STUDIES IN THE STABILITY OF BONDS BETWEEN FIBRE-REACTIVE DYES AND CELLULOSE

A thesis submitted in fulfilment of
the requirements for the degree of

Doctor of Philosophy

by

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TEXT BOUND INTO

THE SPINE

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To the memory of my mother, Amy Kathleen Rocha Gomes.

Summary

A breakdown of the bond between dyes containing a 2,4-fluoro-5-chloropyrimidinyl reactive group and cellulose occurs when the dyeing is treated at room temperature in a detergent containing sodium perborate or an equivalent amount of hydrogen peroxide and is subsequently exposed to a source of heat and light.

Studies of the breakdown of the dyeings have shown that a nucleophilic substitution reaction takes place at the 5 position of the pyrimidinyl ring when the dyeing is treated with hydrogen peroxide, during which the chlorine substituent is replaced by a hydroperoxide group. It has been shown also that the dyeing has to be in its hydrolysed form (Type III) before it can form the hydroperoxide.

Other dyeings have been shown to form hydroperoxides but not all show dye fibre bond breakdown. Dichlorotriazinyl dyeings are in this last category. Dichloroquinoxalinyl dyeings, on the other hand, showed as much breakdown as the 2,4-fluoro-5-chloropyrimidinyl. Three pyrimidinyl dyes were prepared with different substituents in the 5 position of the ring: H, Cl and CN. The 2,4-dichloropyrimidinyl dyeing (with H at the 5 position) did not show any significant breakdown, even at a high pH in the hydrogen peroxide solution, whereas with 2,4,5-trichloropyrimidinyl dyeings the breakdown at pH 12 was significant.

The 2,4-chloro-5-cyano pyrimidinyl dyeing showed the highest breakdown of all, which confirms that the substituent at the 5-position of the pyrimidinyl ring is a determining factor.

The reaction which causes the breakdown of the dye-cellulose bond has been shown to be a radical reaction initiated by the decomposition of the hydroperoxide. The presence of some antioxidants when the hydroperoxide of the dyeing was exposed to the heat and light source was found to reduce the breakdown.

One of the aspects of the breakdown of the dyeings was that it was accompanied by a deterioration in brightness of the colour, and this was very marked with the yellow and orange colours.

Both the deterioration in brightness and the dye-cellulose bond breakdown were reduced by previous alkaline hydrolysis at the 5-position of the pyrimidine ring, thus confirming the relevance of the formation of a hydroperoxide at this position to the breakdown of the dyeings.

One pyrimidinyl dye which showed bond breakdown with hydrogen peroxide but could not fit the above theory was the 2-methylsulphonyl-4-methyl-5-chloropyrimidinyl dye. This dye does not produce the hydrolysed forms of the dyeing and consequently it is noteasily understood why the apparently unreactive 5 position of the pyrimidinyl ring should form a hydroperoxide via a nucleophilic reaction.

INDEX

Chapter III - Results and Discussion

CHAPTER I

INTRODUCTION

Introduction

Before the washing machine became available to most households in the industrialised world, it was common for fabrics to be washed at the boil and for caustic soda and chlorine bleaches to be added to the wash liquor. Only azoic and vat dyes, which were first used at the turn of the century, withstood such conditions. However, conditions of washing became milder with the growth of the use of domestic washing machines in the 1950's, i.e. the temperatures used were much lower and the detergents developed for use with the washing machine did not contain caustic soda nor chlorine bleaches. The first reactive dyes, the Procion M dyes patented by I.C.I. in 1956, were found to be fast to these conditions of washing and thus gained an important share of the market for cotton dyeing, since they were cheaper than vat dyes. Other reactive dyes were developed by other companies and they also showed good fastness to washing.

In 1971 Bayer introduced the Levafix EA range of dyes which were as resistant to alkaline hydrolysis as the Procion M dyes. These dyes had an advantage over the Procion M dyes, which was their higher resistance to acid hydrolysis. However, they were found not to be as fast to washing with domestic detergent. The Drimarene K range of dyes marketed by Sandoz also showed poor fastness to washing with detergents. Both the Levafix EA and the Drimarene K dyes have the

same reactive group, a 2,4-fluoro-5-chloropyrimidine ring. The component of the detergent which was found to be responsible for the loss of dye during the washing was sodium perborate, which is a bleaching agent. However, at the concentration at which sodium perborate is present in detergents, (1-5%) no significant discolouration of the dye is expected. Furthermore, what was observed was loss of dye into the wash liquor, as in the hydrolysis of the dye-fibre bond, and not fading of the colour as would have been expected from the usual action of a bleaching agent.

The effect that perborate salts had on certain dyes, such as Levafix EA (Bayer) and Drimarene (Sandoz), was recognised by the I.S.O. and recently two standard tests were introduced: the 'commercial laundering test' and the 'sensitivity to peroxy compounds' test. In the former test a standard detergent is used with 1g l^{-1} sodium perborate and in the latter only sodium perborate solution (0.4g l^{-1} available oxygen). Given this, it is surprising that no research had been reported on this field until 1979,[1] when Rattee and So tested the dye Levafix Orange E3GA with sodium perborate and with hydrogen peroxide solutions. They started by studying the loss of colour into a solution containing perborate at 50°C and at 70°C, and found that the loss of colour increased with time of reaction and concentration of sodium perborate, and was higher at the higher temperature of 70°C. The possiblity that the loss of colour was caused by the alkalinity of sodium perborate (pH = 10.2, $\pm$ 0.1) was quickly dismissed as a similar test with sodium carbonate (pH = 10.4 $\pm$ 0.1) did not cause any significant colour loss. Results therefore confirmed that sodium perborate did attack these dyes when the dyeings were submitted to washing under warm/hot conditions.

Moreover, it had also been reported by customers that some dyeings, believed to be based on the Levafix EA/Drimarene K range of dyes, which had been washed in perborate containing detergent lost colour when subsequently washed in cold water. In this case it was believed that it was the drying in sunlight that caused the breakdown of the dye fibre bonds and that the unfixed dye came off during the second washing. Rattee and So therefore proceeded to reproduce these conditions in the laboratory. Accordingly, the dyeings were immersed in sodium perborate solutions at room temperature (20°C) and were exposed to u.v. light. Instead of a second 'washing' the removable dye was extracted with solvent and its quantity measured spectrophotometrically. A study of treatment variables showed that an increase in soaking time caused an increase in breakdown, and an increase in light exposure also had the same effect. Intermediate drying before exposure to light had no significant effect on the results but intermediate rinsing with water decreased the breakdown substantially. But what was interesting about the latter effect was that breakdown of the dyeing was not completely eliminated by rinsing. This was taken as indicating the formation of an intermediate compound which was resistant to rinsing, and broke down when exposed to the light source. The heat generated by the light source was proved to be the main energy source of the breakdown of this product, since the breakdown of the dyeing at the same temperature with no light was approximately the same (within experimental error). Hydrogen peroxide was found to have the same effect as sodium perborate and when its effect was measured at two different values of pH (10.2 and 10.4) it was found that the breakdown at the higher value was greater. When sodium perborate was mixed with a standard detergent (without perborate) the relative breakdown of dye-fibre bonds was increased. These two last effects, pH and detergent effect, were not

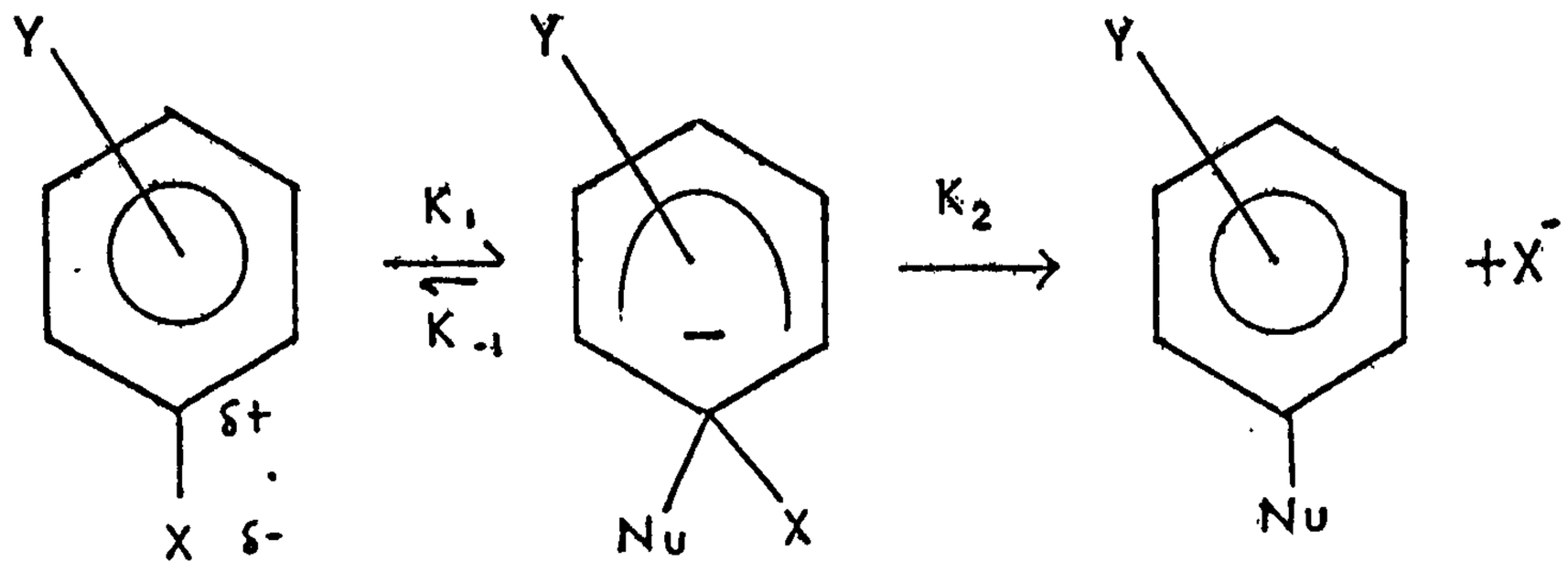
explained and were therefore followed up by Rattee and Gomes (2) in recent work carried out on the same dye. In this work, all the tests were carried out with hydrogen peroxide. The breakdown was observed to increase with increasing alkalinity of the solution. The relationship was not linear but when the corresponding values of the internal pH, computed from the values of the external pH of the solution containing hydrogen peroxide and detergent, were plotted against breakdown, the linearity of the relationship was much more apparent. The detergent was found to have two effects; one which could be attributed to the electrolytes which are part of the detergent and another effect which was suggested to be a specific detergent effect, since other electrolytes did not show it. It was therefore concluded that 2,4-fluoro-5-chloropyrimidinyl dyeings react with hydrogen peroxide and sodium perborate in solution, probably via a nucleophilic substitution reaction. The present work is an attempt at finding out more about this reaction so as to gain an insight into the reasons why this structure of dye is subject to a nucleophilic attack originating from the ionisation of hydrogen peroxide, whereas other structures of reactive dyes are not affected when subjected to the same conditions. Since nucleophilic reactions of halogenated aromatic rings depend on numerous environmental factors, this subject is discussed in detail in 1.1 and 1.2. The chemistry of pyrimidines is also given special attention in 1.3, since most of the present work involved pyrimidinyl dyes. Other subjects which are treated in more detail concern mainly the hydrolysis of reactive dyeings, with emphasis on pyrimidinyl and triazinyl dyeings (1.4), the role of sodium perborate as a source of hydrogen peroxide (1.5) and reactions of hydrogen peroxide with cellulose (1.6) and with heterocylic aromatic compounds (1.7). Finally there is a short discussion on free radical formation on cellulose (1.8), since this is believed to be the cause of the breakdown of the dye-fibre bond.

1.1 Nucleophilic replacement of halogens from aromatic compounds

Nucleophilic reactions can be divided into three categories, designated by SN_1, SN_2 and SN_2(aromatic). In the SN_1 type of reaction the bond to the leaving group is broken before that involving the attacking nucleophile has been formed. In SN_2 the bond with the leaving group is broken and the bond with the attacking nucleophile is formed simultaneously and in the SN_2(aromatic) an intermediate complex (I) is first formed with both the nucleophilic and the leaving group attached to the reaction site before the leaving group breaks away.

With the halogenated aromatic compounds nucleophilic replacement reactions are believed to be of the SN_2(aromatic) type, and there is plenty of evidence to support this, as referred to later. These reactions can be represented as follows:

(1.1)

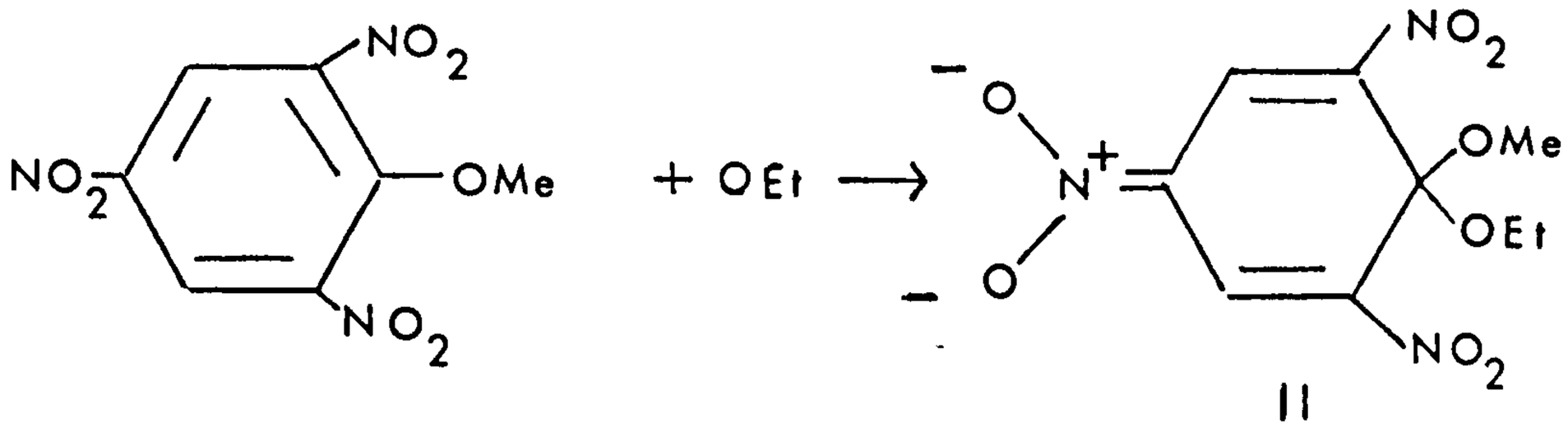


I

where X is the halogen. The presence of another electron withdrawing group, Y, is generally necessary to render the ring sufficiently active for nucleophilic attack. A group which is often used for this purpose is the nitro group, NO_2. Most nucleophilic replacement reactions on aromatic rings are in fact halogen replacement reactions. This is because the halogens, fluorine, chlorine, bromine and iodine are strongly electronegative and therefore electron withdrawing. Their

electronegativities decrease in the order F>Cl>Br>I and as a general rule this is also the order of the ease of their replacement from aromatic rings by nucleophiles although there are exceptions, as seen later.

One of the first pieces of evidence for an SN_2(aromatic) type of reaction was the identification of the intermediate complex (II) below by Jackson and Meisenheimer.[3,4]

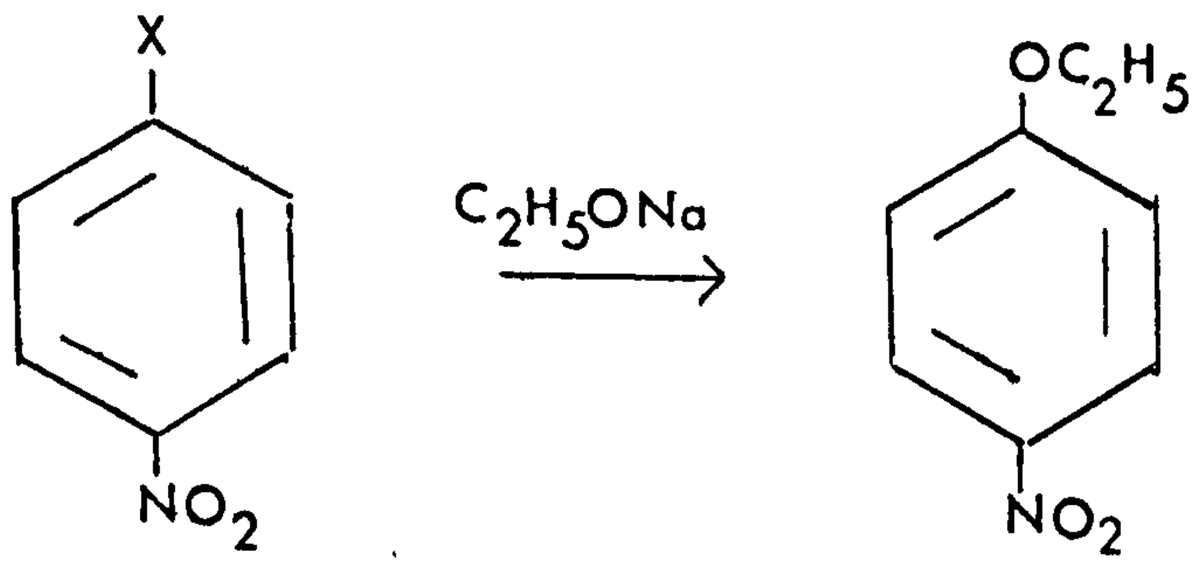


II

Further evidence for the SN_2(aromatic) mechanism has been produced by the vast number of reactions which since the identification of the 'Meisenheimer' complex have been reported to fit second order kinetics.[5] These have been compiled in a number of reviews by Bunnet. One of the first of such reactions which was studied thoroughly was the reaction of 1-chloro-2,4 dinitrobenzene with sodium alkoxide and more recent studies on reactions of 2,4-dinitrobenzenes with different substituents on the 1-position have given fresh evidence for the SN_2(aromatic) mechanism.[6]

These rections can also be called addition-elimination reactions, a term derived from the two steps of the reaction. From the equation representing these types of reaction (Equation 1.1) it is apparent that the rate determining step might lie on either side of the central intermediate (I). This in turn might influence the order of replacement of the halogens.

