Dyes and Pigments 21 (1993) 45–66

Structure Reactivity Correlations of Azo Reactive Dyes Based on H-acid. II. Dye Degradation by Hypochlorite[1]

Karl Bredereck* & Christian Schumacher

Institut für Textil- und Faserchemie, Universität Stuttgart,
Pfaffenwaldring 55, 7000 Stuttgart 80, Germany

(Received 5 August 1992; accepted 14 September 1992)

ABSTRACT

In this paper we report on substituent effects on the degradation of azo reactive dyes based on H-acid by hypochlorite in aqueous solution and on cellulosic substrates. Based on the pH dependence of the fading reaction, we establish a new perception which says that in the pH range above 5 only the dissociated form of the corresponding ortho-*hydroxyazo dyes undergoes the degradation, and thus the dye's pKa value becomes a decisive criterion for the fastness to hypochlorite. With this background at hand, we use an expanded version of the Hammett equation, including the dyes' pKa values, to yield a linear free energy relationship. Also, the effect of dyestuff aggregation on the fading is investigated.*

1 INTRODUCTION

The demand for reactive dyes is increasing year by year. Yet one has to cope with some major challenges, notably the fixation yield in exhaustion-dyeing, the levelness of the dyeings, and problems concerning some fastness requirements. Among the problems which can occur in the fastness of reactive dyeings, the fastness to chlorinated water, perspiration–light and peroxide washing are considered very important.[2] Yet our present knowledge about the chemical and physical background concerning these key fastness requirements is sparse.

The fading of dyed textiles by chlorine or hypochlorite is still a serious

---

* To whom correspondence should be addressed.

problem in countries with highly chlorinated tap water, like Japan or the USA. In the USA, chlorine is still the principal disinfectant for the treatment of drinking water, due to the low costs and the effectiveness in destroying bacteria.[3] For this purpose, *c.* 1 ppm of active chlorine is added to the tap water for sterilization. However, chlorine affects certain dye/fibre combinations, resulting in a reduction of colour. Especially the fastness properties of many reactive dyes on cotton fabrics are often poor.[4] Over the years, the dye chemist has become conversant with numerous empirical rules, yet present knowledge about the chemical and physical background is more limited.

Most of the work that has been done on the fastness to chlorine has covered the fading of commercial dyes, while the chemical structures of the investigated dyes were only partially related,[3,4] or only the reactive groups were varied while the chromophore was maintained.[5] However, in the oxidative degradation of dyestuffs the chromophore is, in general, the weak part that is being destroyed.[6] Our prime objective is to look for correlations between the dye constitution and fading behaviour, e.g. in terms of linear free energy relationships with substituent constants. This is only possible on the basis of a series of very closely related dyestuff structures.

One of the first publications dealing with the destruction of azo dyes by chlorine was the paper of Schmidt, who reported on the regeneration of the diazonium salt during this reaction.[7] Later this was confirmed by other research.[8–10] The regeneration of the diazonium salt was found in other oxidative degradation reactions as well, e.g. by chromic acid or cerium salts,[6] by nitric acid,[11] by singlet oxygen,[12] by N_2O_3[13] and by bromine.[14] On the side of the coupling component, chlorinated quinones[10,15] or phenols,[7,9] respectively, were reported as degradation products of chlorination.

There are some discrepancies in the literature concerning the mechanism of the degradation by chlorine. According to Shilov,[9] HOCl is added across the N=N double bond in the initiating step, leading to the degradation. In contrast to this finding, Gregory and Stead postulated Cl^+ as the reactive species, which then would react with the azo dye to yield an *N*-chloro compound.[15] The species Cl^+, however, is too thermodynamically unstable to be involved in any reaction.[16] Furthermore, the hydride anion was postulated as the leaving group by Gregory and Stead.[15] It was suggested that the hydrazone tautomer reacts predominantly in oxidative fading,[6] which was reported to be valid for the fading by HOCl as well.[15]

Gregory and Stead[15] reported on substituent effects on the degradation of anionic azo dyes in aqueous solution. A favourable retarding effect was observed when bulky substituents are located *ortho* to the azo linkage, but yet some questions are still unanswered. Unfortunately, the authors published only reaction half-times rather than kinetic rate constants, and the concentration of the active chlorine was changed several times during their experiments, which does not particularly enhance the clarity. Also, no consideration was made about dyestuff aggregation which was suggested to have a stabilizing effect upon the hypochlorite degradation by Broecker *et al.*[17] and again in a recent paper.[18]

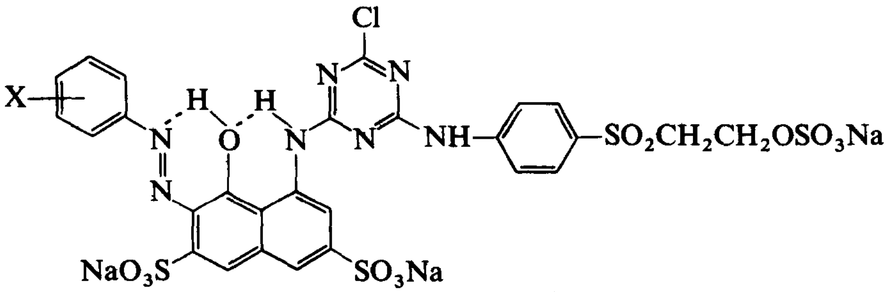
Some of our former work concerning the mechanism of fading of azo dyes on the exposure to hypochlorite covered the degradation of arylazophenols and -naphthols by *tert*-butylhypochlorite in organic solvents.[19,20] *Ipso*-substitution by chlorine and concomitant arylazo rearrangement was found to be a major pathway in some cases.

In this paper we report on the kinetics and the mechanism of the degradation of monoazo reactive dyes based on H-acid with systematically varied substituents in the diazo moiety, *ortho* and *para* to the azo linkage, by the action of hypochlorite. Our investigations deal with the fading of dyes both in aqueous solution and in the chemically fixed state in cellulose after reactive dyeing. Apart from the influence of substituents on the degradation, we also investigated the effect of further important factors on the degradation in aqueous solution, such as the pH dependence and the effect of additives that either favour or disfavour the aggregation of dyestuffs. Other important dye properties, the p*K*a values and the dye aggregation, have already been discussed in Part I[21] and are now linked with the dye degradation.

2 EXPERIMENTAL

2.1 Dyes and dyeings

The dyes used for our investigations were monoazo dyes based on H-acid with bifunctional reactive groups whose structures are shown as follows:



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**)

The preparation, characterization and purification of the dyestuffs as well as their dyeing behaviour were described in Part I.[21]

The dyeing of cotton fabric was performed in an all-in exhaustion process in an Ahiba-Turbomat (Ahiba, Birsfelden, Switzerland) with 1% o.w.f. (the dyes with poor fixation yields, **9** and **11**, were dyed with 2% o.w.f.), at a liquor ratio 1 : 10, in a three-step process: dyeing by heating up to 60°C within 30 min with 50 g/litre NaCl and 5 g/litre sodium carbonate; this temperature was then held for 30 min, then 1 ml/litre of 32·5% sodium hydroxide solution was added and the dyeing was continued for a further 45 min. After the dyeing the dyed samples were extracted with dimethylformamide (DMF)/water (1 : 1) at room temperature overnight in order to remove the unfixed dyestuff. The cotton samples so dyed contained *c.* 10^{-5} mol/g of dyestuff.

