$ mol/litre, $[Dye] = 10^{-4}$ mol/litre; 60°C, pH 10·5.

similar to the results obtained in the hypochlorite fading for dyes **1–12**.[3] Figure 3 shows a correlation for the rates of these two degradation reactions for the dyes **1–12**. Evidently, this correlation is very good and thus we suggest that, in both fading processes, we face similar criteria of dye stabilities, despite the clearly slower dye degradation by peroxide than by hypochlorite. From this correlation we conclude that the pK_a values of the dyes, referring to the dissociation of the NH hydrazone group,[2] should be decisive in the case of the peroxide degradation, in the same way as observed in the hypochlorite series,[3] and that the degradation should progress via the dissociated form of the dyes. Figure 4 illustrates the relationship of dye fading by hydrogen peroxide and the pK_a values of the dyes.

The correlation between $\log k$ and pK_a (Fig. 4), with the expected negative slope, is quite reasonable for a great number of dyes. However, some dyes deviate significantly (**6**, **10**, **13–15**). We suggest that several reasons may be responsible for the deviation, namely differences in the physical state (aggregation) despite the application of DMA[3] (**6** and **10**), further steric, electrostatic and electronic effects. As an example, dyes **13–15** clearly show higher degradation rates than dyes **9** and **12** which have comparable high pK_a values. This may be explained by the strong electron donating effect of

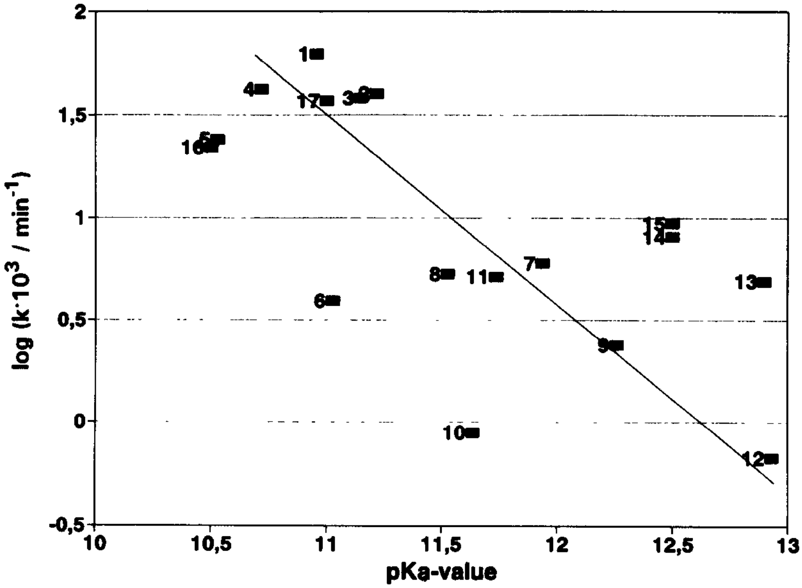


Fig. 4. Influence of the pK_a value of dyes **1**–**17** on the reaction rate constant (pseudo-first order) of the degradation by peroxide in aqueous solution (10% DMA). $[H_2O_2] = 0{\cdot}02$ mol/litre, $[\text{Dye}] = 10^{-4}$ mol/litre; 60°C; pH 10·5.

the amino and alkylamino groups attached to the naphthalene ring of the chromophore in dyes **13**–**15** which favours oxidative degradation; on the other hand, replacing the alkylamino groups by the less electron donating acetylamino groups (**16**, **17**) the peroxide fading is accelerated rather than reduced. Apparently, the clearly lower pK_a values are now decisive.

In order to unequivocally underline this, it is significant that, in the series of dyes with various substituents at the N-atom of the H-acid (**13**–**17**), dyes **13**–**15** with hydrogen and methyl substituents show, due to their high pK_a values, a retarded degradation compared to dyes **16** and **17**, both of which contain an acetyl substituent.

We have shown (Fig. 2) that the dyes with para-substituents in the diazo compound, **1**–**5**, do not give a reasonable linear relationship with respect to the Hammett plot. If we assume, however, that degradation by peroxide predominantly progresses via the dissociated form of the dyestuffs, in analogy to the hypochlorite fading,[3] differences in the equilibrium concentrations of the dissociated dyes have to be taken into account. This consideration leads to an expanded Hammett plot[3] according to eqn (1), which was discussed in detail in connection with the hypochlorite fading of the dyes in Part II.[3]

$$\log\frac{k}{k_o} + pK_a - pK_{a,o} + \log\frac{1 + 10^{pH - pK_a}}{1 + 10^{pH - pK_{a,o}}} = \rho \cdot \sigma \qquad (1)$$