Taking fluorine and chlorine as examples of leaving groups, if the rate determining step is the formation of the complex, it would be expected that fluorine would be replaced more easily since it is more electronegative and this is generally the case. For example, Bevan[7] found that in the reaction shown below (Equation 1.2) the rate of reaction when X was fluorine was 230 times faster than when it was chlorine.



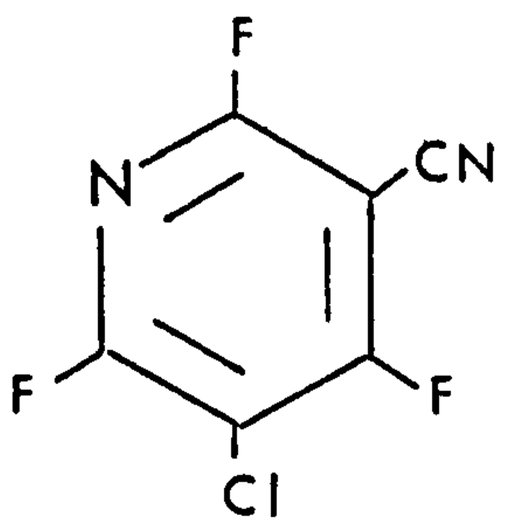
(1.2)

However, the many studies of the comparative displaceability of the halogens in various aromatic nucleophilic reactions make it clear that the four halogens do not stand in any constant order of replaceability. For example, in contrast to the reaction above (Equation 1.2) chlorine is displaced from chlorobenzene much more easily than fluorine from fluorobenzene in reaction with sodium methoxide at 165°C, and with piperidine at 210°C[8] and with potassium amide in liquid ammonia at -33°C.[9]

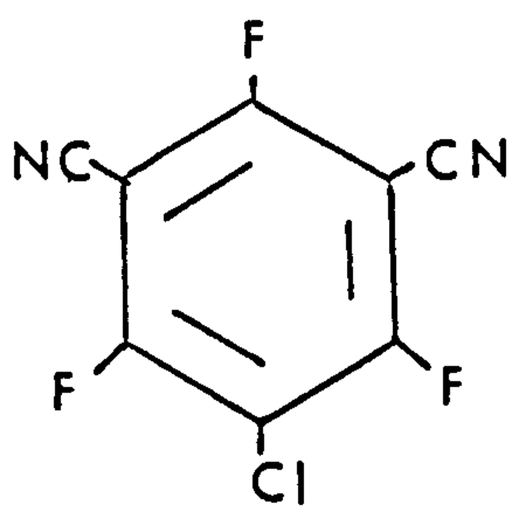
On the other hand when the halogen is in an activated situation such as fluorine in 1.2 above, fluorine seems to be by far the most easily replaced halogen. Thus, ortho-fluoronitrobenzene reacts approximately 700 times faster than ortho-chloronitrobenzene with methanolic methoxide at 25°C.[10][11] There are also important variations in the mobilities of the other halogens and the nature and degree of activation of the nucleophilic reagent. The order I>Br>Cl is displayed

in reactions of unactivated halides with piperidine and methoxide.[8] However, from activated positions the order is reversed, as for example in the reaction of alcoholic ammonia with 1-halo-2,4-dinitrobenzenes.[12]

The nature of the attacking nucleophile can also alter the order of mobilities of the halogens. For example, in attempts at condensing compounds III and IV (below) with the amino group of chromophores to produce reactive dyes, it was realised that they do not condense as easily as the corresponding chloroheterocycles.



III



IV

However, reactive dyes with fluorine containing heterocycles react with cellulose more readily than their chloro analogues. This was explained by C.V. Stead[13] as being due to a preference of the soft amino containing nucleophile for the displacement of the softer chlorine rather than the hard fluorine and that this preference is reversed in the fixation stage when the hard alkoxide ion prefers to displace the hard fluorine. A hard base, has been so called to indicate that it holds on to its electrons very strongly, is not easily oxidised and is not polarisable.[14] Bases in which the donor atom is F, O or N are examples of hard bases. Soft bases have the opposite characteristics. Lewis acids, in which the acceptor atom is small in size, of high positive charge and which lacks unshared pair of electrons in their valence shell, are found experimentally to form

more stable complexes or compounds with hard bases than with analogous soft bases. Such acceptors are called hard acids, since they also would hold on to their remaining electrons very tightly and would be non polarisable. Lewis acids, in which the reverse is true, are called soft acids. Experimentally they are found to form more stable complexes with soft bases than with similar hard bases. Thus in a SN_2 reaction, if the electrophilic centre is hard, then hard bases such as F, OH, and NH_3 will be good nucleophiles. Moreover, electron withdrawing groups make a carbon atom, for example, harder.

The issue is further complicated by the effect of solvent. The reaction involving the condensation of amines with 1-chloro-2,4-dinitrobenzene in ethanolic solution is retarded when benzene, chloro-benzene and nitrobenzene are added,[15] these being poorer ionising solvents than ethanol. However, the condensation of phenoxide ion with the same compound is less ready in methanol than in ethanol,[16] and methanol is a more ionising solvent. Cooper et al[17] predicted such effects of solvents by considering the charge magnitudes and distributions in the initial and transitional states. They divided these reactions into several types, and in type 1 the reactants could be represented by $(Y^- + RX)$ and in type 2 by $(Y + RX)$. In type 1 a more ionising solvent would decrease the rate and in type 2 it would increase it. The reaction of amine with 1-chloro-2,4 dinitrobenzene is of type 2, since the amine has no charge, whereas the reaction of the phenoxide ion is of type 1. Thus the reactions seem to confirm the predicted effect, even though this effect was originally predicted for aliphatic reactions only.

Similarly, if the rate determining step of the reaction (equation 1.1) is the second step, i.e. the decomposition of the intermediate complex with separation of the leaving group, the solvent is also expected to influence the rate of reaction. Taking fluorine and chlorine as examples of leaving groups, a change of solvent can affect them differently and can therefore alter the reactivity ratio K_{ArF}/K_{ArCl} and in some cases even reverse the order of mobility. For example, F. Pietra[18] found that the leaving group ability when computed as the ratio of the reactivities K_{ArF}/K_{ArCl} for the reactions of para-nitro benzenes with piperidine in benzene followed the order Cl>F. But he also found that the change from a non-polar aprotic solvent, like benzene, to dipolar aprotic or protic ones has a dramatic influence on the kinetics of the above reactions. Thus second order overall kinetics are observed both in dimethyl sulphoxide and in methanol. He suggested that the kinetics for the reaction in benzene were first order, and that is because non-polar aprotic solvents do not catalyse the reaction of 4-fluoro nitrobenzene, but such catalysis occurs in dipolar solvents, such as dimethylsulphoxide and methanol. He also found that the reaction of 4-chloronitrobenzenes is not catalysed by these dipolar solvents, and the mobility order in these cases was F>Cl.

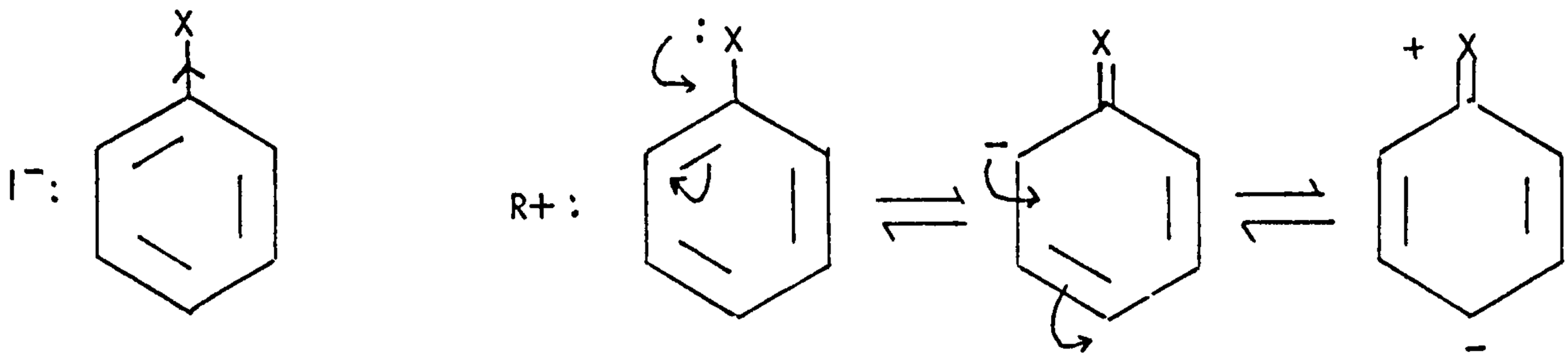
F. Pietra had shown earlier that fluoro-2,4-dinitrobenzene (FDNB) and chloro-2,4-dinitrobenzene (CDNB) also showed this pattern with 2 methylpiperidine[19] and piperidine.[20]

Hammond and Parks[21] had also observed that for reactions of FDNB and CDNB in ethanol at 50°C the ratio of the second order rate coefficients K_{ArF}/K_{ArCl} was 63 and 0.7 with aniline and N-methyl-aniline respectively, while the same ratio was only 0.07 for the reactions of N-methylaniline in nitrobenzene.

1.2 Directing, activating and deactivating effects of halogens

As already mentioned, the electronegativities of the halogens decrease in the order F>Cl>Br>I. Because of their high electronegativity they increase the electrophilic character of the molecule to which they are attached. The effect is stronger for fluorine than for chlorine, bromine or iodine in the series and decreases with the distance of the halogen from the reacting centre. This type of interaction, usually classified as the inductive effect (I) is the most general one. Thus, in an aromatic ring, the inductive effect (I) of the substituent, in this case a halogen, originates in the polarisation of the electrons in the o bond connecting it to the ring. The effect of this primary induction on the benzene ring can occur in three different ways.[22] These are as follows: by direct electrostatic interaction through space (symbol D), by successive polarisations of adjoining σ bonds in the framework of the benzene ring, (symbol Iσ), and by interaction with the aromatic $\tilde{\pi}$ system, (symbol $I_{\tilde{\pi}}$). It has been suggested by some authors[23] that $I_{\tilde{\pi}}$ is insignificant as the σ orbital adjoining the substituent to the ring is orthogonal to the aromatic $\tilde{\pi}$ bonds and interaction would be expected to be minimal. This has, however, been disputed by Chambers,[106] who suggests that the higher than expected activation of a trifluoromethyl group on the benzene ring and the deactivation effect of the fluorine when connected directly to the ring, are both due to the $I_{\tilde{\pi}}$ effect. The deactivating effect of halogens on the ortho and para positions of the ring had otherwise been attributed to the resonance effect R which involves interaction between orbitals in the substituent which are in the same plane as the $\tilde{\pi}$ electron orbitals of the benzene ring.

The two effects can be represented in the following way:



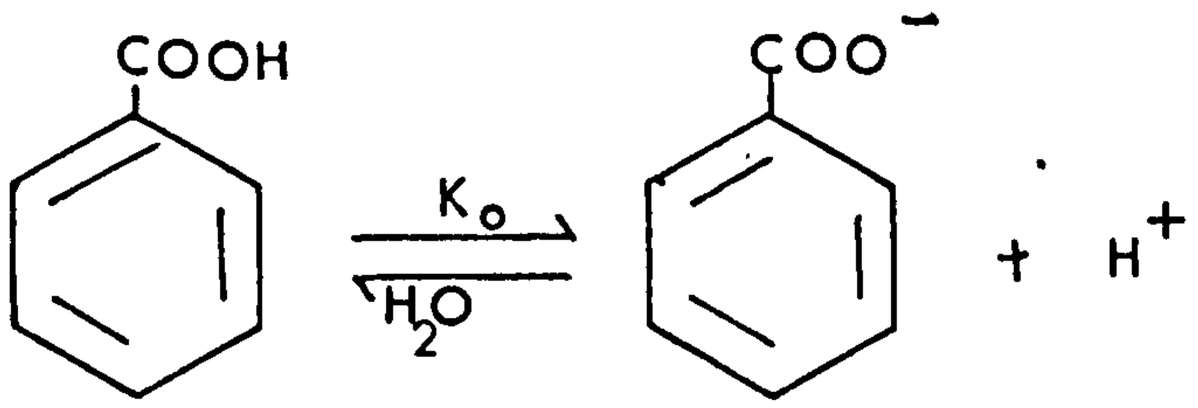
Where I and R are the inductive and resonance effects, X is the halogen, and - (minus) means that it is an electron withdrawing effect and + (plus) an electron donating effect.

The resonance effect decreases in the same order as the inductive effect i.e. I>Cl>Br>I. The effects (I- and R+) conflict with each other but the I- effect is stronger and in the majority of cases it is prevalent. The position para to the halogen is of course the furthest away and therefore the inductive effect will be weaker than in the other positions. The resonance effect on the other hand does not diminish with distance in the benzene ring and as a result of this the para position to the halogen is the least activated towards nucleophilic attack, and in some fluorine compounds it is actually deactivated. A fluorine in 1,2,4,5,6 fluorobenzene, for example, which has another fluorine para to it, is less readily replaced by a methoxide ion than a fluorine para to H in pentafluorinated benzene.(24)

The classical way to express the polar effects is by use of the 'sigma' σ substituent constants, or Hammet σ values as they are also called, in honour of the man who first suggested the relationship from which these values are calculated(25) and which is as follows:

$$\log K/Ko = \sigma \rho \qquad \text{(Equation 1.3)}$$

where K is the rate constant for the ionization reaction of a m- or p- substituted benzoic acid and Ko is the rate constant for the unsubstituted benzoic acid. The ionization reaction of benzoic acid was chosen as it is unlikely that steric factors influence it. The reaction can be represented as follows:



(Equation 1.4)

Electron withdrawing substituents, such as the halogens, increase the equilibrium constant Ko because they stabilise the carboxylate anion. Thus the pK_a is numerically smaller than that for benzoic acid and σ is consequently positive. Electron donating groups, CH_3 for example, decrease the equilibrium constant, and so their values are negative. When graphs are plotted by applying the Hammet equation to reactions of ionisation of benzoic acids with different substituents, a straight line is obtained of slope $\rho = 1$. On the other hand, if ratios of log K/Ko for other reactions are plotted against σ values corresponding to the same substituents, then ρ will vary from reaction to reaction; ρ is called the reaction constant and has been interpreted as a measure of the susceptibility of the reaction to substituent effects. The σ values represent the measurement of the charge distribution by attachment of a reacting side chain to the m- and p- positions, and is the overall sum of all the electronic influences of a substituent, which as already mentioned, can be considered to be divided into inductive and resonance effects. σ values can be divided into σ_m and σ_p values, to represent the effects of substituents at positions meta and para respectively to the carboxylic group in the reaction 1.4.above

The resonance effect from a substituent acts at the ortho and para positions to that substituent, and the inductive effect acts equally in all positions of the ring. The σ_m value is therefore an approximate measure of the inductive effect and $(\sigma_p - \sigma_m)$ is an approximate measure of the resonance effect.

The σ values representing the effect of a substituent in the ortho position, are not as valid mainly because they do not account for steric effects. With some compounds it has been necessary to correct the σ values of some substituents. The discrepancies have been suggested to be caused by through conjugation and were first dealt with by Van Bekkum et al in 1959 [26] and the corrections developed mainly by Taft.[27] Thus σ^o values were calculated for the ionisation reaction of $C_6H_4CH_2COOH$, where the role of the CH_2 group was to isolate the COOH group from the benzene ring and to avoid in this way 'through conjugation', σ^- values were attributed to the ionisation reaction of anilines[28] and σ^+ values for the SN1 hydrolysis of substituted phenyldimethyl-carbinyl chlorides in 90% aqueous acetone.[29]

The σ values refer to reactions of side chains on the benzene ring, and in a large review of reactions that obeyed the Hammet equation, Jaffe (1953)[30] did not find very good correlation of the reaction rates of reactions involving substitution in the benzene ring, with σ constants. But nucleophilic substitution reactions were later found to give good linear relationships with the substituent constants σ^-. The fact that in rections such as that of 1-chloro-2,4-nitrobenzene with piperidine[31] a linear relationship is obtained from values of the second order rate constant vs. σ^- is also proof that the mechanism obeys second order kinetics, as expected.

Johnson[22] explained that the reason why σ^- values fit better than σ values is because of the similarities between the resonance forms of the intermediate complex (I) formed in the SN_2 (aromatic) type of reaction and those of nitroaniline from which σ^- values are obtained. The Hammet σ values can also be exxtended to heterocyclic compounds by considering the nitrogen atom as a substitute on a benzene ring, the so called aza substituent. The σ values of such substituents are obtained from the dissociation constant of nicotinic acid. For heterocycles with more than one nitrogen atom the total σ value can be obtained by adding the single σ values of each nitrogen. The additivity of σ values has been confirmed by Jaffe[30] when he compared calculated total σ values to observed multisubstituted σ values of experiments carried out by a number of workers. By taking all these factors into consideration the Hammet equation can be used to predict reaction rates. In 1953 the available data allowed the prediction of 42,000 rate constants.[30] The Hammet equation is also useful, as mentioned previously, in providing information on the inductive and resonance effects of substituents and on reaction mechanisms.

In the particular case of SN_2 (aromatic) nucleophilic reactions the effect of substituents can also be predicted by considering the stability of the carbanion formed in the first step of the reaction. (Equation 1.1).