The dyeing of ®Cellophane film was conducted in a thermostat under vigorous shaking at a liquor ratio of 1 : 40 by use of the same temperature–alkali programme. The higher liquor ratio was necessary to achieve level dyeings for the ®Cellophane film, and lower fixation yields caused by the higher liquor ratio were compensated by applying 2% o.w.f. on ®Cellophane. With this procedure we obtained dyed samples on ®Cellophane with approximately the same amount of dye as on cotton (10^{-5} mol/g).

2.2 Hypochlorite degradation in aqueous solution

Chlorine bleach liquor was generated by injecting gaseous chlorine into an aqueous solution containing sodium hydroxide. This liquor was then stored in a refrigerator. The content of chlorine was regularly estimated before use by means of iodimetric titration.

The hypochlorite degradation reactions were conducted as follows: a solution of 50 ml of water containing a discrete amount of chromatographically purified dyestuff at a concentration of 5×10^{-5} mol/litre in water and 10% of buffer solution (e.g. Merck ®Titrisol, pH 7) (Darmstadt, Germany) was placed in an Erlenmeyer flask and allowed to cool in an ice bath for *c.* 3 h. To this solution was then added at 0°C a discrete volume of chlorine bleach liquor. The content of chlorine was, in all experiments, 5×10^{-4} mol/litre (40 mg/litre of active chlorine) to achieve a defined 10-fold excess relative to the dyestuff. The vigorously stirred solution was continuously pumped into a flow cell connected to a Perkin Elmer Lambda 2 spectrophotometer (Offenbach, Germany), and the asorbance was monitored throughout the whole course of the reaction by software control (Tdrive program of the PECSS-system). The fading curve so obtained was then stored as an ASCII (JCAMP) data file (*c.* 500 data points per curve) and further evaluated by means of other tailor-made computer programs which we have developed.

Additional fading curves were obtained for water containing 10% (v/v) dimethylacetamide (DMA), 10% ethanol, 10% DMF, 10% acetonitrile, 0·1 to 1 g/litre NaCl and 50 g/litre sodium sulphate. Discrete amounts (1 to 5 equiv.) of additives which are suspected to catalyse the fading, e.g. *p*-(β-sulphatoethyl)sulphonylaniline (VS-amine), were added as well.

For the reactions the following chloride-free buffer systems were applied: pH 1–4 citric acid/sulphuric acid/sodium hydroxide, pH 5–7 phosphate (®Titrisol from Merck), pH 9·6 sodium carbonate/sodium bicarbonate, pH 11 sodium carbonate and pH > 11 citric acid/sodium hydroxide. In all cases the pH value was measured before and after the reaction to confirm constancy in the pH value and to exclude errors due to changes in the pH value.

2.3 Hypochlorite fading on dyed cellulosic substrate

The fading experiments on dyed cotton (1% o.w.f., *c.* 10^{-5} mol/g of dyestuff) were conducted at a goods-to-liquor ratio of 1 : 100 at 22°C and the same hypochlorite concentration and pH value of 7 as in aqueous solution (see section 2.2) (40 mg/litre active chlorine).

The experimental procedure was as follows: in 500 ml Erlenmeyer flasks were placed six samples of dyed cotton fabric. To each flask was then added 450 ml of water and 50 ml of pH 7 buffer solution. After 10 min the appropriate amount of chlorine bleach liquor was added and the flasks (one per dye) were transferred to a mechanical shaker. Shaking at room temperature was maintained for a total reaction time of 4 h. After defined reaction times, samples were taken to monitor the reaction. The samples were rinsed in a liquor containing 1 g/litre of sodium sulphite (anti-chlorine) and several times with water. After drying overnight the reflectance curves were obtained with a Datacolor texflash equipment. The computer evaluation was performed with the ®Osiris program by Datacolor (Datacolor AG, Dietlikon, Switzerland). From the reflectance spectra obtained the Kubelka–Munk function ($K/S = (1 - R)^2/2R$; K = absorption, S = scattering, R = reflectance, $K + S + R = 1$) was calculated and only the K/S value at the reflectance minimum was used for further evaluation.

The fading experiments on dyed cellulose film were conducted under the same conditions, except for the liquor ratio which was 1 : 250 in this case. The degradation of the dyed film was measured with a Perkin Elmer spectrophotometer.

2.4 Kinetic evaluation

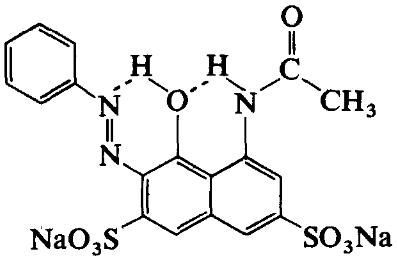
The pseudo reaction order of the degradation reactions in aqueous solution was obtained from the slope of the log–log plot of the rate law in differential form (log $\Delta(E/E_0)/\Delta t$ versus log E/E_0; E means the absorbance at λ_{max}).[22] This procedure was only possible because a sufficient number of data points (500) was collected for each curve, of which 50 were then used for the calculation by a computer program.

Most reaction rates were evaluated by means of pseudo first-order kinetics for the first phase of the fading (*c.* 250–500 s). Thus, the rate constants were obtained from the initial slope of the corresponding ln E/E_0 versus t plot. Reaction half-times were determined graphically from the E versus t plot ($t_{1/2}$ at $E = E_0/2$).

3 RESULTS AND DISCUSSION

3.1 Influence of additives on dyestuff degradation by hypochlorite in aqueous solution

According to preliminary experiments we expected that the fading behaviour of the azo dyes would be very sensitive to additives and catalytic effects. It is possible that either dyestuff aggregation or the catalysis by certain compounds affect the rate constants or even the mechanism of the fading reaction. Thus, we chose to evaluate the nature of the degradation reaction for a simple model dye without reactive groups, Acid Red 1 (phenylazoacetyl-H-acid), whose structure is shown as follows:



In the first part of this series of papers a method to assess aggregation, by means of deviations from the Lambert–Beer law of absorbance, was introduced.[21] Here, we report about the influence of aggregation on the hypochlorite fading reaction. For this purpose the fading kinetics of Acid Red 1 was investigated with respect to the presence of substances that either favour aggregation (salt) or such compounds that disfavour aggregation

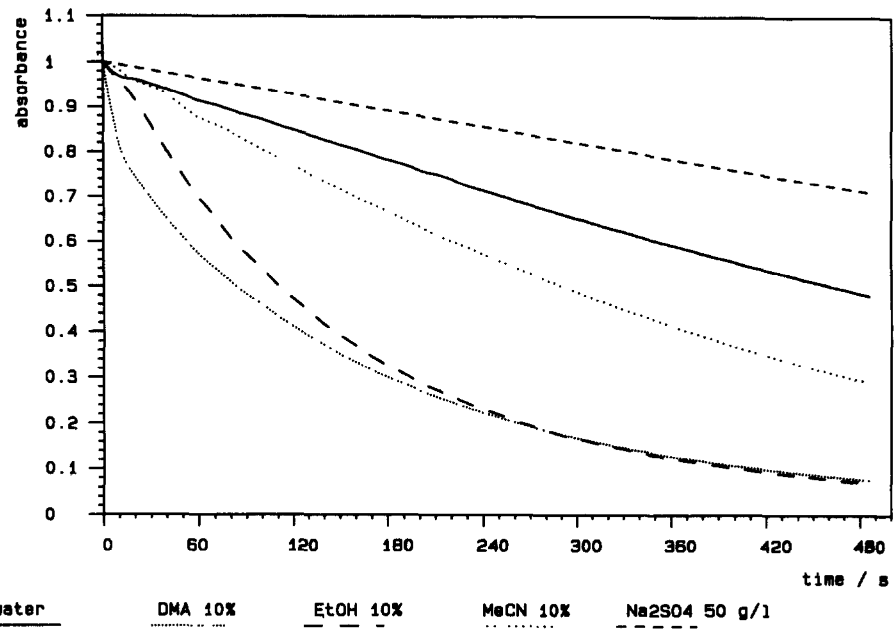


Fig. 1. Influence of solvent additives and salt on the hypochlorite degradation of Acid Red 1, at [dye] = 5×10^{-5} mol/litre, pH 7, 0°C, [HOCl] = 5×10^{-4} mol/litre.