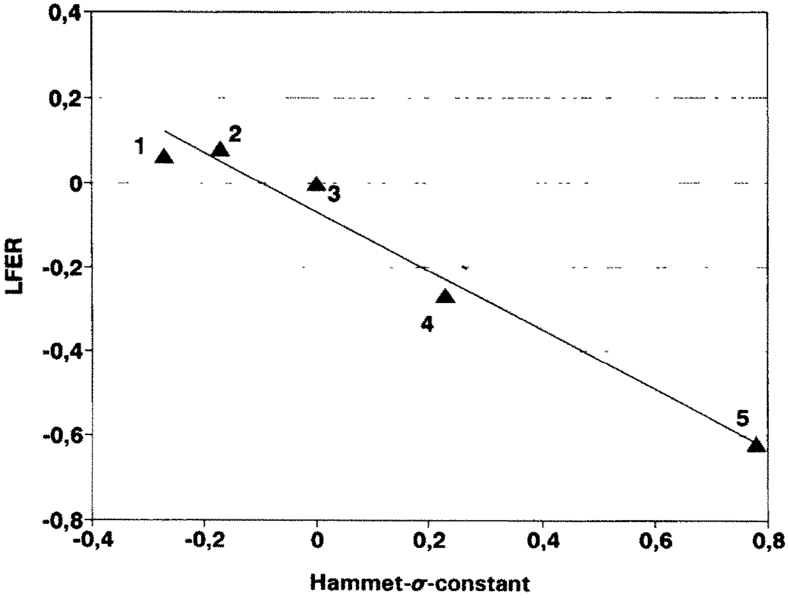


Fig. 5. Expanded Hammett plot according to formula (1) for the peroxide fading of **1**–**5** in aqueous solution (10% DMA) $[H_2O_2] = 0{\cdot}02$ mol/litre, [Dye] = 10^{-4} mol/litre; 60°C; pH 10·5; LFER—left side of eqn (1).

'o' refers to hydrogen as substituent (dye **3**). The correction of the original Hammett correlation (Fig. 2) with consideration of the pK_a values of the dyes than yields a more reasonable linear relationship (Fig. 5, $\rho = -0{\cdot}705$). As in the case of hypochlorite fading, we therefore conclude that the dissociated hydroxyazo dye is predominantly relevant to the peroxide degradation reaction.

3.3 Dye degradation on cellulose substrates

Dye degradation by peroxide on cellulose film is much slower than in aqueous solution. In general, the influence of the substituents in the chromophore on the degradation (Table 2) is similar to the results we found in aqueous solution (see Section 3.2), with dyes **10** (*o*-SO_3H) and **12** (*o*-COOH) being the most stable, followed by the other ortho substituted dyes **7**–**9**; dyes with para substituents in the diazo component are somewhat less stable. However, there are some significant discrepancies between the dye degradation on cellulose and in aqueous solution, which is very likely due to differences in the physical state. Furthermore, differences in the dye distribution in cellulosic substrates, covalently bound on the surface of the materials, in greater voids, or in small micro pores, may have an influence on

TABLE 2

Degradation of **1–17** by Hydrogen Peroxide on Cellulose Film. Dye Degradation in Per Cent after 3 h of Peroxide Treatment. $[H_2O_2] = 0{\cdot}06$ mol/litre, pH 10·5, $[\text{Dye}] \approx 10^{-5}$ mol/g; 60°C, 0·15 g/litre $MgCl_2$, 1·2 g/litre Sodium Silicate

Dye	*Degradation* (%)
1	24·3
2	15·2
3	12·7
4	14·8
5	15·6
6	16·4
7	9·2
8	9·9
9	9·3
10	5·2
11	13·4
12	3·4
13	11·9
14	11·5
15	20·0
16	24·4
17	24·6

the degradation by chemicals diffusing into the film or the fibres, respectively.

In Fig. 6, the fading (percentage dye destruction after 3 h exposure) of the dyes by hydrogen peroxide in cellulose film is plotted versus the pK_a values of the dyes. Many dyes correlate fairly well, while others are degraded faster than expected from their pK_a value (**1**, **13**–**17**). For dyes **1** and **13**–**15**, the electron donating effect of the *p*-methoxy group in the diazo moiety and the (alkyl)amino groups attached to the naphthalene ring (**13**–**17**) may have an additional effect on the oxidative dye degradation, as in aqueous solution (Section 3.2).

Furthermore, it can be seen from Fig. 6 that dyes **2**–**12**, containing a bifunctional monochlorotriazinyl/vinylsulphonyl reactive system, correspond to the linear relationship (percentage dye fading versus pK_a). On the other hand, the monofunctional vinylsulphonyl dyes **13**–**17** do not fit this correlation, while they are degraded faster. According to these results, it seems that a bifunctional reaction of dyes with cellulose may reduce the sensitivity of the dyes to degradation reactions by chemicals, and thus

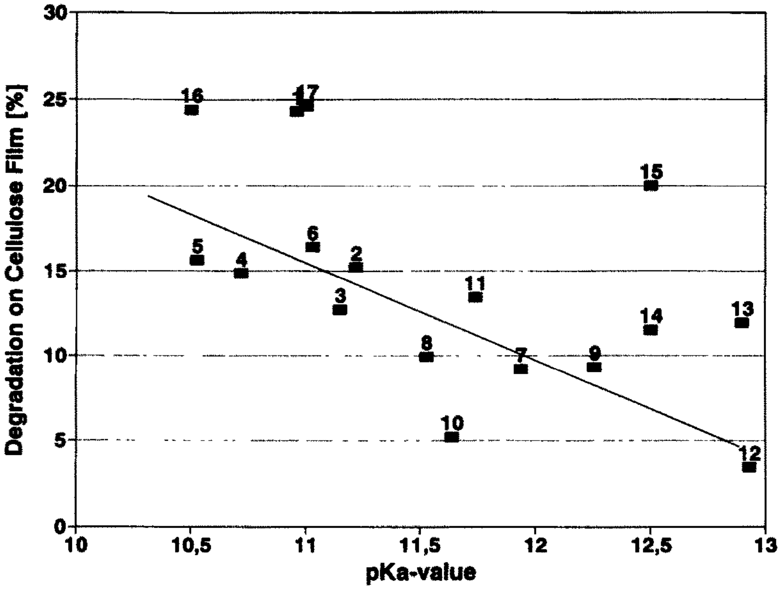


Fig. 6. Influence of the pK_a value of dyes **1–17** on dye destruction (%) on cellulose film after 3 h of exposure to aqueous hydrogen peroxide solution (Table 2).

enhance the corresponding colour fastness, but, further studies are necessary to further clearly elaborate this.

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