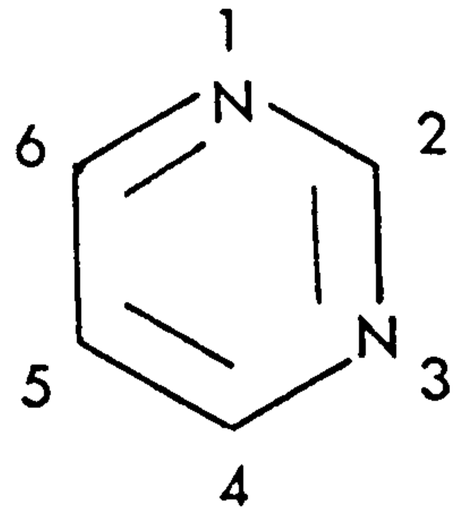
Electron withdrawing groups stabilise carbanions and as predicted by the order of their electronegativities, fluorine is by far the best stabilising substituent. This can be assessed by the acidity of the halogenated benzenes, which in turn have been obtained from rates of exchange of denterohalobenzenes. With this technique Heine[32] obtained the following order of acidities: meta $-C_6H_4F_2$ > meta-C_6H_4ClF > meta-$C_6H_4Cl_2$.

Wittig et al[33] reported a reaction rate 15 times higher for 1-Fluoro 4 methoxybenzene with phenyl lithium than for the corresponding chloro compound. The acidifying influence of fluorine falls off in the order ortho>meta>para. Evidence of this preference has been provided by several workers. Roberts[34] and co-workers have shown that the rate coefficient of deuterium exchange for fluorobenzenes in liquid ammonia in the presence of sodamide when fluorine was ortho to another fluorine in the benzene ring was 4×10^{-1} s^{-1}, whereas for fluorine in the para position it was 2×10^{-5} s^{-1}, a huge difference. A difference of approximately the same order ws also found by Streitwieser and Mares[35] when applying base catalysed deuterium exchange to ortho and para deuterofluorobenzenes. In both experiments the deuteration meta to the fluorine was found not to differ greatlyfrom para deuteration which implies that the inductive influence is by far the dominant one.

However, more recently, it has been found that with polyfluorinated benzenes a methoxy anion prefers to displace a fluorine meta to another fluorine than ortho to it.[24] This was suggested to be caused by electron pair repulsion by the fluorine on the carbon atom it is attached to, which offsets the strong inductive force of the fluorine. This inductive effect however, would not be affected at the adjacent carbon atom, thereby explaining the stronger stabilisingeffect on a negative charge at the ortho position (carbanion). On the other hand, the para position was found to be deactivating towards nucleophilic substitution as mentioned previously, (see page 12). The order of reactivity ortho> para cannot, however, be explained in the same manner as meta>ortho. It has been explained before as being due to the resonance effect overcoming the inductive effect. An alternative explanation was given by Chambers,[24] based on experiments with many polyfluorinated rings, including heterocycles, which was that the nucleophile will attack at the site which maximises the number of activating fluorines.

1.3 The chemistry of pyrimidines and the synthesis of pyrimidinyl reactive dyes.

Pyrimidine is the compound 1,3-diazine, and may be regarded as being derived from benzene by replacement of two meta -CH= groups by -N=. It can be represented as shown below. (V)



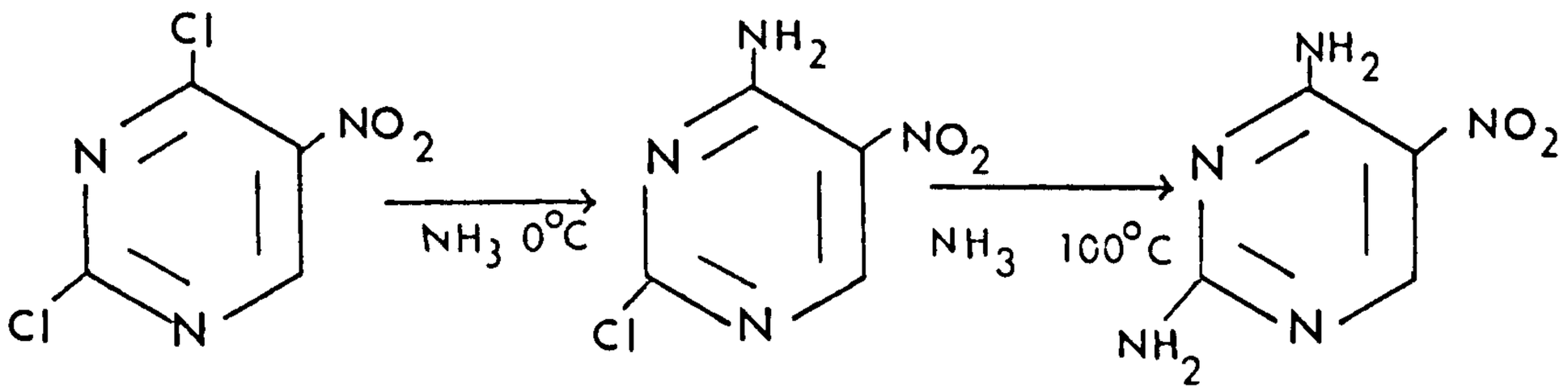
V

In a review of the chemistry of pyrimidine, Hurst[36] considers several general principles which should be taken as a guide for a student of pyrimidine chemistry and can be summarised as follows: the 2,4 and 6 positions of the pyrimidine ring have a strong $\tilde{\pi}$ electron deficiency due to the presence of nitrogen in the 1 and 3 positions and this deficiency makes these positions susceptible to attack by nucleophiles; however the 5 position of the pyrimidine ring resembles more a true 'aromatic position' and is only slightly $\tilde{\pi}$ electron deficient by induction. In this position, for example, halogens are much more resistant to nucleophilic replacement than in positions 2,4 and 6.

The presence of electron attracting substituents enhances the $\tilde{\pi}$ electron deficiency in the pyrimidine ring and make the ring more susceptible to nucleophilic attack, and electron releasing substituents have the opposite effect, as expected. In the reaction of 2,4-dichloro-5-nitropyrimidine (VI) with ammonia, for example, 4-amino-2-chloro-5-nitropyrimidine (VII) forms readily at 0°C but once the electron donating amino group is introduced, it is necessary to heat

the reactants to 100°C before the replacement of the second chlorine at the 2 position takes place.[36] (equation 1.5 below)

(1.5)

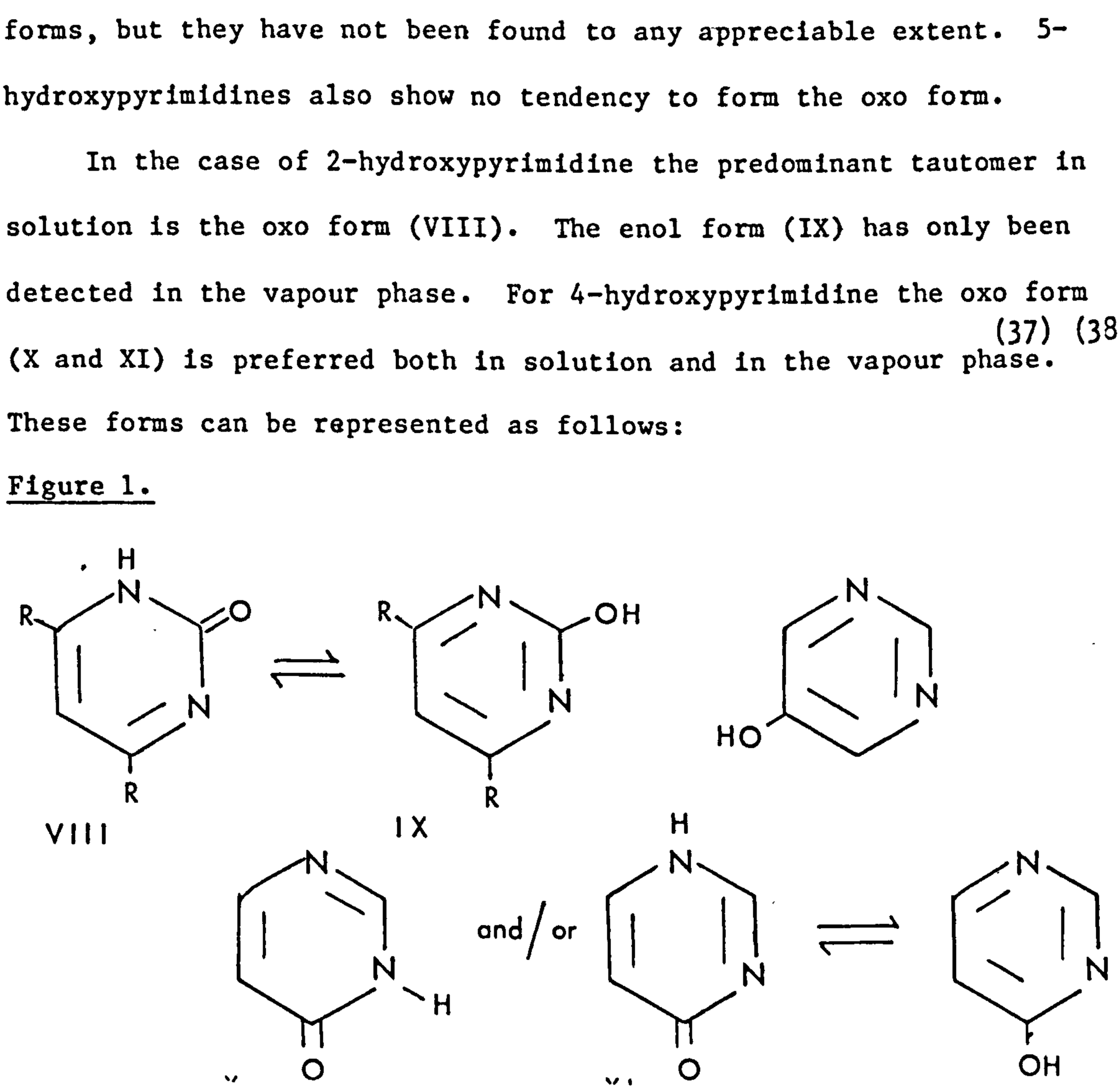


VI VII

Pyrimidine and pyrimidine derivatives can exist in more than one form, due to the possibility of conjugation between a mobile hydrogen atom and the π bond. These tautomeric forms of pyrimidine have been identified mainly by spectroscopic methods, for pyrimidines with hydroxy and mercapto substituents ortho to the nitrogen atoms. In theory it is posible for amino pyrimidines to exist in tautomeric forms, but they have not been found to any appreciable extent. 5-hydroxypyrimidines also show no tendency to form the oxo form.

In the case of 2-hydroxypyrimidine the predominant tautomer in solution is the oxo form (VIII). The enol form (IX) has only been detected in the vapour phase. For 4-hydroxypyrimidine the oxo form (X and XI)[37] [38] is preferred both in solution and in the vapour phase. These forms can be represented as follows:

Figure 1.

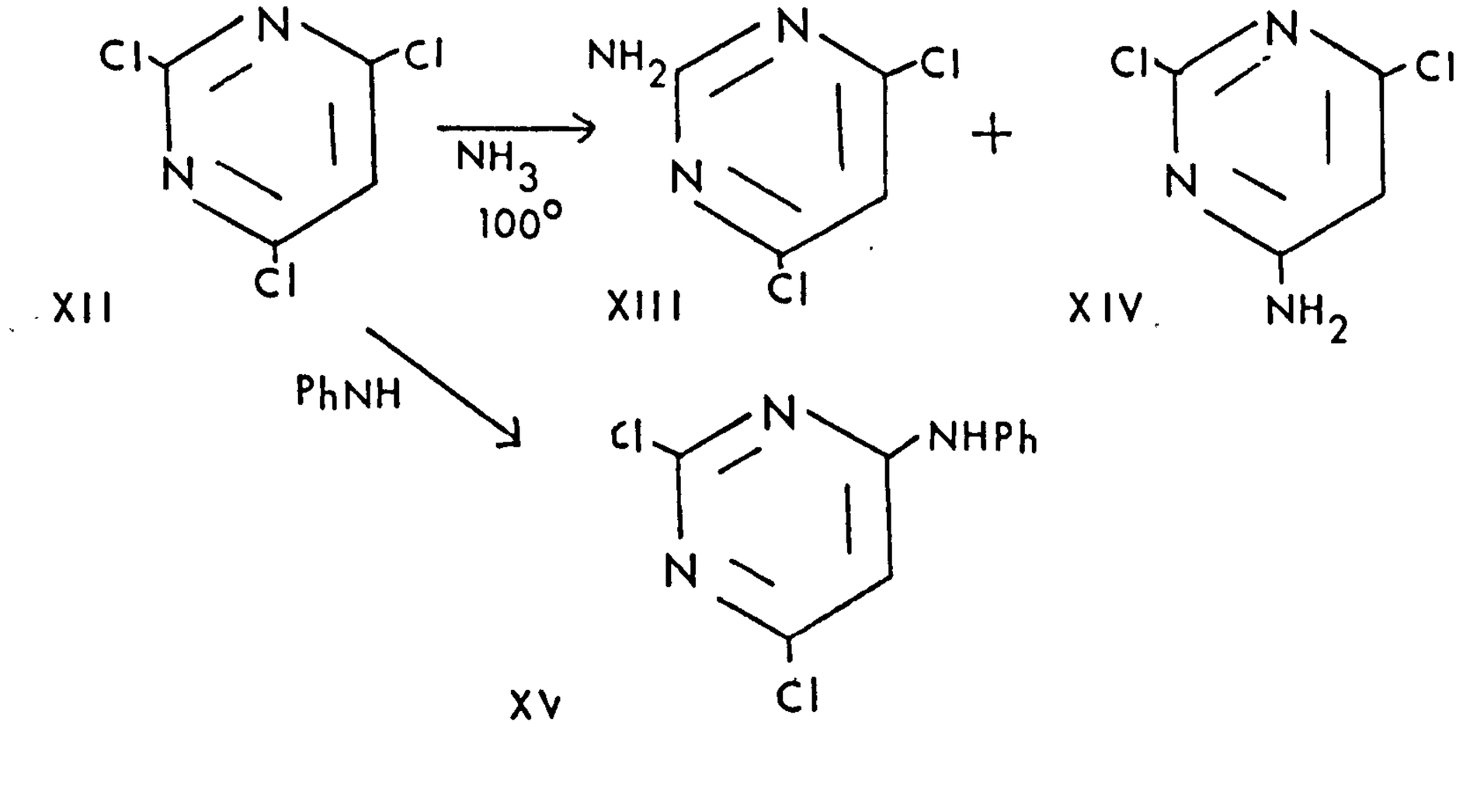


The hydroxypyrimidines shown above can also ionise as acids, 2-and 4- hydroxypyrimidines have pK_a values similar to phenol (9.17 and 8.59 respectively).

The introduction of electron attracting substituents increases the acidity. For example, the pK_a value for 2-hydroxy-5-chloropyrimidine is 7.35.[39] Predictably the introduction of electron releasing groups has the opposite effect.

In the nucleophilic replacement of halogens from pyrimidines, the 4 position seems to be the preferred site of attack and this has been exemplified already in Equation 1.5. Other examples of this preference have been reported. Thus, 2,4-dichloropyrimidine reacts with sodium methoxide at room temperature to form only 2-chloro-4-methoxypyrimidine[40] and 2-amino-4-chloropyrimidine forms 2-amino-4-hydroxypyrimidine on boiling in water for one day, whereas 2-chloro-4-aminopyrimidine is unchanged under these conditions.[41] Ackermann and Dussy[42] also found that on reacting tetrochloro-pyrimidine with aniline in water/acetone medium at 50°C at pH 6-7 only the 4-amino derivative was obtained. Similarly with fluoropyrimidines,[43] 2,4,5,6 fluoro-pyrimidine reacts with sodium methoxide in methanol and THF at 0°C to form 4,6 methoxy-2,5 fluoropyrimidine and only under reflux the reaction produces 2,4,6 methoxy-5-fluoropyrimidine. Moreover, 2,4,5,6 fluoropyrimidine forms a mixture of 4-amino-2,5,6 fluoropyrimidine and 4,6 amino-2,5 fluoropyrimidine on reacting with aqueous ammonia. However, reactions are also known where the 2 position is attacked preferentially: on treating 2,4-dichloropyrimidine with alcoholic ammonia at room temperature and allowing it to stand for some time a mixture of 2,amino-4-chloro (60%) and 4-amino-2-chloropyrimidine (40%)[36] is obtained, and on treating 2,4,6-trichloropyrimidine (XII) with ammonia at 100°C substitution also

occurs in both the 2 (XIII) and 4(XIV) position.[44] But on reacting 2,4,6-trichloropyrimidine with aniline, substitution only occurs at the 4 position. (XV).[45]

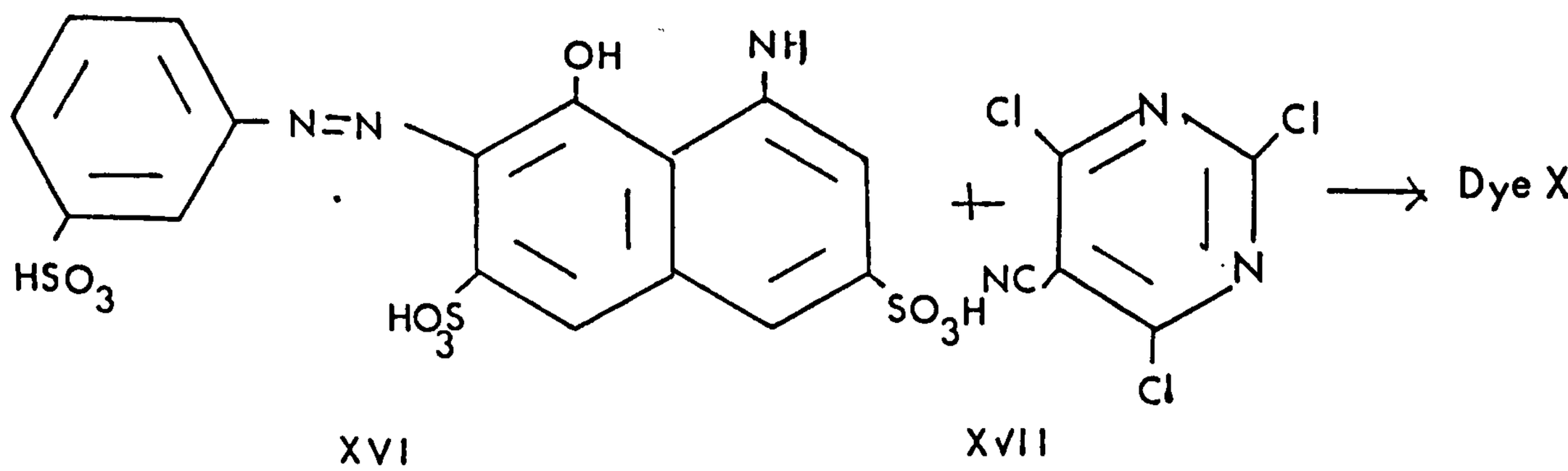


The amination of halopyrimidine is important to the preparation of pyrimidinyl reactive dyes, since the reaction to link the chromophore to the pyrimidine ring is a condensation reaction involving the amino group of the chromophore and the halogen of the pyrimidine ring. Most of the evidence suggests that this reaction would take place preferentially at the 4 position of the ring.