(organic solvents), as is shown in Fig. 1. Table 1 contains the reaction half-times obtained and the calculated reaction orders.

It is well documented in the literature that Acid Red 1 tends to aggregate.[23-25] The total aggregation parameter according to the evaluation used in Part I,[21] is $\Phi_{tot} = 0{\cdot}92$ and, therefore, one can assume that this dye is at least partially aggregated under the applied conditions of the degradation reaction (5×10^{-5} mol/litre at 0°C in water). This has an effect on the fading kinetics as is expressed in the reaction order of 0·36 (Fig. 1, Table 1). A dramatic increase in the reaction rate is observed when solvents like acetonitrile, ethanol and DMA are added, resulting in a shift of the reaction order in the area close to 1 (Fig. 1, Table 1). This is a consequence of the deaggregating effect of such solvent additives, which is also underlined by the fact that the weakly or nonaggregating dyes **10** and **12** are not significantly affected by the solvent additives. However, the other, stronger aggregating dyes of this series are highly affected (change in fading rate upon addition of DMA; see Table 3 in Section 3.3 and ϕ values[21]).

On the other hand, one may expect a decrease in the fading rate and the reaction order approaching zero upon the addition of electrolytes (Na_2SO_4) due to the increase of aggregation. In fact, this assumption is true, as can be seen from the example of Acid Red 1 (Table 1, Fig. 1).

TABLE 1
The Influence of Additives on the Degradation of Acid Red 1 by Hypochlorite at a Dye Concentration of 5×10^{-5} mol/litre, in Water at pH 7, 0°C, [HOCl] = 5×10^{-4} mol/litre

Additive	$t_{1/2}$ *(s)*	*Pseudo-reaction order*
None	505	0·36
NaCl (0·1 g/l)	476	—
NaCl (1 g/l)	280	—
VS-amine[a]	230	—
Na_2SO_4 (50 g/l)	830	0
None	505	0·36
DMF (10%)	324	—
Acetonitrile (10%)	294	0·72
Ethanol (10%)	114	1·20
DMA (10%)	86	1·18

[a] VS-amine = *p*-(β-sulphatoethyl)sulphonylaniline (10^{-4} mol/litre).

However, it has to be mentioned that the fading is accelerated by the addition of NaCl. Apparently, the concentration of Cl_2 is increased by the addition of chloride ions caused by a shift of the equilibrium of the pH-dependent chlorine disproportionation, and chlorine is a stronger bleaching agent than HOCl and especially OCl^-.

In the very early stage of this work, we found that dyestuff degradation by hypochlorite is faster if the dye concentration is increased, which is very surprising. However, we could demonstrate that carefully purified samples (*via* column chromatography on RP-18 silica gel) of the dyestuffs did not show any significant concentration dependence of the fading any more. The effect is recorded in Table 2 for the *para*-substituted dyes. Hence, we must conclude that the fading behaviour of the dyes is affected by catalytic effects. The nature of this catalysis, however, is not yet completely clear. We tried to elucidate this effect by adding discrete amounts of suspect compounds, e.g. metal salts and hydroquinone, to check for a possible radical pathway (which, however, did not have a significant effect) and by adding condensation products of cyanuric chloride with different amines, including the VS-amine, and the VS-amine itself, to the reaction (Schumacher, C., unpublished). It turned out that the concentration effect exists only if the VS-amine is involved, either present in small amounts in the crude dyestuff (when no thorough purification occurs) or added as a discrete species as catalyst (see Table 1). Thus, the inference to be drawn is that a catalysis caused by impurities, arising from the VS-amine, is involved.

It is also very likely that catalytic effects can accelerate the dyestuff

TABLE 2

Pseudo First-order Rate Constants for the Hypochlorite Degradation of the Dyes 1–5, in Comparison of the Crude Dyes ($\epsilon = 1{\cdot}6$–$1{\cdot}9 \times 10^4$ litre/mol cm, 50–60% purity) with the Chromatographically (on RP-18 silica gel) Purified Dyes ($\epsilon = 3$–$3{\cdot}5 \times 10^4$ litre/mol cm, 80–90%), at Different Dye Concentrations of $[D]_1 = 2{\cdot}5 \times 10^{-5}$ and $[D]_2 = 10^{-4}$ mol/litre, in Water at pH 7, 0°C, [HOCl] $= 5 \times 10^{-4}$ mol/litre

Dye	*Crude dyes (k (10^{-3}/s))*		*Pure dyes (k (10^{-3}/s))*	
	$[D]_1$	$[D]_2$	$[D]_1$	$[D]_2$
1	3·48	9·23	2·31	2·59
2	3·11	6·34	0·71	0·45
3	2·67	6·61	0·81	0·66
4	2·23	5·00	2·07	2·43
5	1·73	2·62	2·63	3·04

degradation by chlorinated water in textile goods, depending on the environmental conditions during the exposure to chlorinated water; e.g. Perenich *et al.* recently reported on light-fading in the presence of chlorinated water.[26]

3.2 The pH dependence of the hypochlorite fading and a mechanistic interpretation

According to Gregory and Stead,[15] who investigated the degradation of a *para*-aminoazo dye, the reaction rate should be slower in alkaline medium and faster in acidic medium. On the other hand, the contrary was found for azopyrazolone dyes,[27] and catalysis by NaOH for the fading of azo dyes by HOCl has also been mentioned in the literature.[8]

The pH dependence of the hypochlorite degradation of Acid Red 1 is illustrated in Fig. 2. The increased degradation in acidic medium is consistent with the results of Gregory and Stead,[15] and very likely due to the reaction of chlorine (Cl_2) with the dye molecule. In a pH-dependent equilibrium, in the presence of chloride ions, we must always consider the appearance of HOCl, OCl^- and Cl_2 (Fig. 3) as expressed in the following equations:[28]

$$Cl_2 + 2NaOH \rightleftarrows NaCl + NaOCl + H_2O, \qquad K = 4{\cdot}5 \times 10^{-4}$$

$$NaOCl + H_2O \rightleftarrows HOCl + NaOH, \qquad K_a = 3{\cdot}2 \times 10^{-8}$$

The concentration of chlorine rises significantly at pH values lower than 5 (Fig. 3). This explains the faster fading in acidic medium. However, the observed accelerated fading in alkaline medium, with a maximum at