As has already been mentioned nucleophilic substitution at the 5 position of the ring is much more difficult than at the other positions and generally requires vigorous reaction conditions. It has, however, been reported that a number of 5-bromopyrimidines can be aminated with comparative ease[36] and 5-bromo-pyrimidine reacts with sodium methoxide at 100°C to give 5-methoxypyrimidine.[46]

Another untypical reaction of the 5-position of pyrimidines is the hydrolysis of 5-bromo-2,4-dihydroxypyrimidine (5-bromouracil) which is converted to 2,4,5 trihydroxypyrimidine merely on boiling in sodium bicarbonate solution.(47)

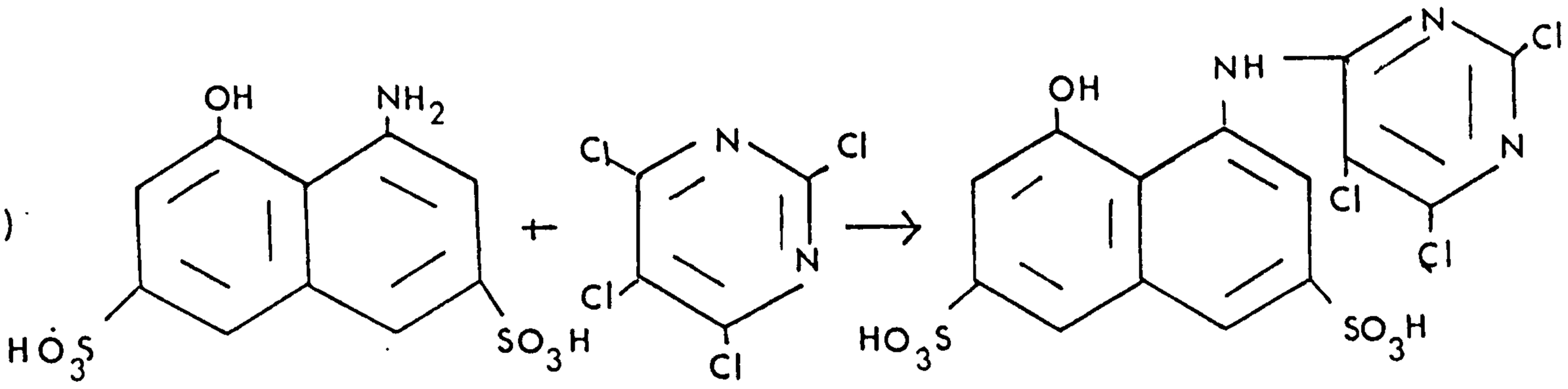
Since the hydrolysis of halopyrimidines in water is fairly easy, there are two competing reactions in the reaction of synthesis of halopyrimidinyl dyes : the condensation reaction with the amino group and the hydrolysis of the halogen. This has to be taken into consideration when synthesising these dyes, and the alkalinity of the solution has to be carefully controlled. The route of synthesis has also to be chosen, taking this factor into consideration. Thus, other things being equal, it is often preferred to choose the method in which the reactive group is introduced in the final stage, to minimise the danger of hydrolysis.(48) This is the case with 5-cyano-2,4- chloro-pyrimidine (XVII) which is condensed with the chromophore (XVI) to form dye X. (equation 1.6 and section 2.1)



XVI XVII

However, with less reactive halopyrimidines such as 2,4,6-trichloro and 2,4,5,6-tetrachloropyrimidine (XVIII) the reaction with the already formed chromophore, (XVI) is very difficult and an intermediate (XX) from a dyebase (XIX) is first prepared, e.g.

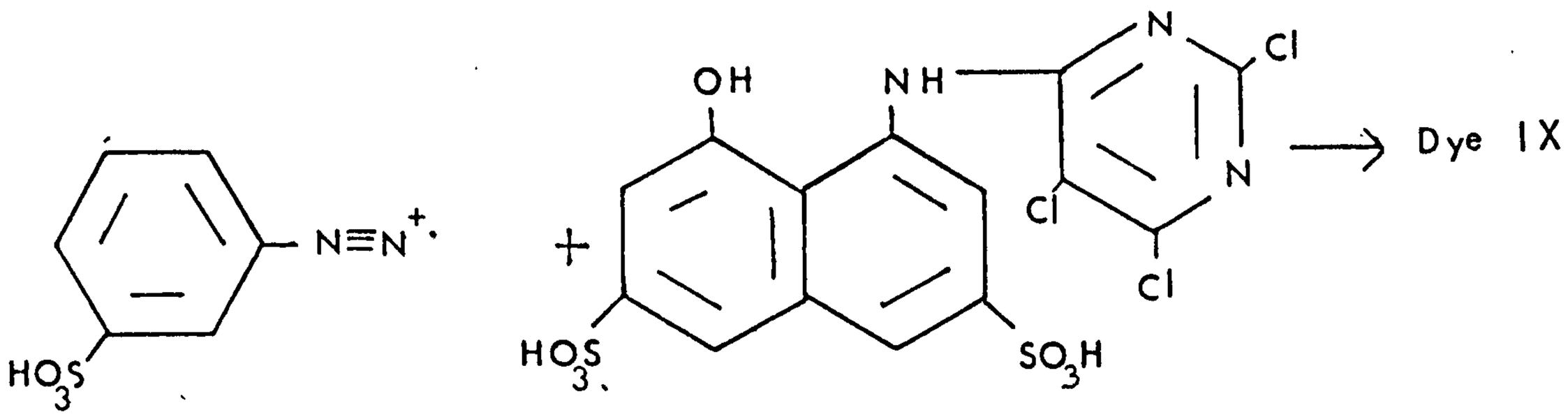
(1.7)



XIX XVIII XX

The intermediate is then coupled to a diazonium salt (XXI). With compound (XX) above the reaction can be represented as shown below. (equation 1.8 and section 2.1)

(1.8)

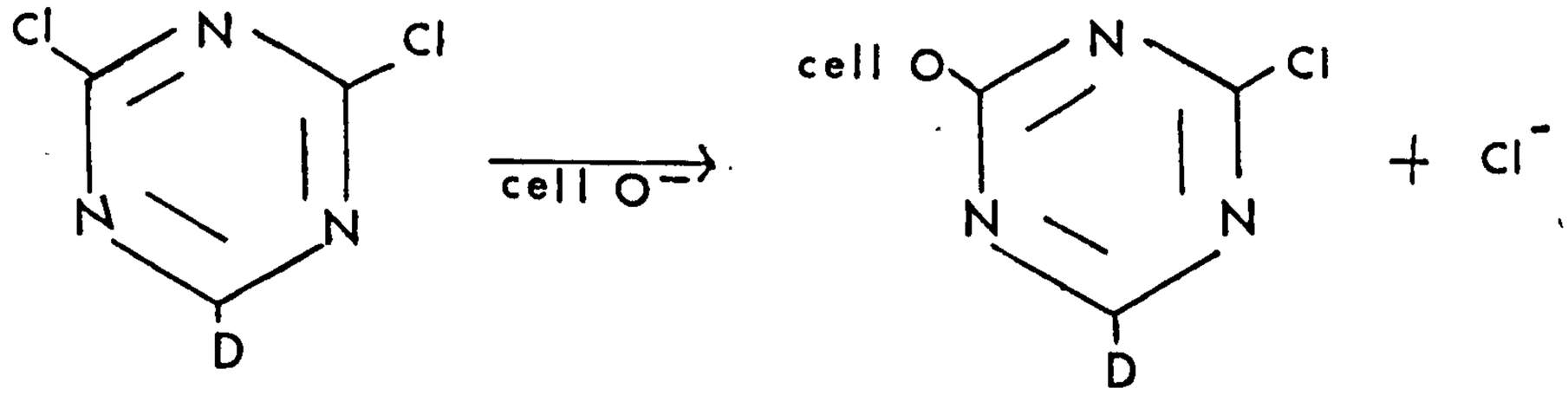


XXI

The corresponding dichloropyrimidinyl dye (dye VIII, Section 2.1) is synthesised via the same route. Both these pyrimidines are more stable to hydrolysis than 5-cyano-2,4 chloropyrimidine (XVII) and so the risk of hydrolysis, due to the extra step in the sequence of reactions, is less.

1.4 Reaction of pyrimidinyl and triazinyl dyes with cellulose and hydrolysis of the dyeings during and after dyeing.

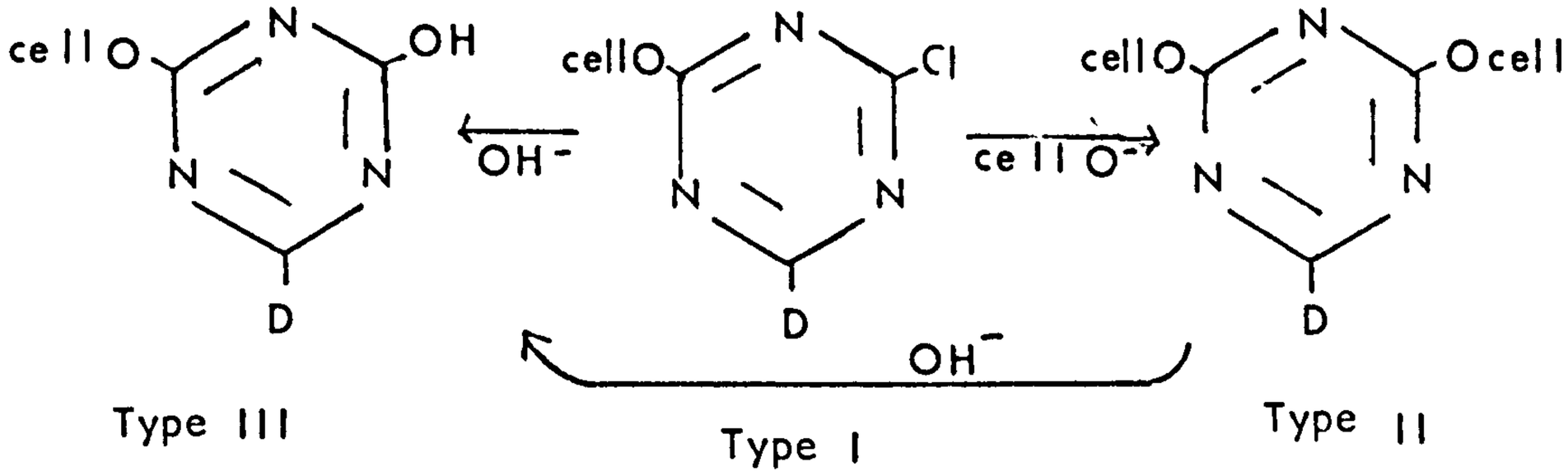
During the dyeing of cellulose with heterocycle containing reactive dyes, the cellulose ionises under the alkaline conditions used and the cellulosate anion replaces one (or two) of the electron withdrawing labile groups ortho to a nitrogen heteroatom, in much the same way as other nucleophiles already considered in the previous section. Taking dichlorotriazinyl dyes as an example, the reaction can be represented as shown below.



D = chromophore

These dyes were first marketed under the commercial name of Procion MX dyes (I.C.I). In contrast to the pyrimidines, with dichlorotriazines there is no argument as to where the nucleophile, the cellulosate anion, attacks, due to the symmetry of the dichloro triazine ring. The reaction can proceed further since there is still a labile chlorine in the ring.

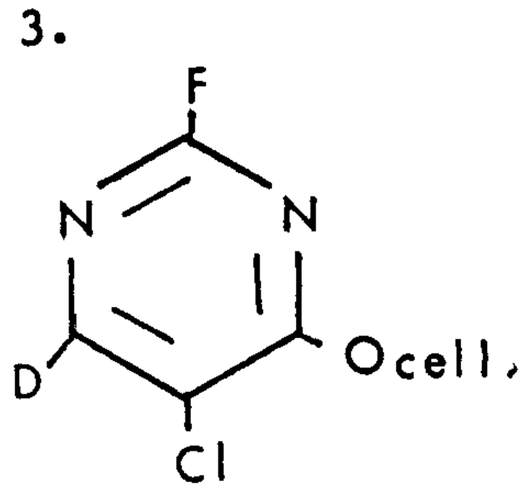
Thus it can either react with the cellulosate ion again, or be hydrolysed.
Fig 2



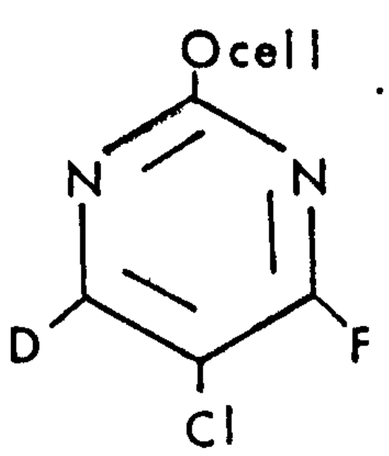
Type III Type I Type II

The products of these three reactions are known as Types I, II and III as shown above. Dyeings of Type I and III are soluble in cuprammonium hydroxide, whereas Type II is not.[49] Preston and Fern[50] found that Procion Brilliant Orange MG (dichlorotriazinyl) dye formed different proportions of type I, II and III dyeings, depending on the dyeing method used. There was slightly less of Type I, for example in exhaustion dyeing (cold), than in pad-batch (cold). This was because more cross-linking was formed in the exhaustion dyeing than in the pad-batch. Type III was about the same in both methods of dyeing. More vigorous methods, such as pad-bake and pad-steam, formed a lot more Type III, approximately the same of Type II and less of Type I than either of the other two (cold) methods. Rattee[51] has suggested that 2,4-fluoro-5-chloropyrimidinyl dyes also formed three analogous types of dyeings during dyeing. In fact besides these three types, two others are possible because of the assymetry of the ring, as shown overleaf. (Figure 3).

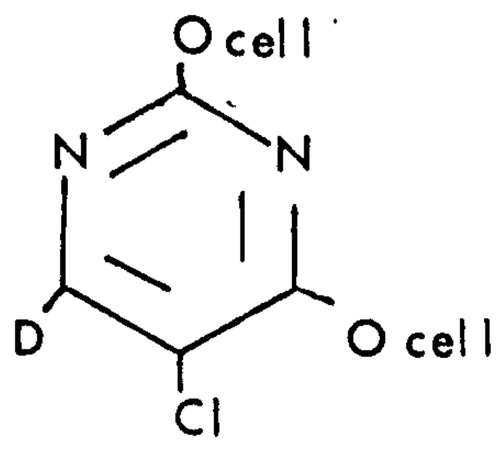
Figure 3.



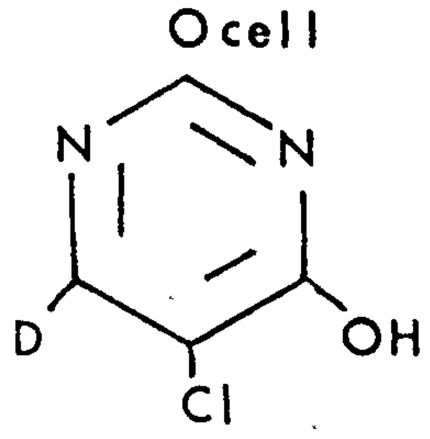
I_a



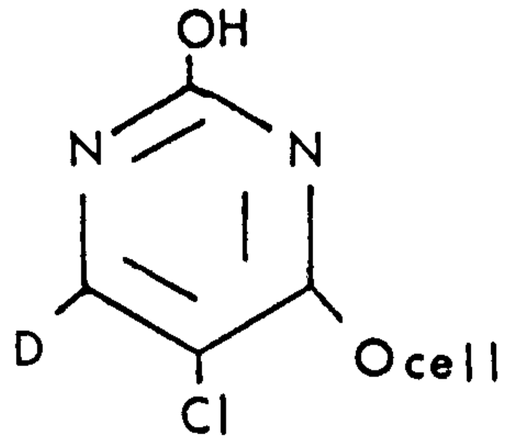
I_b



II



Type III_a

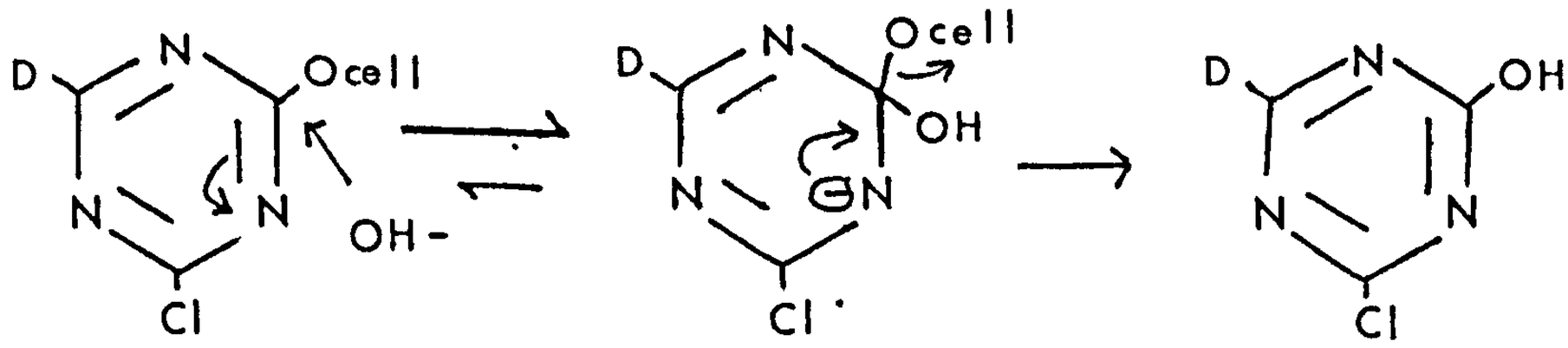


Type III_b

D = chromophore

Types 3a and 3b can take another resonance form, the oxo form. As already shown in 1.3, the analogous oxo form of 2 hydroxypyrimidine is believed to be the predominant one in solution. The possibility of the 2nd fluorine reacting again with cellulose is supported by analogous reactions of 2,4-difluoro-5-chloropyrimidinyl dyes. Thus, Datyner et al[52] found that a partially hydrolysed difluoropyrimidinyl dye is still fairly reactive to wool, and Yushu[53] showed that these dyes form cross-links with silk fibroin. Type I dyeings are less stable to nucleophilic attack than the other types, due to the electron-withdrawing substituent still remaining. They can form Type III as shown above but hydrolysis can also occur at the dye-cellulose bond. Assuming this reaction is of the SN_2 (aromatic) type as it seems likely (see 1.1) it can be represented as follows:

1.9



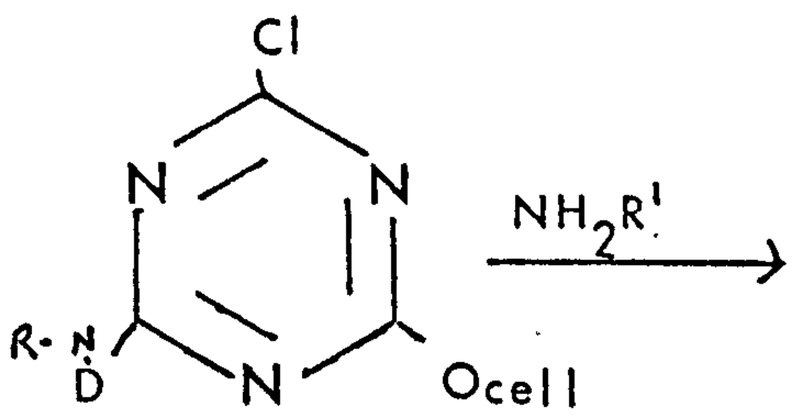
D = Chromophore

and similarly for 2,4-fluoro-5-chloropyrimidines.

Acid hydrolysis with breakdown of the dye-cellulose bond is more problematic than alkaline hydrolysis. Preston and Fern found that the Type III dye-cellulose bond is hydrolysed more in acid conditions than either Type I or II.

To improve the washfastness to acid hydrolysis, a Type I dyeing can be given an aftertreatment with an amine, which will replace most of the labile chlorine and will form what is called the Type IV dyeing.

(1.10)

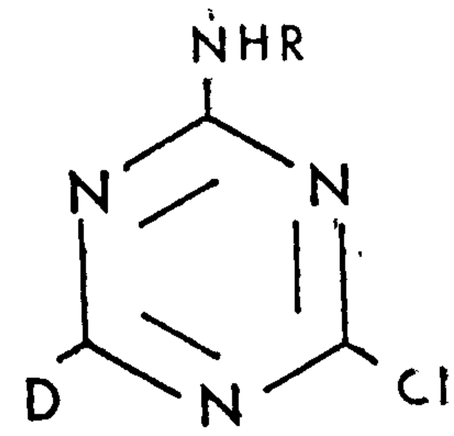


D = chromophore

R = Hydrogen or alkyl

R^1 = alkyl or aryl

In this way the ring will become more stable to nucleophilic attack due to the electron donating characteristics of the imino group. Monochlorotriazinyl dyes, (XXI) of the Procion H (I.C.I) and Cibacron (CIBA) range of dyes, already have an imino group instead of a second chlorine.



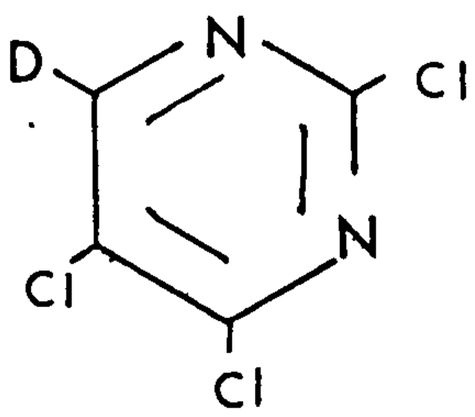
D = chromophore

R = Hydrogen or alkyl

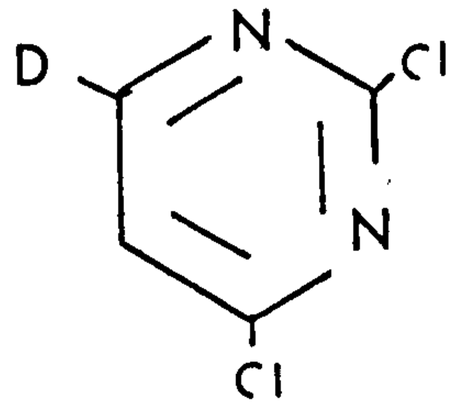
XXI

These dyes produce dyeings more stable to acid hydrolysis since Type III will not be formed, but which do not appear to be more stable to alkaline hydrolysis.(54) Dyes of this type have the disadvantage of a lower reactivity and have to be applied at higher temperatures.

Trichloro (XXII) and dichlorotriazinyl dyes (XXIII) are also less reactive than dichlorotriazinyl dyes which is expected since the pyrimidine ring only has two nitrogen heteroatoms. Reactive (Geigy) and Drimarene(S) dyes have within their range both these two types of dyes. Their structures can be represented as follows:



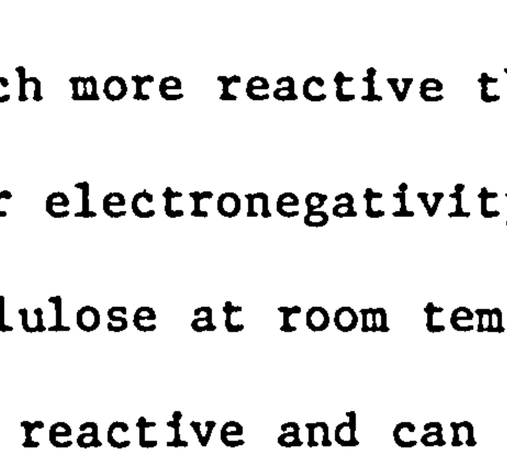
XXII



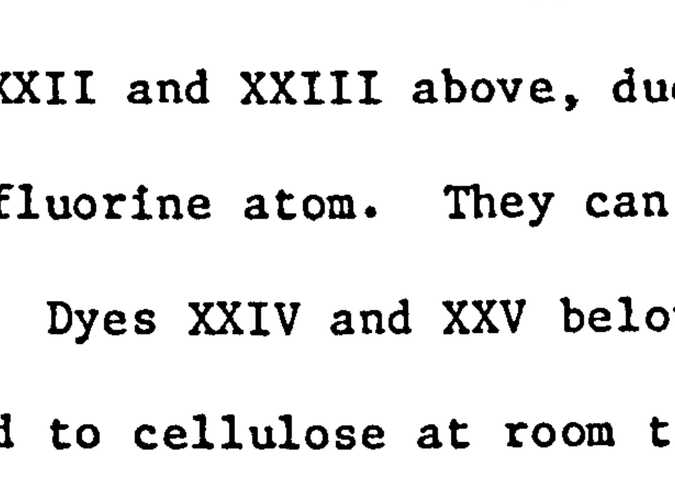
XXIII

D = chromophore

The above pyrimidinyl dyes also show a higher resistance to alkaline hydrolysis at the dye-cellulose bond than the mono and di-chlorotriazinyl dyes.(54) However 2,4 difluoro-5-chloropyrimidinyl dyes are much more reactive than dyes XXII and XXIII above, due to the greater electronegativity of the fluorine atom. They can be applied to cellulose at room temperature. Dyes XXIV and XXV below are also highly reactive and can be applied to cellulose at room temperature.



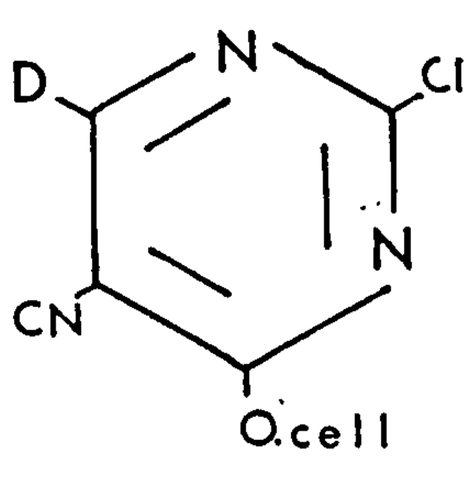
XXIV



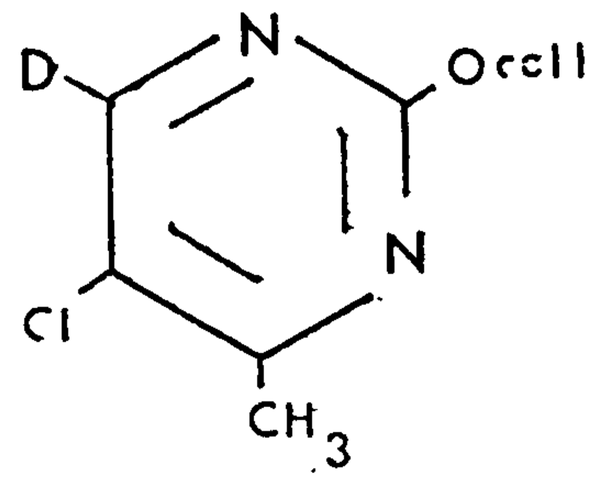
XXV

D = chromophore

Dye XXIV has not been reported as a commercial dye. This is probably because its wash fastness to alkali is low. Dye XXV is marketed under the name Levafix P by Bayer. Its wash fastness to alkali is high. On dyeing with Dye XXV above, the cellulose atacks at the 2 position, leaving a dyeing with an unreactive ring, whereas with Dye XXIV the cellulosate ion attacks at either the 2 or 4 position and the ring is still left with activating substituents, i.e. CN at the 5 position, and a chlorine at the 2 or 4 position. Assuming the cellulosate ion attacks at the 4 position in Dye XXIV (Equation 1.9) the dyeings can be represented as follows:



XXVI



XXVII

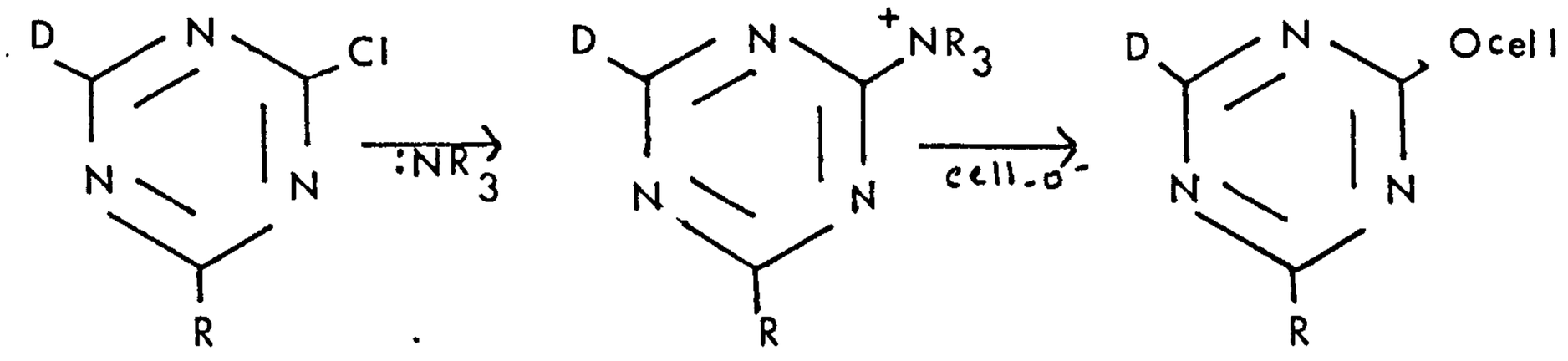
D = chromophore

R = Hydrogen or alkyl

Hence, it can be said that as a general rule dyes that do not completely lose their reactivity during dyeing will undergo hydrolysis at the dye-cellulose bond than dyes that lose most of their reactivity during dyeing. It is also apparent that the extra nitrogen heteroatom in the triazine ring of a dichlorotriazinyl dyeing makes the dyeing less resistant to alkaline hydrolysis than di and trichloropyrimidinyl dyeings. (Equation 1.9).

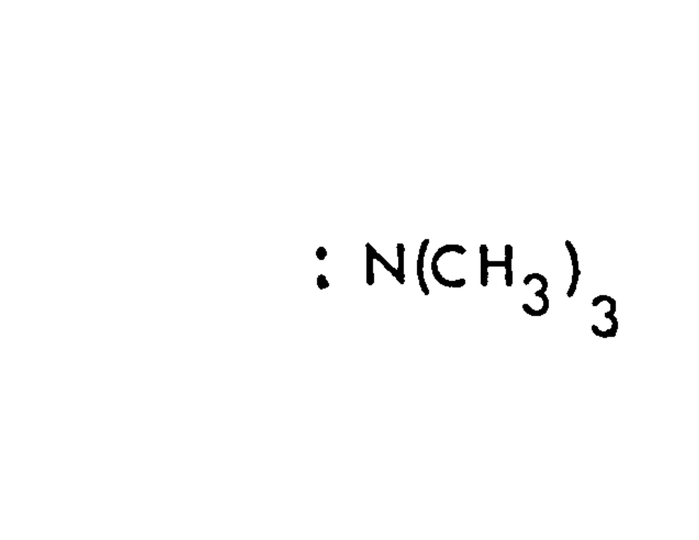
When one or more of the activating substituents is labile, it can be replaced by electron donating substituents which will increase the stability of the ring towards nucleophilic attack. It has already been mentioned that dichlorotriazinyl dyeings can be made more stable

towards acid hydrolysis by reacting the dyeing with a primary amine. (Equation 1.10). Tertiary amines have also been shown to increase the stability of dyeings. Hughes[55] treated a 5-cyano-2,4-chloro-pyrimidinyl dyeing (XXVI) with a series of tertiary amines and obtained a higher resistance to hydrolysis with most of them. Tertiary amines can be used to catalyse the dyeing of cellulose with heterocycle containing reactive dyes of low reactivity, such as monochlorotriazinyl and di and trichloropyrimidinyl. Catalysis of monochlorotriazine dyes by tertiary amines takes place by quarternisation followed by reaction of quarternised species with the cellulose, tertiary amine being released and then becoming available to produce further quarternised dye. These reactions may be represented as follows:



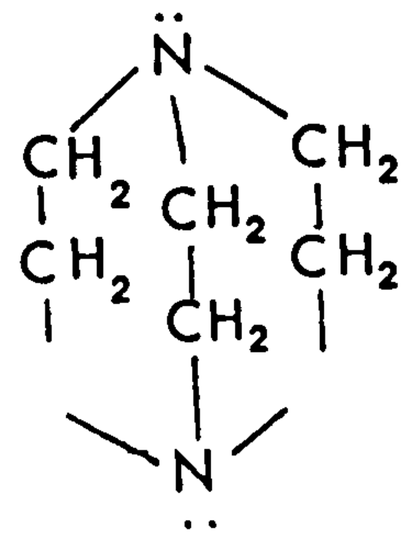
D = chromophore

Dawson[56] measured the rate constants of quanternisation with various tertiary amines and found that both the basicity and the bulk of the amines were influential factors. Of the amines tested, 1,4 diaza-2:2:2 bicyclooctane, (DABCO) XXIX and trimethylamine (XXVIII) were found to give the highest rates of quarternisation.