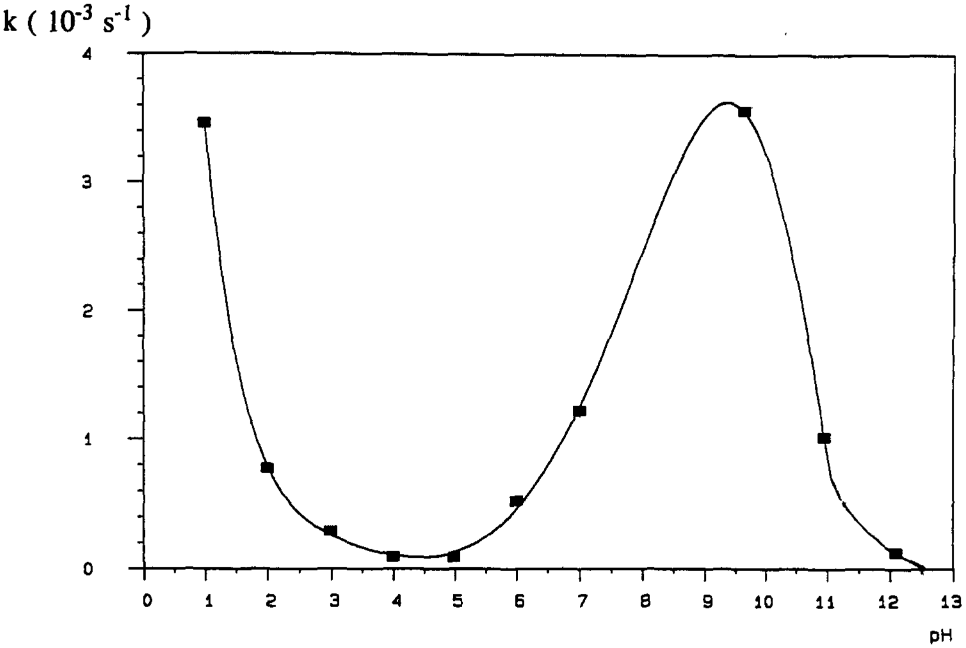


Fig. 2. pH dependence of the hypochlorite degradation of Acid Red 1, at [dye] = 5×10^{-5} mol/litre in water, 0°C, [HOCl] = 5×10^{-4} mol/litre.

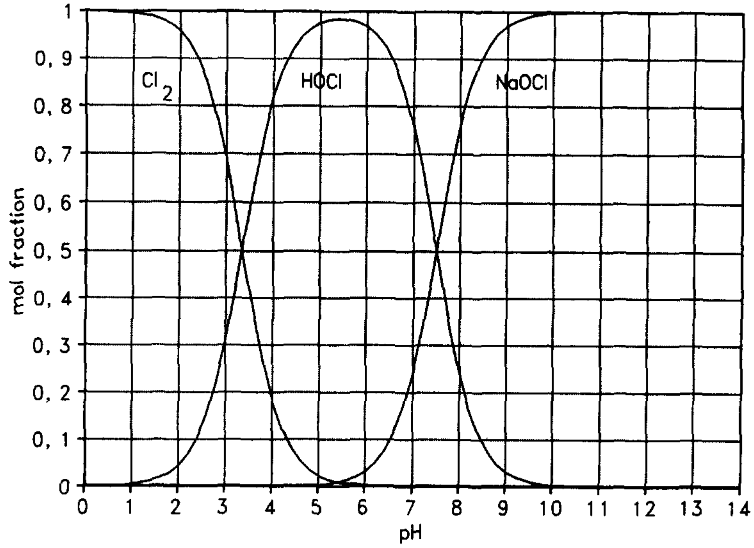


Fig. 3. Composition of the hypochlorite bleach liquor as a function of the pH value.

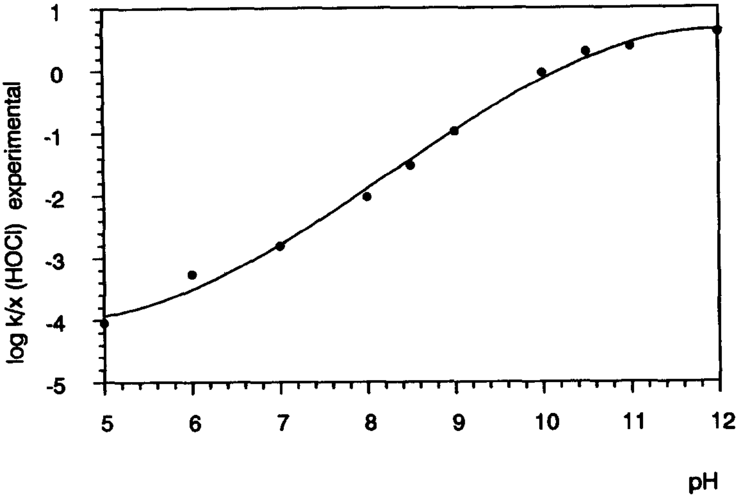


Fig. 4. log (k_{ps}/x_{HOCl}) vs. pH plot for the experimentally obtained data for Acid Red 1, [dye] = 5 × 10^{-5} mol/litre in water, 0°C, [HOCl] = 5 × 10^{-4} mol/litre.

approximately pH 9·5 (Fig. 2) must be explained differently, and will be subject to further evaluations in this section.

The decrease in the pH range above 10 may be explained by the dissociation of HOCl. In order to take this into consideration, the k/x_{HOCl} value (x_{HOCl} is the mole fraction of HOCl) was observed instead of the real rate constants k. The experimentally obtained k/x_{HOCl} values plotted versus pH (Fig. 4) yields a nearly linear correlation with a slight curvature. This observation is definitely the key kinetic result and any kinetic model must account for this result.

Based on pH-dependent rate constants, we used the following simple kinetic evaluation. In the approach to be presented here, we assume a possible parallel reaction of either the undissociated hydroxyazo dye HD (rate constant k_1) or its dissociated anion D^- (rate constant k_2). However, we can only measure the total reduction in colour and thus we observe the total dye concentration ([D] = [HD] + $[D]^-$) from the absorbance at λ_{max}. The rate law can then be written as

$$-\frac{d[D]}{dt} = k_1[HD] \cdot [HOCl] + k_2[D^-] \cdot [HOCl] \quad (1)$$

The equilibrium concentrations [HD] and $[D^-]$ were then expressed by their mole fractions x_{HD} and x_{D^-}(x_{HD} = [HD]/[D], x_{D^-} = $[D^-]$/[D]). Thus, eqn (1) is transformed into

$$-\frac{d[D]}{dt} = (k_1 x_{HD} + k_2 x_{D^-})[D][HOCl] \quad (2)$$

The fractions of x_{HD} and $x_{\mathrm{D^-}}$ were calculated by using the determined p*K*a values (p*K*a = 10·5 for Acid Red 1) of the dyes (for method see Part I[21]):

$$x_{\mathrm{HD}} = \frac{1}{1 + 10^{\mathrm{pH-p}Ka}}, \qquad x_{\mathrm{D^-}} = \frac{10^{\mathrm{pH-p}Ka}}{1 + 10^{\mathrm{pH-p}Ka}} \tag{3}$$

In the same manner the pH dependence of HOCl ($\mathrm{p}Ka_{\mathrm{HOCl}} = 7{\cdot}45$) is accounted for ($[\mathrm{HOCl}] = x_{\mathrm{HOCl}}[\mathrm{HOCl}]_0$). With this procedure the rate law yields (the p*K*a values in the formula refer to the p*K*a values of the dyes):

$$-\frac{\mathrm{d}[\mathrm{D}]}{\mathrm{d}t} = x_{\mathrm{HOCl}} \cdot [\mathrm{HOCl}]_0 \frac{k_1 + k_2 \cdot 10^{\mathrm{pH-p}Ka}}{1 + 10^{\mathrm{pH-p}Ka}} \cdot [\mathrm{D}] \tag{4}$$

The integration of eqn (4) is simple since only [D] changes with time. The kinetic evaluation according to pseudo first-order kinetics—$[\mathrm{HOCl}]_0$ is put into the pseudo rate constant—the pseudo first order rate constant k_{ps} is obtained:

$$\frac{k_{\mathrm{ps}}}{x_{\mathrm{HOCl}}} = \frac{k_1 + k_2 \cdot 10^{\mathrm{pH-p}Ka}}{1 + 10^{\mathrm{pH-p}Ka}} \tag{5}$$

The mole fraction of HOCl in the denominator of eqn (5) considers the pH-dependent HOCl dissociation.