: $N(CH_3)_3$

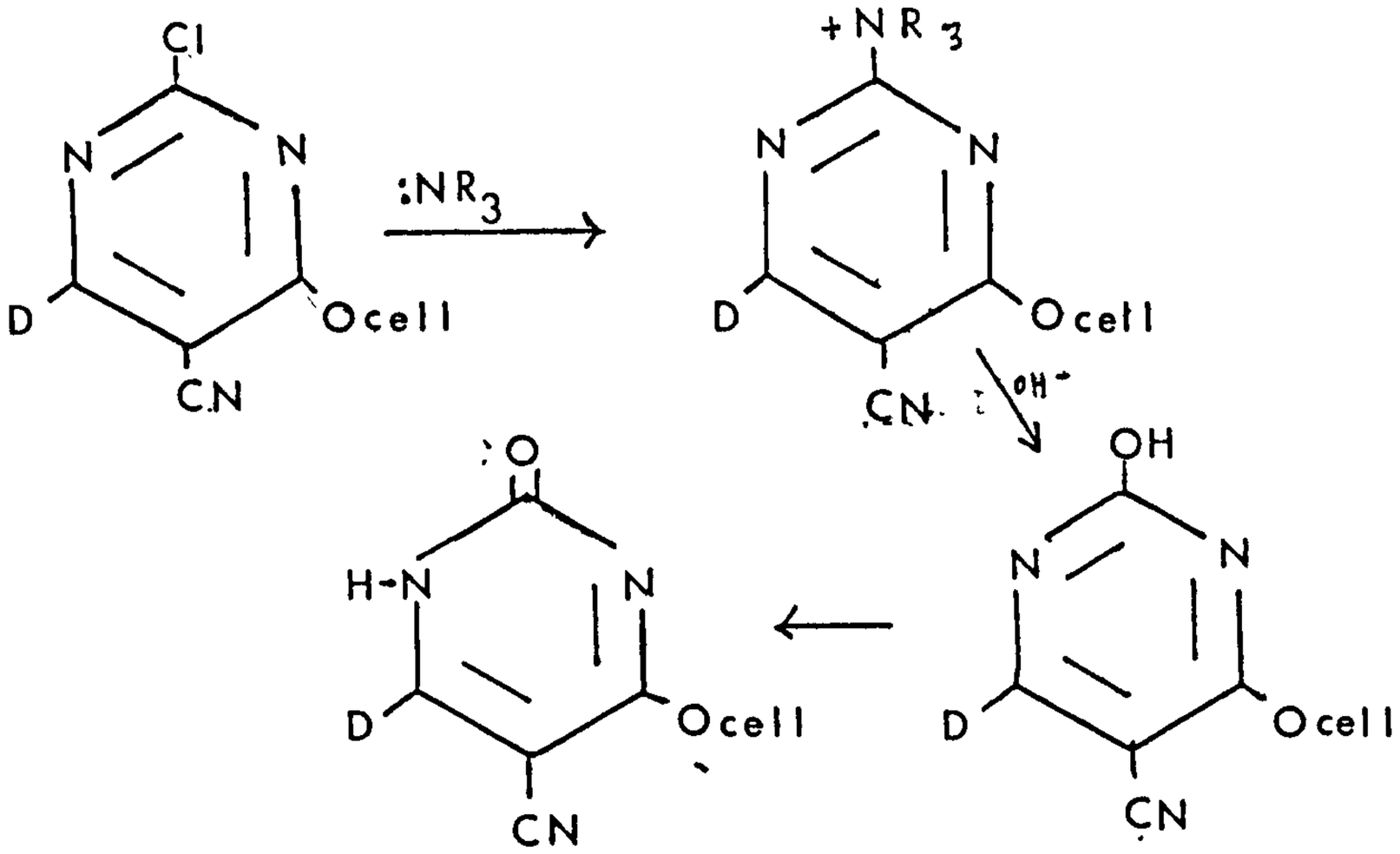
XXVIII



XXIX

Similarly, the reaction of 5-cyano-2,4-chloropyrimidinyl dyeings with tertiary amines under alkaline conditions is believed to be as follows:(55)

(1.11)



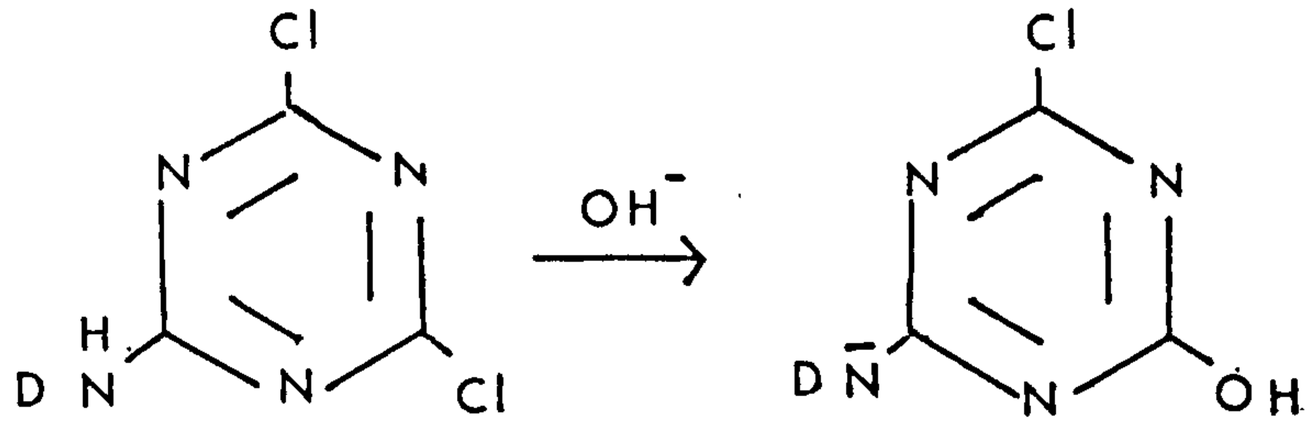
XXXI

The 2 hydroxy form exists mainly in the keto form (XXXI). The dyeing is then stable to alkaline hydrolysis, since the ring conjugation is lost and therefore the activating effect of the -CN group on the carbon-cellulose bond is less.(57)

Dyes having the same reactive group may still vary a lot in their reactivity and in the resistance of the dyeings to hydrolysis. These variations have in part been attributed to the ionisation of the imino group linking the chromophore to the ring. Ingamells and co-workers(58) tested a number of triazinyl dyes and found that those which

had an alkyl or aryl substituent on the bridging nitrogen showed a bimolecular rate constant during alkaline hydrolysis and the rate of hydrolysis increased linearly with pH. However, with dyes where the imino bridging group was unsubstituted, and above a certain pH ($>$ 11) the rate of hydrolysis hardly increased with increase in pH. This (59) was suggested by Horrobin as being due to the ionisation of the imino group, which would deactivate the ring towards any further nucleophile attack. (1.12).

(1.12)

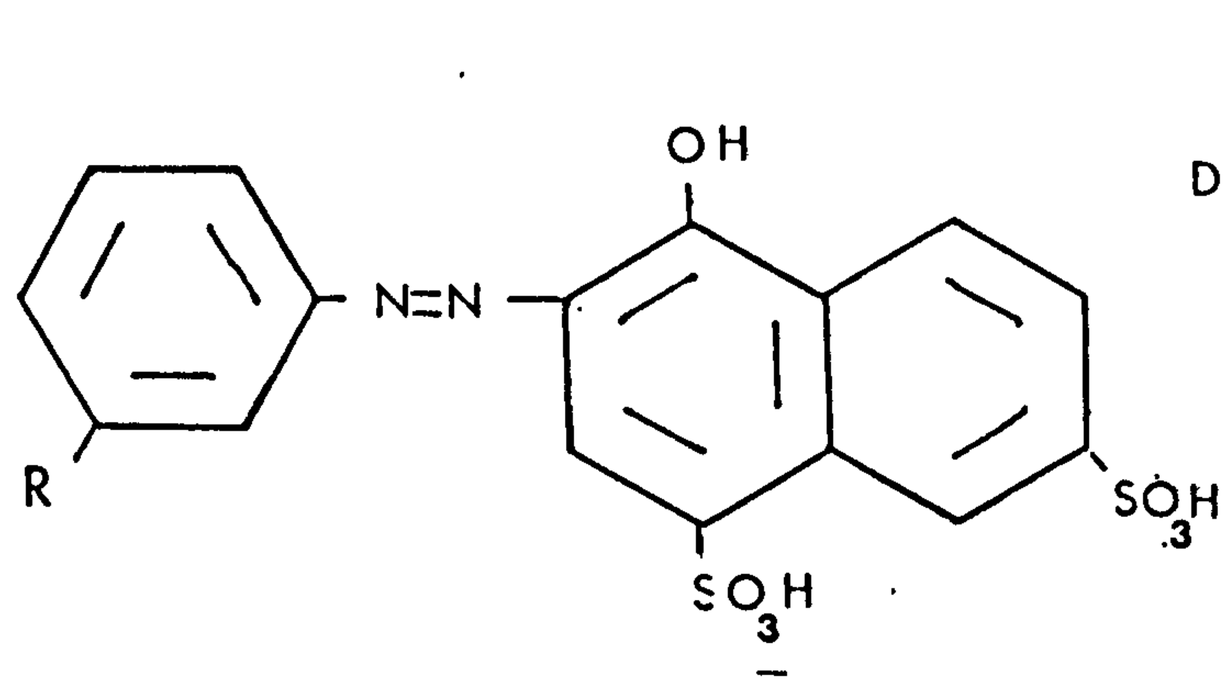


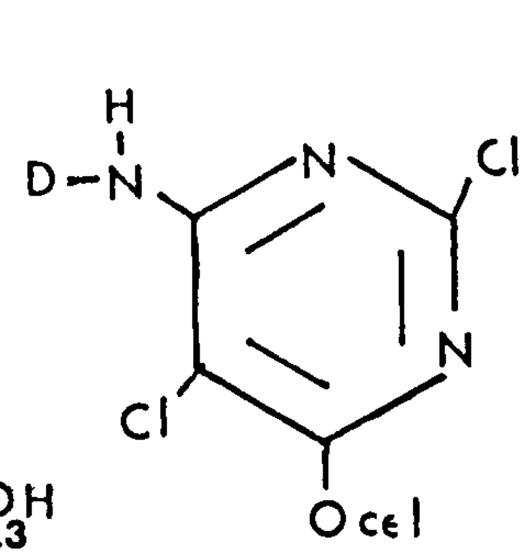
XXXII

D = chromophore

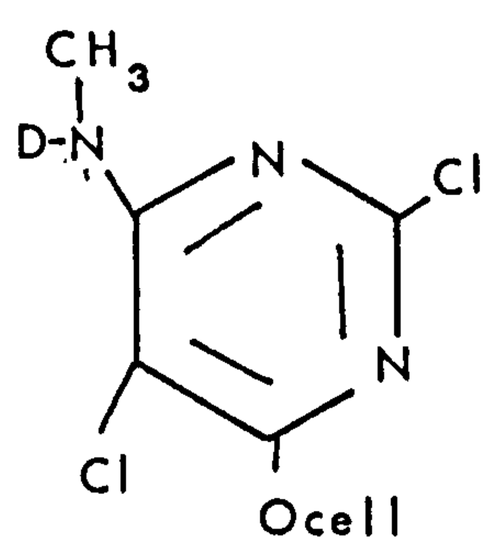
Benz also found that dyeing XXXIII with an imino group showed less alkaline hydrolysis at the dye-cellulose bond than dyeing XXXIV with a substituted imino group.

Chromophore D — Reactive group R





XXXIII

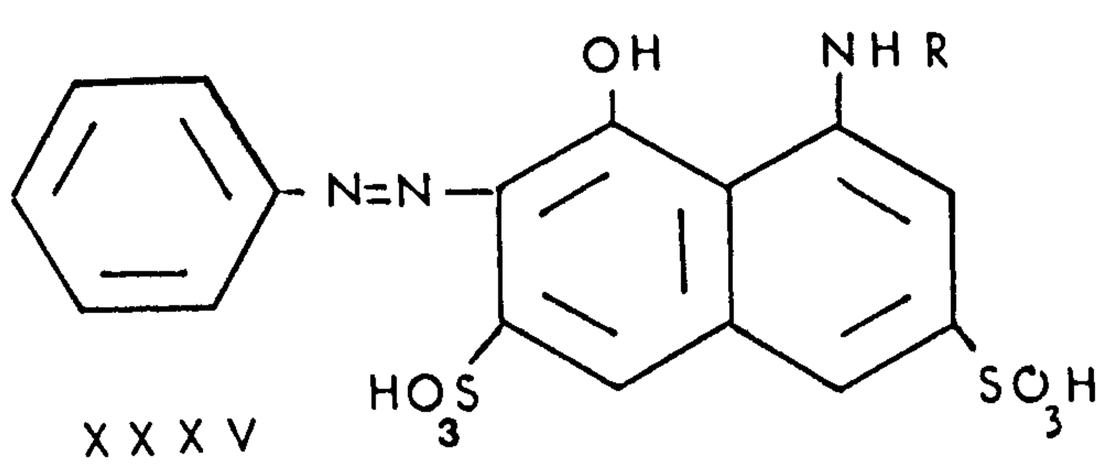


XXXIV

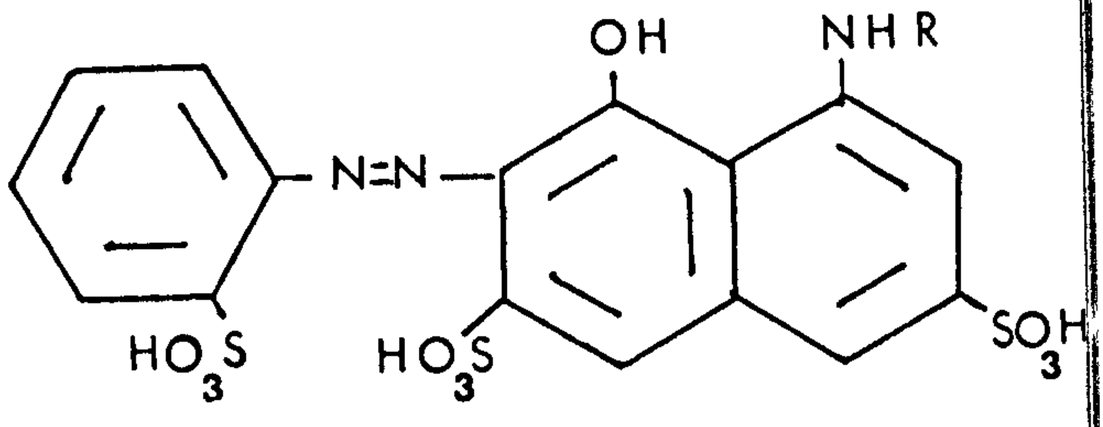
This difference in reactivity towards OH- can also be explained by the ionisation of the imino group.

Since the hydrolysis of dyeings takes place in a heterogeneous medium, i.e. at the surface of a fibre, other factors, characteristics of such reactions, come into play, which are not present in the hydrolysis of dyes in solution. The surface potential has to be considered and in the case of cellulose it will cause the repulsion of anions, and the attraction of cations. This is due to the ionisation of cellulose and of carboxyl groups present in the cellulose (See for example, Ref. 60). Moreover, when the cellulose is already dyed with an anionic dye, the dye will enhance this effect. Neale and Stringfellow, for example,[61] found that the absorption by cellulose of dyes containing 4 sulphonic acid groups was about half of that obtained with dyes containing only 2. This is because as the dye is absorbed by the cellulose, its negative charge repels any further absorption of dye. The more negatively charged the dye is, the more it shows this effect. Since the acidity of the sulphonic acid groups is influenced by the other substituents in the ring, this will in turn affect such heterogeneous reactions as the hydrolysis of dyeings.

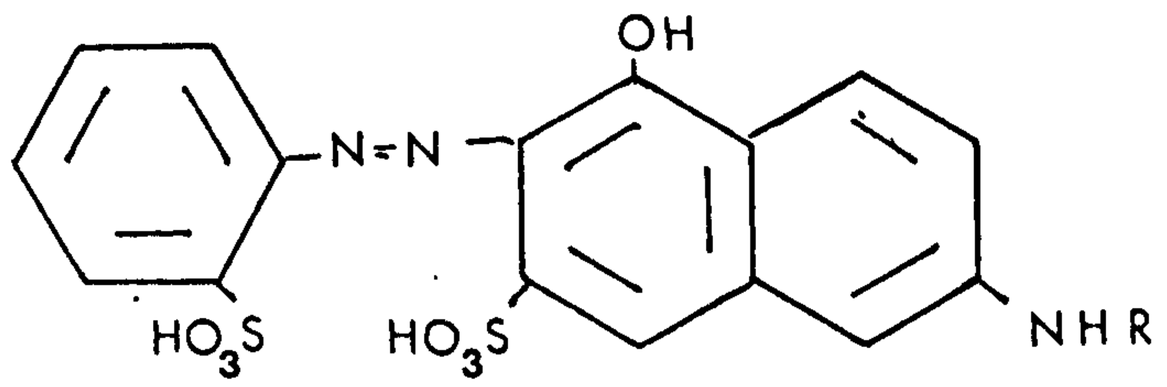
Johnston,[62] for example, found that dichlorotriazinyl dyeing (XXXV) and (XXXVI) with chromophores containing a naphthalene ring with two sulphonic acid groups suffered greater acid hydrolysis at the dye-cellulose bond than another dichlorotriazinyl dyeing (XXXVII), which had the sulphonic acid groups on two separate rings. The structures of the dyes were the following: (overleaf)



XXXV



XXXVI



XXXVII

Johnston suggested that this was because the two sulphonic acid groups in the same ring reinforced each other's acidity through conjugation. This would in turn increase the concentration of protons in the fibre which catalyse acid hydrolysis. Acid hydrolysis of dichlorotriazinyl dyeings which had previously been found by Pierce[63] and Rattee[64] to obey first order kinetics, was later shown by Johnston and Rattee to be a second order reaction. They found that the reaction constant was proportional to the calculated proton concentration inside the fibre, or the 'internal pH', as it is also called. Pierce and Rattee[64] had used buffer solutions in the experiments but found that different buffers gave different results, even though the pH of the test solution was the same. This was because the ionic strengths of the buffers differed and this altered the internal pH. These experiments by Pierce, Johnston and Rattee brought to light the importance of electronic effects of ions present in the solution when doing hydrolysis experiments on dyeings. The effect of the ionisation of the imino group (Equation 1.12) can also be explained by a decrease in internal pH which would decrease alkaline hydrolysis.

Electrolytes, on the other hand, increase the internal pH of a cellulose dyeing, bringing it nearer to the external pH and therefore enhance the alkaline hydrolysis of the dye-cellulose bond. (See, for example Ref. 60).