Theoretically, there are several marginal cases, using different approximations, which seem to be conceivable for the right-hand side of equation (5):

(a) The denominator of the right-hand side of eqn (5) equals *c.* 1 for the pH range to be considered here (pH 5–10).

(b) In the case of $k_1 \gg k_2 \cdot 10^{\mathrm{pH-p}Ka}$ one may write $k/x_{\mathrm{HOCl}} = k_1$. According to this, the rate should be independent of the pH value, which does not correspond to the reality at all. In other words, the mere reaction of HD with HOCl does not explain the pH dependence of the reaction.

(c) In a second approach it seems reasonable to assume that $k_1 \ll k_2 \cdot 10^{\mathrm{pH-p}Ka}$, then eqn (5) can be transformed to yield eqn (6) after logarithmation:

$$\log \frac{k_{\mathrm{ps}}}{x_{\mathrm{HOCl}}} = \log k_2 + \mathrm{pH} - \mathrm{p}Ka \tag{6}$$

This expression explains the experimentally observed pH dependence of the fading reactions very well. Apparently, the dye anion reacts at a much higher reaction rate than the undissociated dye.

The rate constant k_2 was then determined from the log k/x versus pH

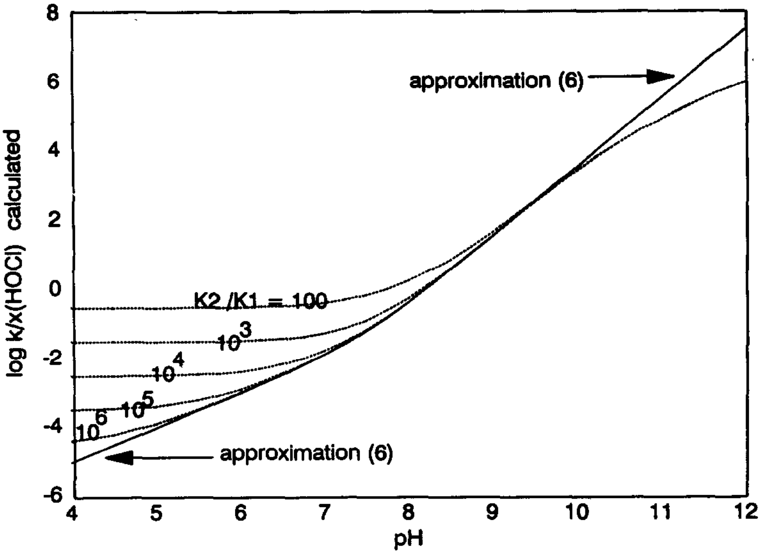


Fig. 5. log (k_{ps}/x_{HOCl}) vs. pH plot for calculated values of k_2/k_1 ratios (parameter fitting for k_1), for the exact eqn (5), (– – – –); k_2 was obtained from the experimental plot at pH 5; the parameter k_1 was then varied in order to fit the approximized function, eqn (6) (———).

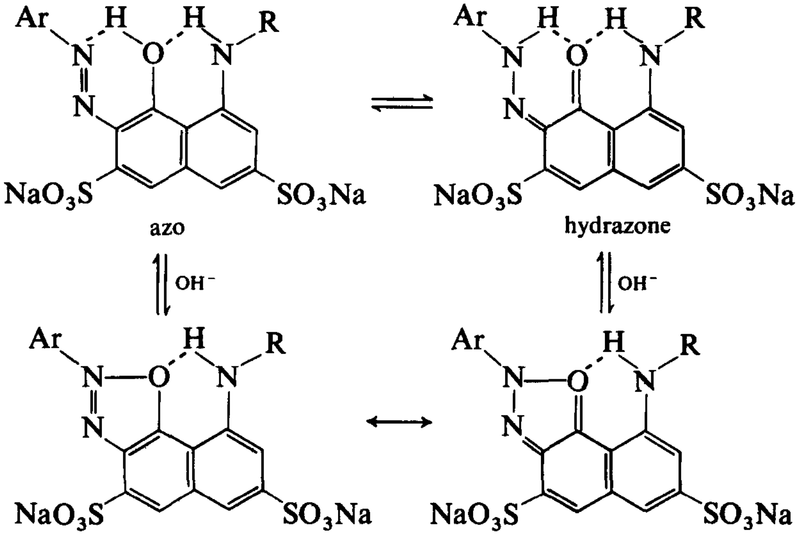
plot at pH = 5 (when x_{HOCl} = 1, see eqn (6)). The constant k_1 was estimated by parameter fitting. For this purpose, the parameter k_1 in the logarithmic expression on the right-hand side of eqn (5), the correct function, was varied to fit eqn (6), the approximation, which resembles the experimental curve (Fig. 4). The values so obtained are $k_2 = 25\ s^{-1}$ and $k_2/k_1 \geq 10^{-6}$. In other words, the dissociated dye reacts at least 10^6 times faster with hypochlorite than the undissociated dye. Consequently, even in the pH range 5–7 only the reaction of the dye anion of the hydroxyazo or hydrazone dye, respectively, is relevant for the hypochlorite degradation.

The inference to be drawn from the above observations is that practically only the dissociated form of the dye undergoes the fading reaction by hypochlorite. The exclusive reaction of the dye anion makes the p*K*a values of the dyes a decisive criterion for a dye to be fast to chlorine or hypochlorite, respectively.

The observed curvature in the experimental values (Fig. 4) is in fact realistic since x_{HOCl} also depends on the pH value and the calculated curve (Fig. 5) also shows the same curvature.

The absolute data values of the calculated curve, eqn (5) (Fig. 5), and the experimentally observed curve (see Fig. 4) do not correlate at high pH values. This may be due to dye aggregation, which decreases the reaction order below 1 (see Table 1). Our model, however, assumes a pseudo first-order reaction, which does not correspond to the reality, but, nevertheless, it allows us to evaluate the fading reactions in the initial phase by a simple first-order kinetics.

Azo–hydrazone tautomerism



Mesomeric equilibrium

In general, there is much controversy in the literature whether the azo or hydrazone form are degraded faster. This concerns not only the hypochlorite fastness, but many other oxidative fading reactions as well. However, at least here this point is of no relevance because the dissociated dyes of either the azo or the hydrazone dye are mesomeric and, therefore, undistinguishable.

3.3 Substituent effects on the hypochlorite degradation and structure–reactivity correlations

The pseudo first-order rate constants obtained for the 12 reactive dyes are shown in Table 3. The relative rate constants refer to dye 3 with hydrogen as substituent. The data measured in a water–DMA mixture are rate constants for the dyes in an almost nonaggregated physical state. Finally, the ratio k_{DMA}/k_{H_2O} directly shows the effect of dyestuff aggregation on the reaction rate.

The series of dyes with *para* substituents (**1–5**) does not yield a linear energy relationship according to the Hammett plot (Fig. 6). This holds for the data in water and the DMA series as well. In the Hammett approach, differences in the equilibrium concentrations of the dissociated forms of the dyes are not yet taken into account. However, this must be

TABLE 3
Effect of Substituents on the Pseudo First-order Rate Constants for Dyestuff Degradation of the Dyes 1–12 by Hypochlorite, at a Dye Concentration of 5 × 10^{-5} mol/litre (Dyes Purified by Chromatography), in Water at pH 7, 0°C, [HOCl] = 5 × 10^{-4} mol/litre

Dye	*k (10^{-3}/s)*		k_{rel}		k_{DMA}/k_{H_2O}
	Water	*DMA (10%)*	*Water*	*DMA (10%)*	
1	2·30	46·0	3·30	1·67	21
2	0·54	27·9	0·79	1·01	52
3	0·68	27·6	1·00	1·00	41
4	2·24	47·0	3·32	1·70	21
5	3·32	46·8	4·92	1·70	14
6	0·17	1·29	0·25	0·047	7·5
7	0·26	3·22	0·39	0·117	12
8	0·28	3·27	0·41	0·119	12
9	0·10	0·68	0·15	0·025	6·9
10	0·18	0·09	0·27	0·003	0·5
11	0·41	1·85	0·61	0·067	4·5
12	0·11	0·12	0·16	0·004	1·1

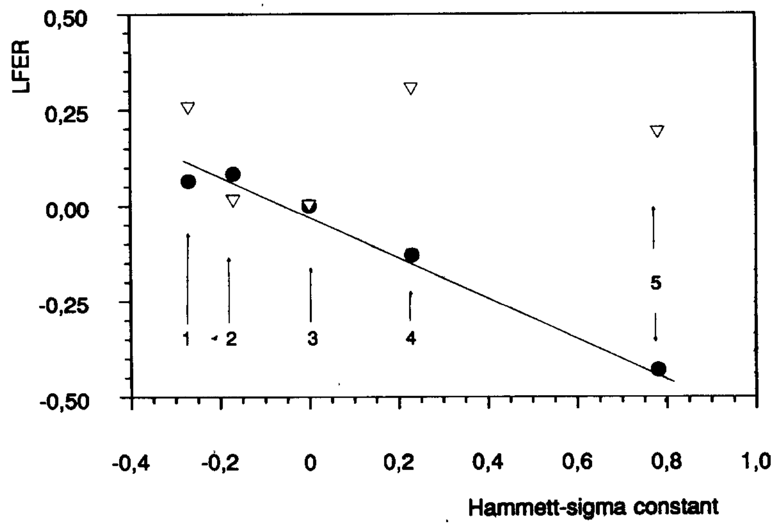


Fig. 6. Linear free energy relationships for the hypochlorite degradation of the para substituted dyes 1–5: Hammett plot (▽) and expanded Hammett plot (●); the rate constants were determined in water containing 10% (v/v) DMA at [dye] = 5 × 10^{-5} mol/litre in water, 0°C, pH 7, [HOCl] = 5 × 10^{-4} mol/litre.

considered since our findings suggest that the degradation by hypochlorite exclusively progresses via the dissociated form of the dyestuffs (Section 3.2). As was shown already in Part I,[21] the p*K*a values of the dyes highly depend on the substitution pattern. Therefore, it is understandable why the 'ordinary' Hammett correlation is not valid.

On the other hand, we can calculate the fraction of dissociated dye and check whether a LFER can be obtained for it. The fraction of the dissociated dye anion is

$$x_{\mathrm{D}^-} = \frac{10^{\mathrm{pH-p}Ka}}{1 + 10^{\mathrm{pH-p}Ka}} \tag{7}$$

If one replaces the rate constant k in the Hammett expression by the ratio k/x_{D^-}, a new expanded Hammett equation is obtained (the denominator in eqn (7) is *c.* 1 at pH 7):

$$\log \frac{k}{k_0} - \mathrm{p}K_{\mathrm{a},0} + \mathrm{p}K_{\mathrm{a}} = \rho\sigma \tag{8}$$

Again, the index 0 refers to the reference dye **3** (hydrogen). The expanded Hammett plot according to eqn (8) is shown in Fig. 6.

As a matter of fact, the correction of the original Hammett correlation with consideration of the dyes' p*K*a values, and depressing the dye aggregation by the addition of DMA, does now yield a linear relationship ('expanded Hammett plot'). The slope of the expanded Hammett plot is negative ($\rho = -0{\cdot}503$). This indicates a nucleophilic centre in the dyestuff molecule reacting with an electrophile (probably HOCl).

This correlation not only shows the effect of the substituents, but with this concept it also underlines very clearly the validity of our suggestion of a mere reaction of the dye anion.

Finally, it must be emphasized that the expanded Hammett correlation is only relevant in the series containing DMA, probably due to differences in the physical state (aggregation) of the dyes in water. The fading rates of the dyes are significantly enhanced by the addition of DMA, accelerating the degradation up to 50 times (Table 3).

A large influence of *ortho* substituents on the hypochlorite fastness has previously been reported by Gregory and Stead.[15] Yet some questions remained open in their work, e.g. dyes with an *ortho*-$COOC_2H_5$ substituent were reported to be degraded many times faster than dyes with *ortho*-COOH substituent which cannot be rationalized on the basis of only steric effects. This question can now be understood based on our results, since we show that the *ortho*-COOH group is engaged in a very strong bifurcated hydrogen bonding, leading to a significant increase in its p*K*a value.[21]

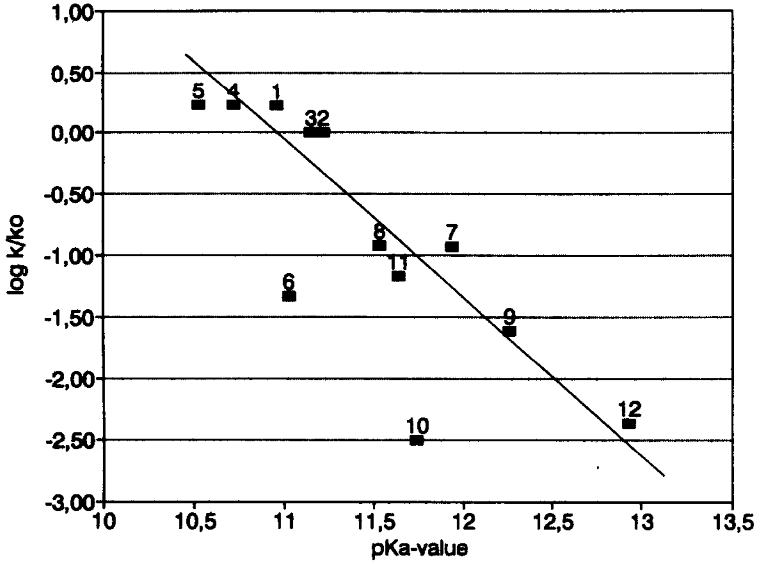


Fig. 7. log k/k_0–p*K*a plot for the dyes **1–12** with both *ortho* and *para* substituents; the rate constants were determined in water containing 10% (v/v) DMA at [dye] = 5×10^{-5} mol/litre in water, 0°C, pH 7, [HOCl] = 5×10^{-4} mol/litre.

The *ortho*-substituted dyes are indeed degraded much slower than the corresponding *para*-substituted dyes (Table 3) with all k_{rel} values being clearly smaller than 1.

Very large differences in the p*K*a values as a function of *ortho* substituents were found (Part I[21]). Now it seems conceivable to fit the *ortho*-substituted dyes (**6–12**) into a common linear free energy relationship (LFER) framework, together with the *para*-substituted dyes (**1–5**). The basis for this concept are the p*K*a values as a decisive parameter. Figure 7 correlates the rate constants with the p*K*a values of the dyes. The *para*-substituted dyes lie in the upper left corner of the diagram. A distinct scattering of the data points is encountered. This is partially due to electronic effects that are directed in the opposite direction, e.g. the electron withdrawing nitro group (dye **5**) decreases the p*K*a value relative to **3**, while a decrease in electron density lowers the reaction rate at the same time (negative slope in the expanded Hammett plot).