In previous work on the reaction of the dyeing with hydrogen peroxide,[2] the breakdown was found to increase with the concentration of electrolyte, which was also considered to be an internal pH effect, since the reaction on the dyeing is a nucleophilic attack by the perhydroxyl anion HO_2^-.

1.5 Sodium perborate as a source of hydrogen peroxide

Sodium perborate should be represented by the formula $NaBO_2.H_2O_2.3H_2O$, since its properties appear to be those corresponding to an addition product of hydrogen peroxide rather than to a salt of some hypothetical peroxyboric acid.[65] In alkaline medium sodium perborate liberates hydrogen peroxide. The amount of hydrogen peroxide which corresponds to a certain amount of sodium perborate can be calculated from the formula above. For example, for a 5g/l solution of perborate the concentration of hydrogen peroxide is:

$$5 \times \frac{34.016}{153.86} = 1.105 \text{ g/l.}$$

The concentrations of stock solutions of hydrogen peroxide are usually expressed in 'volume strength'. This is defined as the volume of oxygen gas measured at 0^oC and 1 atmosphere, available from the complete decomposition of one volume of hydrogen peroxide solution also measured at standard conditions.[66] The weight percentage of a hydrogen peroxide solution can be derived from a graph of weight percentage vs. volume strength, plotted from values taken from a table such as that given by Schumb.[66] For example, the weight percentage of a 100 volume solution is 27.5 w/v. Thus, from the example above, a 5 g/l sodium perborate solution would correspond approximately to 4 ml/l of a 100 V hydrogen peroxide solution, i.e.

$$\frac{1.1054 \times 100}{27.5} = 4.02 \text{ ml/l.}$$

These concentrations of sodium perborate and hydrogen peroxide were used throughout previous work done on the stability of 2,4-fluoro-5-chloropyrimidinyl dyeings to sodium perborate and hydrogen peroxide.[1][2]

1.6. Reactions of hydrogen peroxide in an alkaline medium

Hydrogen peroxide ionises in water to form perhydroxyl ions. The rection of ionisation can be represented as follows:

$$(1.13)\ldots \quad H_2O_2 \underset{k_2}{\overset{k_1}{\rightleftharpoons}} H^+ + HO_2^- \qquad (1.13)$$

It has been shown that some reactions with hydrogen peroxide involve the HO_2^- ion. Halperin[67] showed that sulphite is oxidised to sulphate via a perhydroxyl mechanism and Davies[68] and co-workers showed that alcohols, carboxylic esters, or olefins reacted with 90% (wt %) hydrogen peroxide to form alkyl hydroperoxides also via a perhydroxyl ion mechanism involving carbonium ions. As early as 1949 Bunton[69] showed that the oxidation of α-diketones by hydrogen peroxide occurred through the action of perhydroxyl ions. Bunton[70] also showed that peroxyacetic acid can be formed by replacement of the hydroxyl group of acetic acid by the perhydroxyl group.

The best known use of hydrogen peroxide is as a bleaching agent. The rate at which hydrogen peroxide bleaches a given substance increases with pH, from which it is inferred that the active species is the perhydroxyl ion HO_2^- which is formed by ionisation of hydrogen peroxide, as shown in equation 1.13 above. From the law of mass action

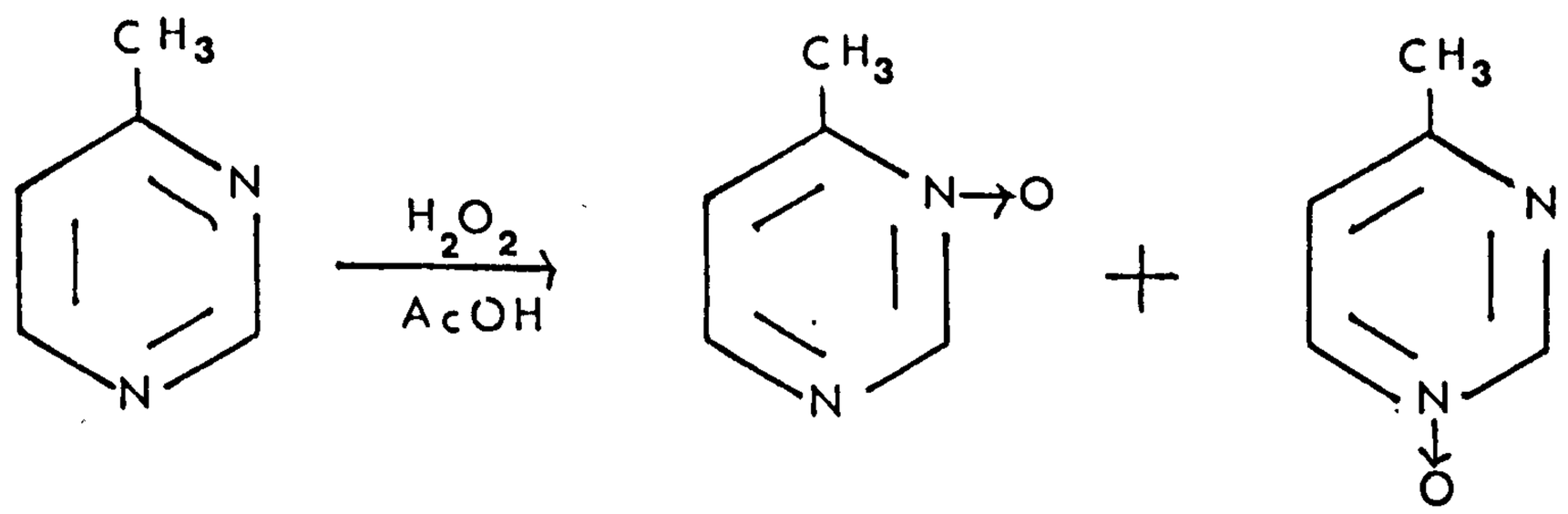
$$k_1 = \frac{[HO_2^-]\ [H^+]}{[H_2O_2]} \qquad [\ ] = \text{conc}$$

The reduction in $[H^+]$ which is implied in an increase in pH requires an increase in HO_2^- ions to keep k_1 constant.

It is well established that the oxygen released by decomposition of a peroxide has, in general, no bleaching action and may in fact cause damage to the cellulose. For example, cellulosic materials in a strongly alkaline (pH > 12) hydrogen peroxide solution, show reduction in the chain length of the cellulose molecules with an accompanying loss in strength.[65] During the bleaching of cellulose, metals such as iron, copper and manganese, even in minute amounts, have also been found to increase the damage to the cellulose.[65] Recently, Ney[71] has found that in the bleaching of cellulose fibres with hydrogen peroxide, the reaction can proceed via the HO_2^- ion or the HOO·radical, and that the coloured impurities can be bleached via the HO_2^- ion without the cellulose being attacked, whereas the HOO·radicals are liable to cause chemical degradation. To prevent the decomposition of hydrogen peroxide, stabilizers are used, one of the most widely used being sodium silicate. A typical bleaching solution will contain 0.1 to 0.4 wt.% hydrogen peroxide, about 1 to 1½% sodium silicate, and sufficient hydrogen peroxide to bring the pH to approximately 11.

1.7 N-oxidation of diazines by hydrogen peroxide and its influence on the rectivity of the ring.

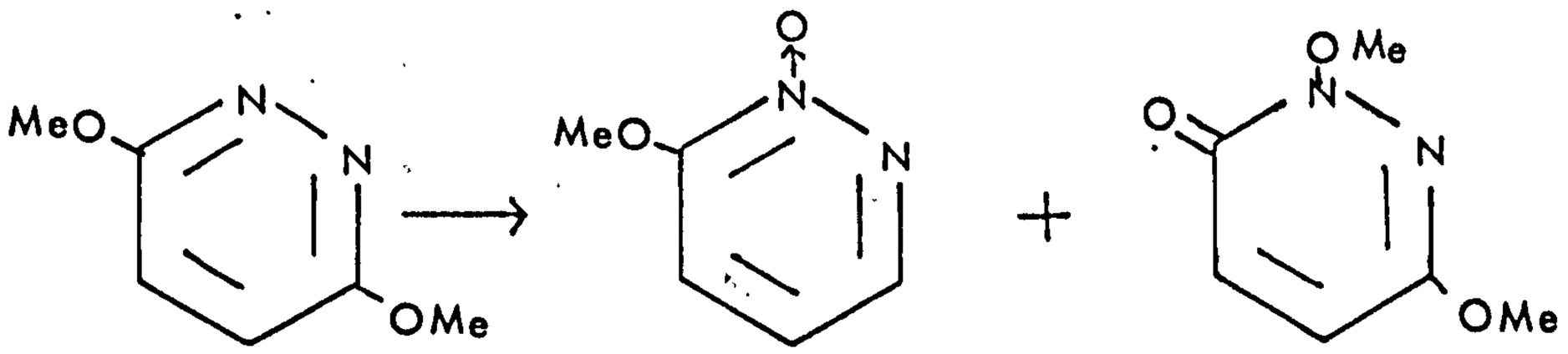
Hydrogen peroxide can oxidise at the N heteroatom of heterocyclic rings, to form N-oxides. This reaction has been shown to be favoured by strongly basic amines. Aliphatic tertiary amines are strongly basic and can be easily converted to the corresponding N-oxide in a comparatively good yield by allowing then to stand at room temperature with hydrogen peroxide solution.[72] Heteroaromatic tertiary amines such as pyridine, have a much weaker basicity and do not undergo this reaction. But, pyridine for example, was found to undergo N-oxidation with hydrogen peroxide when in the presence of a carboxylic acid.[72] With methyl pyrimidine, for example, Ogata et al[73] found that on reacting with hydrogen peroxide in the presence of acetic acid, both 1-oxide (XXXVIII) and 3-oxide (XXXIX) methyl-pyrimidine were formed.



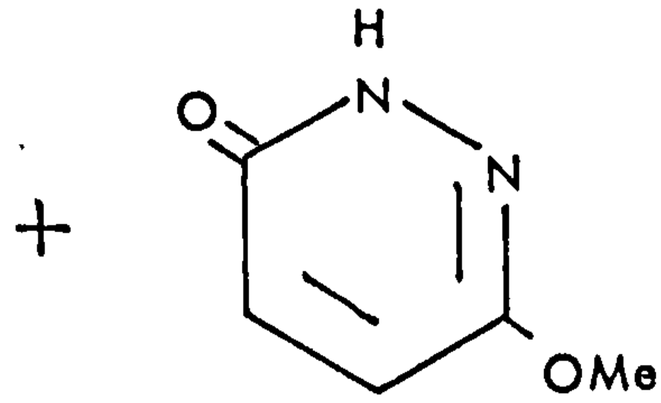
XXXVIII XXXIX

Ochiai[72] suggested that the higher the electron density of a ring nitrogen, the easier N-oxidation takes place. If an electron donor substituent is present at a position adjacent to, or conjugated with, the ring nitrogen, the electron density is elevated and N-oxidation becomes easier. On the contrary, an electron withdrawing substituent

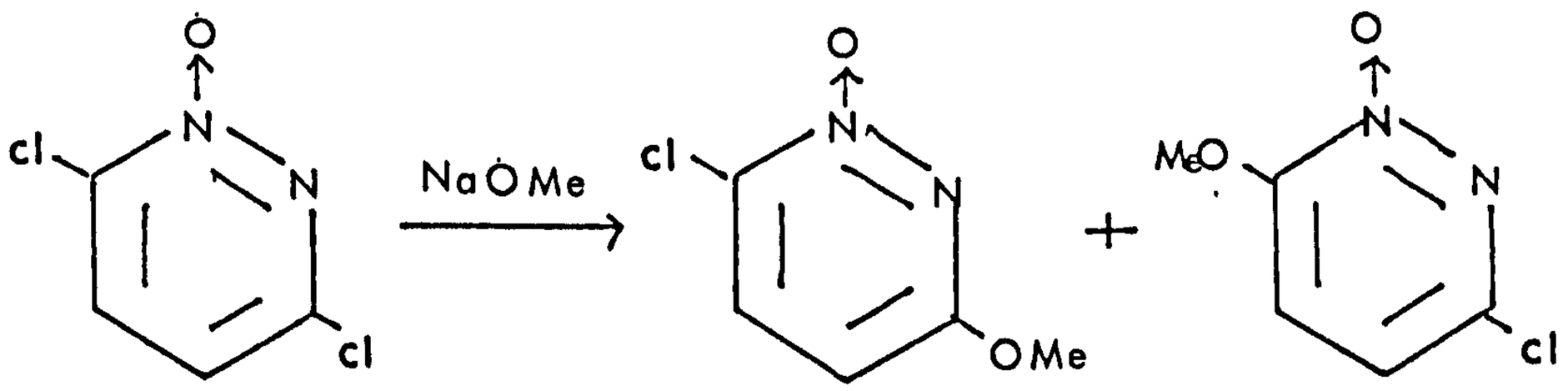
at these positions makes N-oxidation more difficult. For example, 3-methylpyridazine is converted to the N-oxide in good yields, whereas 3-chloropyridazine gives a very small yield of the 1-oxide derivative.(76) Also, 3,6-dimethylpyridazine is N-oxidised more easily in high yields than pyridazine itself.(74) During oxidation of 3,6-dimethoxypyridazine (XL) methyl migration can also occur, with the formation of a keto-methoxypyridazine. Thus, if the N-oxidation is carried out with hydrogen peroxide-maleic acid in dichloromethane, the following products are obtained.(75)



XL



N-oxidation increases the reactivity of the ring towards nucleophilic substitution. For example, 3-chloropyridazine 1-oxide is converted to 3-pyridazinol 1-oxide by heating on a water bath with 5% sodium hydroxide solution and 3,6 dichloropyridazine (XLI) 1-oxide is converted to 3-methoxy-6-chloropyridazine 1-oxide by reacting with sodium methoxide at room temperature:(77)



1.8 Free radical formation on cellulose by peroxides

Hydrogen Peroxide, as already mentioned in 1.6 can decompose at high pH values and high temperatures during the bleaching of cellulose. This decomposition results in a degradation of the cellulose with loss of strength, which has been attributed to the peroxy radical $HOO^{\cdot}$.(71)

Hydrogen peroxide can also produce $OH^{\cdot}$ radicals when in solution with Fe^{II} ions.(78) (79) (80) (81) Higginson and co-workers concluded on the basis of experiment that this reaction proceeded via a one electron transfer, as follows:-

$$(1.14)..... \quad H_2O_2 + Fe^{II} \rightarrow HO^{-} + HO^{\cdot} + Fe^{III}$$

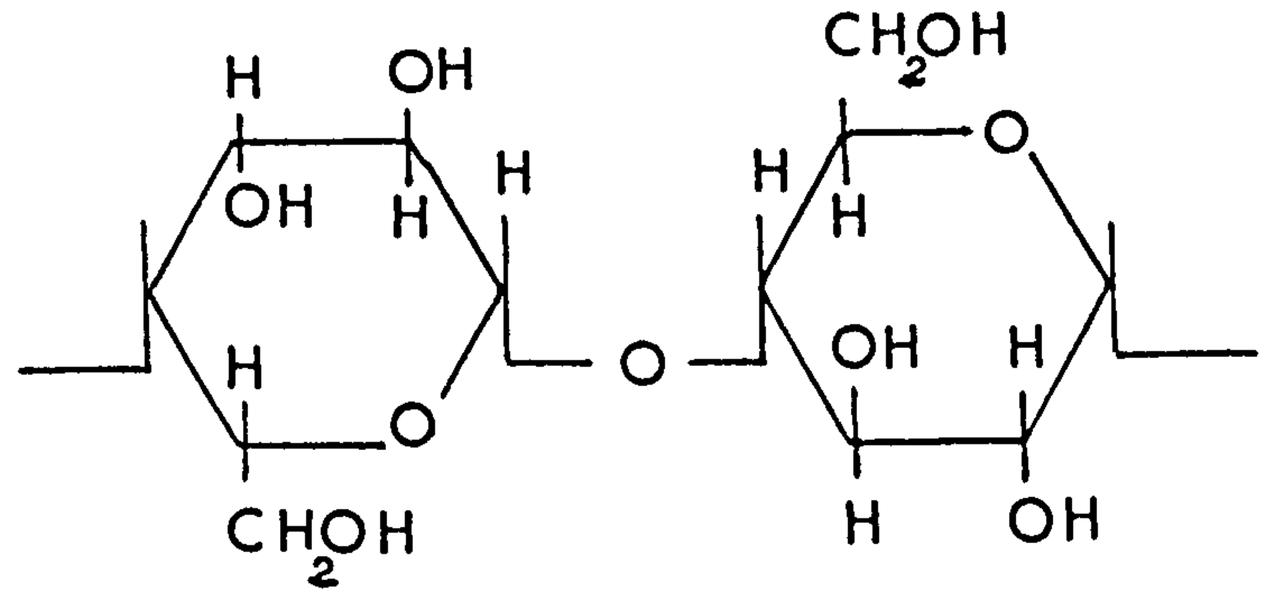
This reaction has been used to produce radicals on cellulose for subsequent grafting with polymers.(82) Arthur and co-workers(79) obtained an e.s.r. spectrum of cellulose treated with Fe SO_4 and hydrogen peroxide.

Since copper and manganese have the same effect as iron on the strength of the cellulose during bleaching with hydrogen peroxide, it may be assumed that they also react with hydrogen peroxide by a one electron transfer reaction as above, with the formation of $OH^{\cdot}$ radicals.

The way in which these radicals form radicals on the cellulose is by abstraction of hydrogen atoms from the cellulose molecule.

The chemical structure of cellulose consists of long chains of -anhydro-D-glycose units combined through a hemiacetal bridge between carbons 1 and 4 (figure below). Two such units form the repeating

unit, since the primary hydroxyl groups lie at opposite sides of the chain.



Theoretically, any of the hydrogen atoms in the molecule of cellulose as represented above can be abstracted.