The *ortho*-substituted dyes are placed along a straight line down to the lower right corner of the plot. Except for the dyes **6** and **10**, all dyes fit this correlation fairly well. The deviation of those two compounds is not yet fully understood. Possibly, there are still aggregates remaining in spite of DMA addition (for differences in the physical state of the dyes, see below), or there are additional effects involved, e.g. further steric effects.

Only the nonaggregating dyes **10** and **12** are not substantially affected by the DMA addition (see k_{DMA}/k_{H_2O} in Table 3). The ratio k_{DMA}/k_{H_2O} is even smaller than 1 for **10**; in fact, the fading rate of this dye is lowered at half the rate it had in water. This is surprising at first glance, but it could also suggest that **10** may form associates with DMA. This would eventually explain the deviation of this dye from the log k/k_0 versus p*K*a correlation. Furthermore, as we shall see, dye **10** will fit a similar correlation on the fibre (see Section 3.4) and hence it is reasonable to assume that our approach with DMA as a deaggregating agent does not work in the case of **10**. We should state here that the fading behaviour of **10** is of great practical importance because most azo dyes with reasonable fastness to chlorine have *ortho*-sulpho groups.

The conclusions from our investigations concerning substituent effects on the degradation by hypochlorite are: the validity of the log k/k_0 versus p*K*a correlation in the first place, and the expanded Hammett plot in the second place, very strongly emphasize that the p*K*a values of the dyes at their *ortho*-hydroxyazo group are the decisive parameters for the hypochlorite fastness.

3.4 Degradation on cellulosic substrates

In this section we report on our results concerning the degradation behaviour of the dyes upon exposure to chlorinated water when they are chemically bound to cellulosic fibres, which is, of course, relevant in practice.

TABLE 4

Kinetic Rate Constants According to Pseudo First-order Evaluation for the Hypochlorite Degradation on Dyed Cellulose (Cotton Fabric and ®Cellophane Film) in Two Reaction Phases (Phase 1: 0–20 min, Phase 2: 30 min–4 h); 1% o.w.f. ([D] = 10^{-5} mol/g); [HOCl] = 5×10^{-4} mol/litre, *c*. 40 ml/litre Active Chlorine, pH 7, 22°C, Goods-to-bleach Liquor Ratio 1 : 100 for Cotton and 1 : 250 for ®Cellophane

Dye	*k (10^{-2} min^{-1})*			
	Cellophane film (E_{rel})		*Cotton fabric (K/S_{rel})*	
	Phase 1	*Phase 2*	*Phase 1*	*Phase 2*
1	1·87[a]	0·36	1·10[a]	0·27
2	1·76	0·43	0·66	0·31
3	1·92	0·54	0·50	0·32
4	2·19	0·50	0·90	0·39
5	2·24	0·66	0·40	0·27

[a] Inaccurate value due to poor straight line in the ln E/E_0 (or ln K/S_{rel}) versus *t* plot.

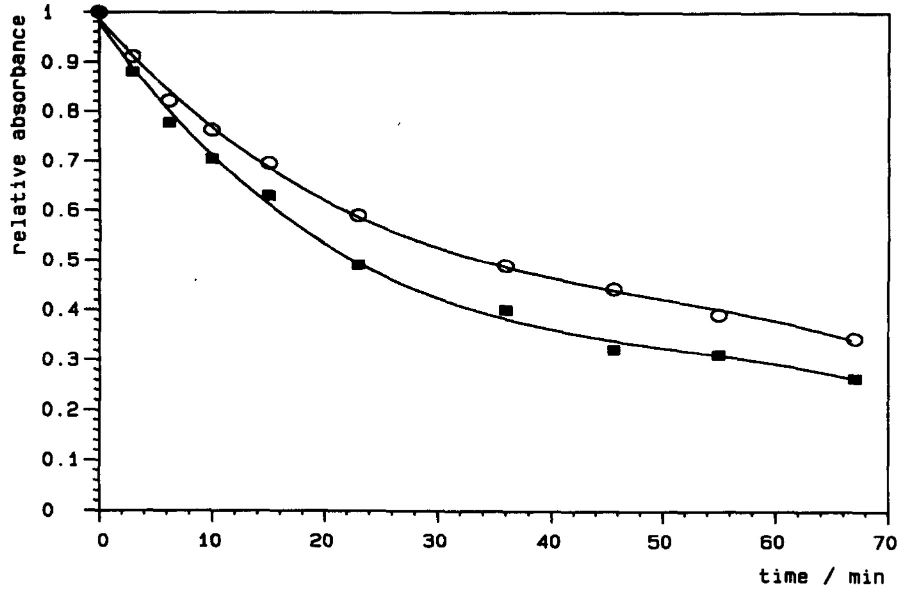


Fig. 8. Hypochlorite fading curve for ®Cellophane film dyed with **2** (○) and **4** (■), respectively; the samples were exposed to chlorinated water, at pH 7, 22°C, [HOCl] = 5×10^{-4} mol/litre.

In practice, e.g. by colour fastness assessment according to DIN 54019 (fastness to chlorinated water), all samples are graded by visual criteria. Instead, in this work only physically measurable data, the *K/S* values, which were calculated from the remission spectra for dyed cotton and the visible absorbance in the case of dyed ®Cellophane film, were used for the rating of the samples.

Figure 8 contains the fading curves in ®Cellophane for two arbitrarily selected dyes (**2** and **4**). The fading in cellulosic substrates, both ®Cellophane film and cotton fabric, is much slower than in aqueous solution. For the dye degradation on the fibre, half-times of *c.* 1 h (*para*-substituted dyes) were measured, while the half-time in solution was only about 200 s. We suggest that the slow diffusion of the active species, presumably HOCl, is responsible for the lower reaction rate in the fibre.

Apparently, we observe two phases of dye destruction in the fibre. After a first period of fast reaction (phase 1) the degradation becomes eventually very slow (phase 2, see Fig. 8). The kinetic rate constants for the two phases, according to pseudo first-order kinetic evaluation, are recorded in Table 4 for the *para*-substituted dyes. After an initial period of fast dye destruction, the rate of fading becomes, eventually, almost equal for all para substituted dyes. This effect is stronger in cotton fabric than in ®Cellophane film, where slight differences are still observed (see

TABLE 5

Dye Degradation by Hypochlorite on Dyed Cellulose (Cotton Fabric and Dyed ®Cellophane Film) (1% o.w.f. [D] = 10^{-5} mol/g); [HOCl] = 5×10^{-4} mol/litre, *c.* 40 mg/litre Active Chlorine, pH 7, 22°C, Goods-to-bleach Liquor Ratio 1 : 100 for Cotton and 1 : 250 for Cellophane

Dye	*Dye destruction after 1 h (%)*	
	®Cellophane film (E/E_0)	*Cotton fabric (K/S_{rel})*
1	51	44
2	47	42
3	49	40
4	55	48
5	56	37
6	42	12
7	20	12
8	14	17
9	5·5	6·5
10	11	3
11	28	28
12	13	13

rate constants in phase 2, Table 4). Obviously, the fading is controlled by diffusion in phase 2 after a fraction of dyestuff in the more easily accessible areas in the cellulose has been destroyed.

The above mentioned pseudo first-order kinetic evaluation for phase 2 is arbitrary, but it allows us to compare the rate constants in phase 2 with the rate constants in phase 1. However, it is equally possible to evaluate the curve according to zero-order kinetics, which would be conceivable for a diffusion controlled reaction.

The fading after 1 h of exposure to the chlorinated water is recorded in Table 5 for both *ortho*- and *para*-substituted dyes on cotton fabric and ®Cellophane film. The degradation is faster in ®Cellophane than in cotton for most dyes (**1**–**4**, especially **5**–**7** and **10**), but very similar for some others (**8**, **9**, **11** and **12**). Dye **10** has the best value of all our dyes on cotton, which is better than expected from its p*K*a value, but much worse on ®Cellophane film. Interestingly, we recall the fading in water/DMA where we observed a degradation behaviour which was better than expected from the theory as well (see Section 3.3).

Very likely, differences in the distribution of the dye in the cellulose matrix is responsible for the different fading in cotton and ®Cellophane for certain dyes. We also want to recall here that the aggregation of the dyes increases the dyestuffs' stability towards fading by hypochlorite.

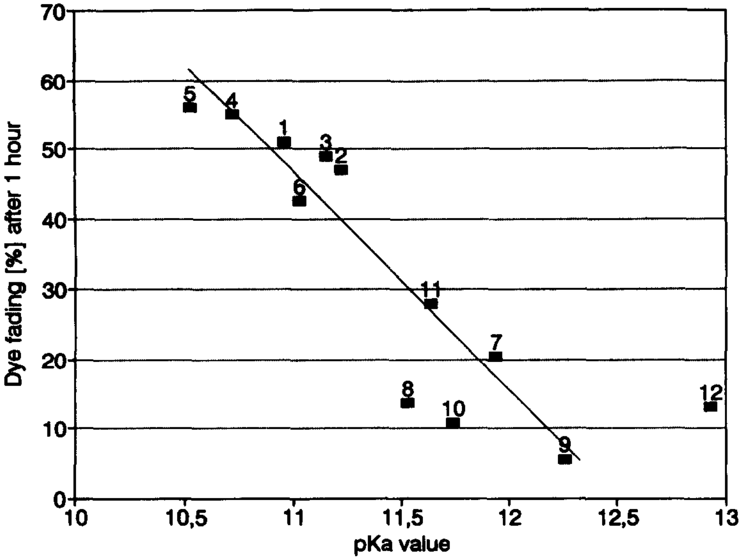


Fig. 9. Hypochlorite degradation of the dyes **1–12** on ®Cellophane film as a function of the dyes' p*K*a values (percentage dyestuff destruction after 1 h of exposure); at pH 7, 22°C, [HOCl] = 5×10^{-4} mol/litre.

The order of fading for the *para*-substituted dyes on ®Cellophane is comparable with the water/DMA series (**2**,**3** < **1** < **4**,**5**, Table 5) and hence it is likely that the physical state in ®Cellophane is more monodisperse than aggregated, which, on the other hand, makes the dyes more susceptible to dyestuff degradation. The lower fading rate on cotton, however, and the change in the order of fading (**5** < **3** < **2** < **1** < **4**, Table 5), in comparison with the water/DMA or ®Cellophane series, renders it likely that there is some degree of dyestuff aggregation in the cotton fibre in spite of the covalent bonds of the reactive dyes and the cellulose chain. Therefore, it is very probable that there is more aggregation in cotton than in ®Cellophane, since we find a remarkable retarding for the fading of some dyes on cotton fibre (**5**, **6**, **7** and **10**, Table 5).

In order to check whether a relationship with the dyes' p*K*a values exists as it did in solution, the fading in ®Cellophane (percentage dye destruction after 1 h exposure) was plotted versus the p*K*a values of the dyes (Fig. 9). As a matter of fact, the relationship is applicable fairly well. Dyes **6** and **10**, which significantly deviated from the correlation in solution, now follow the correlation much better. This supports the above mentioned theory that there is some rest-association for these two dyes, even in the series containing DMA (see Section 3.3). On the other hand, dye **12** is degraded faster than expected from its p*K*a value on cellulosic substrates, both cotton and ®Cellophane, than was suspected from the results in solution. With this correlation, it is shown that the p*K*a value is a characteristic parameter to preassess the fastness to chlorine or hypochlorite, respectively, for *ortho*-hydroxyazo dyes on cellulose.

ACKNOWLEDGMENTS

C.S. expresses his gratitude to the Stipendienfonds der Chemischen Industrie, Frankfurt, for financial support. We specially thank Dr H. Tappe and Dr W. Russ of Hoechst AG, Frankfurt, for their fruitful suggestions during this work.

REFERENCES

1. Schumacher, C., PhD Thesis, Universität Stuttgart, Germany 1992.
2. Abeta, S., Yoshida, T. & Imada, K., *Jpn. Text. News*, **340** (1983) 64.
3. Perenich, T. & Epps, H. H., *Text. Chem. Color.*, **18** (1986) 15.
4. Abeta, S., Yoshida, T. & Imada, K., *Am. Dyest. Rep.*, **73**(7) (1984) 26.
5. Abeta, S. & Fuijoka, S., *Dyes and Pigments*, **3** (1982) 281.
6. Desai, N. F. & Giles, C. H., *J. Soc. Dyers Colour.*, **65** (1949) 639.
7. Schmidt, M., *J. Prakt. Chem.*, **85** (1912) 235.
8. Shilov, E. & Minajev, W., *Melliand Textilber.*, **15** (1934) 224, 266.
9. Shilov, E., *Melliand Textilber.*, **17** (1936) 425, 504, 734.
10. Seyewetz, A. & Chaix, E., *Bull. Soc. Chim. Fr.*, **41** (1927) 332.
11. Schmidt, O., *Ber. Dtsch. Chem. Ges.*, **38** (1905) 3201.
12. Griffiths, J. & Hawkins, C., *J. Chem. Soc., Perkin Trans. II.*, (1977) 747.
13. Huisgen, R., *Liebigs Ann. Chem.*, **574** (1951) 184.
14. Bunce, N. J., *J. Chem. Soc., Perkin Trans. I.*, (1974) 942.
15. Gregory, P. & Stead, C. V., *J. Soc. Dyers Colour.*, **94** (1978) 402.
16. Bell, R. P. & Gelles, E., *J. Chem. Soc.*, (1951) 2734.
17. Broecker, B., Fiolka, P. & Rath, H., *Melliand Textilber.*, **51** (1970) 447.
18. Hamada, K., Nishizawa, M. & Mitsuishi, M., *Dyes and Pigments*, **16** (1991) 165.
19. Bredereck, K. & Schoner, R., *Tetrahedron Lett.*, **51** (1976) 4711.
20. Schoner, R., PhD Thesis, Universität Stuttgart, Germany, 1975; Hassanein, M. T., PhD Thesis, Universität Stuttgart, Germany, 1979.
21. Bredereck, K. & Schumacher, C., *Dyes and Pigments*, **19** (1992).
22. Connors, K. A., *Chemical Kinetics*, VCH, New York, 1990, pp. 17–53.
23. Tull, A. G., *J. Soc. Dyers Colour.*, **89** (1973) 132.
24. Pugh, D., Giles, C. H. & Duff, D. G., *Trans. Faraday Soc.*, **67** (1971) 563.
25. Campbell, D. S. E., Cathcart, D., Giles, C. H. & Rahman, S. M. K., *J. Soc. Dyers Colour.*, **75** (1959) 1631.
26. Perenich, T., Blackburn, R. & Wilkinson, R. P., *Text. Chem. Color.*, **23(8)** (1991) 14.
27. Piehler, G., PhD Thesis, Universität Stuttgart, Germany, 1983.
28. Peters, R. H., *Textile Chemistry*, Vol. II, *Impurities in Fibres, Purification of Fibres*, Elsevier, Amsterdam, 1967, pp. 187–202.