In organic peroxides, the energy required for their dissociation into free radicals is some 20 k cal/mole less than that needed for hydrogen peroxide,[65] and as a consequence, thermally initiated free radical mechanisms are favoured. Among organic peroxide decompositions proceeding via free radical mechanisms occurring by breaking at the O-O bond, two of the most extensively studied have been those of di-tert-butyl peroxide and benzoyl peroxide.[83] Swain and co-workers found that the substitution of electron repelling groups on benzoyl peroxide increases the rate of decomposition, while electron attracting groups decreased the rate.

The lower strength of the O-O bond in organic peroxides also means that they can break down readily when exposed to u.v. radiation. Martin and Norrish (84) showed that the photolytic decomposition of t-butyl hydroperoxide in an inert solvent at 313 nm occurs with a very high quantum yield. More recently, Carlsson and Wiles (85) showed that hydroperoxides present in polypropylene underwent photolysis when exposed to the emission of a 500 W mercury lamp. The maximum energy absorption by the hydroperoxide was found to be 365 nm, and this value was taken as the wavelength of photolysis. From these results they drew the conclusion that photolysis of polymeric hydroperoxides can be expected to play an important part in the deterioration of polypropylene articles under weathering conditions, i.e. exposure to terrestial sunlight. (290 nm) in air.

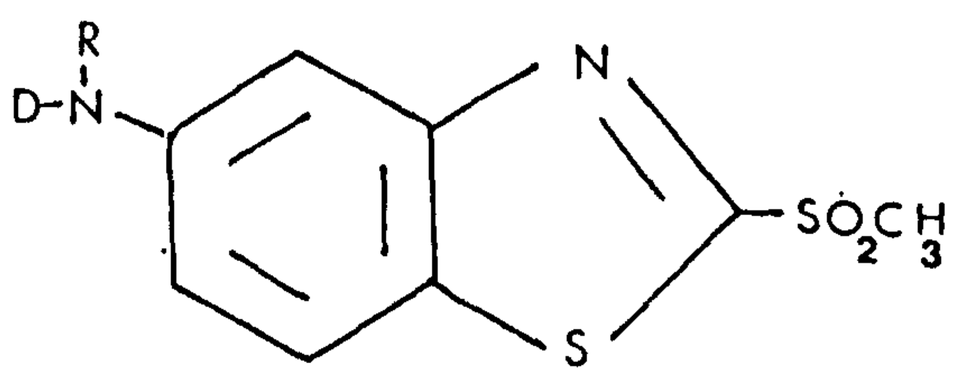
CHAPTER II

EXPERIMENTAL METHODS

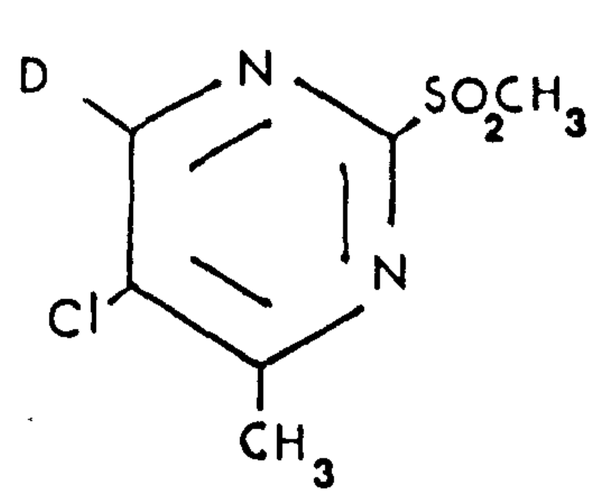
2.1 Identification of dyes

The reactive group of the Levafix EA range of dyes has been disclosed by Bayer, the manufacturers, to be a 2,4-fluoro-5-chloropyrimidinyl ring. Levafix E dyes are older dyes and their structure appears in numerous reviews, including the manufacturers' (Bayer). Their reactive group is a dichloro quinoxaline ring.

When it was thought of interest to this work to test a pyrimidinyl dye with a reactive group, as shown in B, most references pointed to this dye belonging to the Levafix P range of dyes manufactured by Bayer. However, dyes with two kinds of reactive group were reported (86) to be included in this range of dyes. They were as follows:



A



B

In order to identify the structure of the Levafix P dye, the method recommended by Beech was followed.(87) The electrolytes were first removed from the dye as described in 2.2. and an n.m.r. spectrum of the dye was taken. It indicated the presence of two different methyl groups as in B. Some of the dye was then treated with aqueous 2N sodium carbonate for 1 hour. The n.m.r. spectrum now indicated the presence of only one methyl group. Thus it was confirmed that the structure of the Levafix PN dyes used was B above.

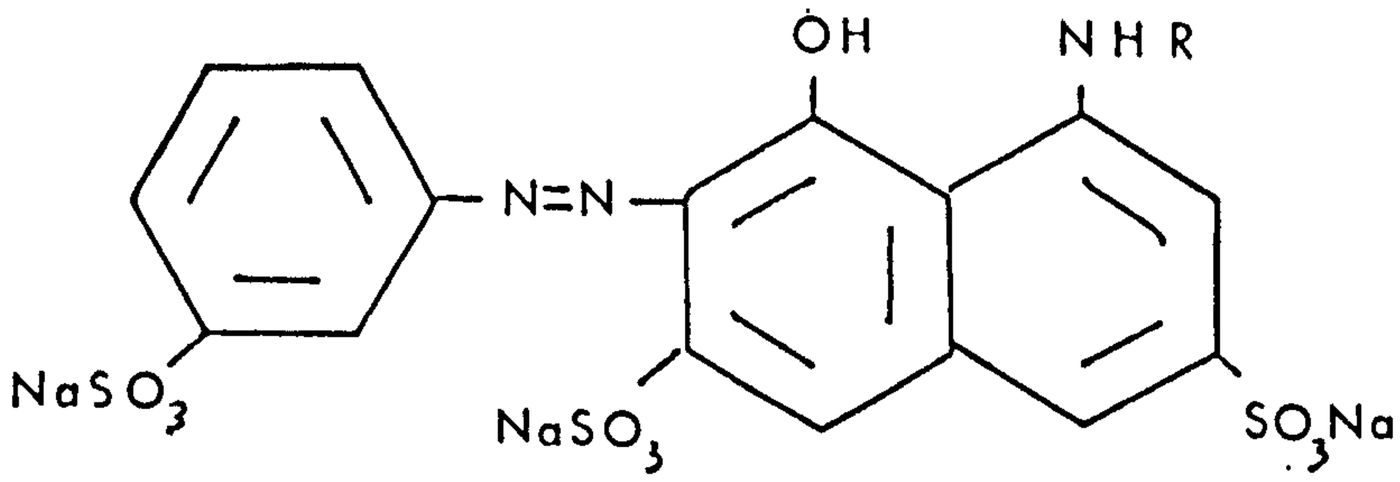
Two other commercial dyes which were thought to be of interest to the present work were the 2,4,5-trichloro and 2,4-dichloro-pyrimidinyl dyes which are known to belong to the Drimarene (S) and Reactone (Geigy) ranges of reactive dyes. However, the two reactive groups are not discriminated. Since it would be difficult to identify them with absolute certainty, they were instead prepared beforehand. (Dye VIII and Dye IX).

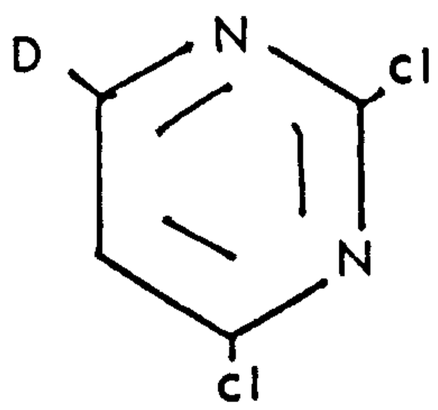
Another dye which was prepared, since it is not known whether it is used commercially, was the 2,4-chloro-5-cyano-pyrimidinyl dye. (Dye X).

Another advantage of obtaining these dyes by synthesis is that it was in this way possible to have three dyes for testing with the same chromophore.

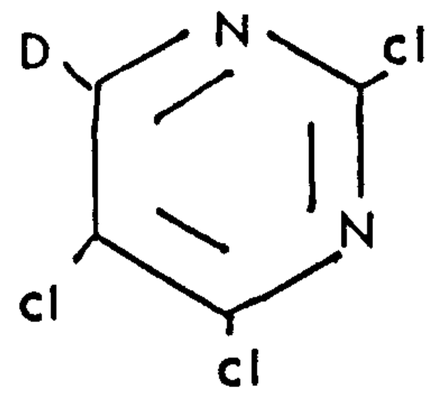
Choromophore D

Reactive group R

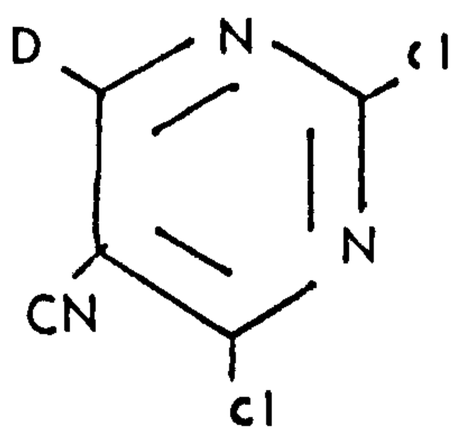




Dye VIII



Dye IX



Dye X

2.2. Synthesis of intermediates and dyes.

2,4,5,6-tetrachloropyrimidine (88)

Barbituric acid (13g) was mixed with phosphorus pentachloride (100g) and phosphorus oxychloride (50g) and the resulting mixture refluxed for 8 hours. The hot solution was poured slowly onto ice and left overnight to produce a yellow solid. The yellow aqueous mixture was steam distilled for several hours until no more colourless oil distilled over. The oil solidified on cooling to give a white solid with a strong odour. The white solid was filtered, washed with water and dried in vacuo over calcium chloride.

The yield was 7g (34% lit 37%) m.p. 62-64 (lit. 66-68°C) ν_{max} 865 (C-Cl) cm^{-1} (I.R.1).

(Found = C, 22.0; N, 13.1; Cl, 64.85. Calculated for $C_4N_2Cl_4$ C, 22.0; N, 12.9; Cl, 65.1%)

This preparation was repeated and done in scale up to four times as big as recorded above, when more of this product was necessary for the synthesis of the dye.

2,4,6-Trichloropyrimidine (89)

A mixture of dimethyl aniline (29.5 ml) and phosphorus oxychloride (52 ml) was poured slowly with mixing onto 17g of barbituric acid. The mixture was then refluxed for half an hour, during which time hydrogen chloride was evolved. The hot solution was poured slowly onto ice and left overnight. The resulting yellow solution was then extracted with 50 ml portions of dimethyl ether and the combined extracts dried over calcium chloride. The ether was then distilled off until the solution became dark and viscous. It was then distilled in vacuo and a colourless liquid distilled over at 98-102°/18 mm.

It solidified when cooled to give a white solid with a characteristic pungent odour, m.p. 20-21 (text 21°C); ν_{max} 860 (C-Cl) cm^{-1} (I.R.2). Yield = 13.7g, 54% (lit. 46%)

This preparation was repeated and scaled up to four times as big as recorded above when more of this product was necessary for the synthesis of the dye.

5-cyano-2,4,6 trichloropyrimidine (90)

A mixture of barbituric acid (19.2g) urea (72g) and potassium cyanate (12g) was heated slowly to 150°C and stirred at this temperature for three hours. Ammonia was given off during this time. After cooling to 100°C, 120 ml of hot water was added and the mixture further cooled to 50°C. Hydrochloric acid (10%, 37.5 ml) was then added. The mixture was cooled to 20°C and the fine white suspension of 5-carbamoylbarbituric acid poured out of the flask, filtered off, washed with water and dried (m.p. 90-91°C). ν_{max} 3400 ($-NH_2$), 1600 (-C=O) (I.R.3). A large solid residue of inorganic material (m.p.> 340°C) left in the flask was discarded.

5-carbamoylbarbituric acid (8.5g) was mixed with phosphorus oxychloride (40g) and then 14g of dimethylaniline was added slowly with stirring over ten minutes. The mixture obtained was refluxed for 45 minutes, during which time hydrogen chloride was evolved. After cooling the brown solution was poured onto ice and left overnight. The precipitated 5-cyano-2,4,6-trichloropyrimidine was filtered off, washed with water and dried. Yield = 6.5g, 65% . The light brown product was further purified by vacuum sublimation to yield a white crystalline solid, m.p. 119-121 (text. 119-121°C) ν_{max} 2220 (-C=N) (I.R. 4). Found: C, 28.5; N, 20.7; Cl, 49.0. Calculated for $C_5Cl_3N_3$ = C, 28.8; N, 20.2; Cl, 51.0)

The scaling up of the preparation of 5-carbamoylbarbituric acid was attempted several times, without success, as it was difficult to heat the mixture uniformly up to the melt temperature of 150°C without charring. It was therefore repeated several times at the smaller scale indicated above whenever more product was needed.

2,4,5-trichloropyrimidin-6-yl-H acid

H acid (1-amino-8-naphthol-3,6-disulphonic acid) was first purified in the following manner. It was dissolved in 10% sodium hydroxide and heated until a dark brown solution was obtained. This solution was then filtered and hydrochloric acid (36%) was added to it to re-precipitate the acid. It was dried below 80°C. 4g of the purified H acid was then dissolved in water (50ml) and acetone (37.5ml) at 50°C and the pH adjusted to 7 with 2N sodium hydroxide.

Tetrachloropyrimidine (5g) in acetone (12.5 ml) was added dropwise with stirring and the solution was further stirred under reflux at 50°C for three hours. The pH was maintained between 6 and 8 by addition of 2N sodium hydroxide. The product was precipitated by pouring the solution into acetone, and filtered. Yield = 4g, 70%. ν_{max} 3350(-NH), 1550 (-C=N-), 850 (C-Cl). (I.R. 5).

2,4-dichloropyrimidin-6-yl-H acid

The same method and weights as in the preparation of 2,4,5-trichloropyrimidin-6-yl- H acid were used but the reaction was more difficult to accomplish and only 2g of product was obtained. (35%) ν_{max} 3400 (-NH), 1570 (-C=N-), 830 (C-Cl). (I.R. 6).

Metanilic acid →2,4,5-trichloropyrimidine-6-yl-H acid (Dye IX)

2.5g of Metanilic acid (1-amino-3-sulphobenzene) were dissolved in a minimum amount of water and sodium carbonate was added until the solution was alkaline. The temperature was kept below 10°C whilst hydrochloric acid (36%) was added until the solution was acid to Congo Red paper. More ice was added and N sodium nitrite was added dropwise with stirring until there was just an excess of nitrite in solution, (tested with starch iodide paper). The resulting yellow solution was stirred at 0-5°C for half an hour and made neutral with sodium carbonate. The diazonium solution was then added slowly to a solution of the 2,4,5-trichloropyrimidin-6-yl-H acid condensate (6g), synthesised previously and already made slightly alkaline with sodium carbonate. A red colour developed immediately and the solution was stirred for a further hour. The dye was salted out by the addition of sodium chloride, filtered, washed with a 20% solution of sodium chloride and dried at 50°C. It was then purified by dissolving it in dimethylformamide and precipitating with acetone. (See 2.2). Finally it was filtered and washed with acetone. Weight of dye = 4g. (60% yield). ν_{max} 3400 (-NH), 1600 (-C=N-), 850 (C-Cl) cm^{-1}. (I.R. 7).

Metanilic acid→2,4-dichloropyrimidin-6-yl-H acid (Dye VIII)

The same method was used as for making the dye with 2,4,5,6-tetrachloropyrimidine but only 3g of 2,4-dichloropyrimidin-6--yl-H acid condensate were used. After purification with dimethylformamide the dye weighed 2g (60% yield). ν_{max}: 3400 (-NH), 1580 (-C = N-), 850 (C-Cl) cm^{-1}. (I.R. 8).

Metanilic acid→2,4 chloro-5-cyano-pyrimidin-6-yl-H acid (Dye x)

Metanilic acid was diazotised in the same way as for the other dyes and was added dropwise to an alkaline solution of H acid, with stirring, at room temperature. The resulting red solution was stirred for a further hour and the dye was then salted out. The dye was purified in dimethylformamide and dried at 50°C. This chromophore was then used more than once for making the dye as follows: 6g of H acid-metanilic acid were dissolved in water (100 ml) and stirred at room temperature. 5-cyano-2,4,6-trichloropyrimidine (2g) was dissolved in acetone (50ml) and water (25ml), and added dropwise to the chromophore (3g) with stirring, at room temperature. The pH was maintained at 5-6 by the addition of sodium carbonate solution (10%), while the solution was kept stirring for a further 2 hours, approximately. When the pH stopped dropping, the reaction was considered finished. The excess pyrimidine was filtered off and the dye was salted out. It was purified in the same way as the other dyes, with dimethylformamide and dried at 50°C. Yield (3g, 60%). ν_{max} = 3400 (-NH), 2200 (C-C $\equiv$ N), 850 (C-Cl) cm^{-1}. (I.R. 9).

2.3 Purification of dyes

The commercial dyes from the Levafix EA, Levafix E and Levafix P ranges were obtained from Bayer and those from the Procion MX and Procion H ranges from Imperial Chemical Industries Ltd. It was necessary to remove impurities such as buffer salts and other electrolytes and the method quoted by Mehta et al[91] was used as follows:

The dye was dissolved in the minimum quantity of cold dimethylformamide and the solution was filtered. Excess dimethylformamide was evaporated off in a rotary evaporator and the dye was precipitated by adding acetone. It was filtered, washed with fresh acetone and dried at 70°C.

In the case of one dye, Levafix Blue E3GA, another method, first used by Robinson and Mills[92] was followed, since this dye was not soluble in dimethylformamide. The dye was precipitated from water with sodium acetate and filtered. Sodium acetate was removed from the precipitate by warming in ethanol to remove the excess electrolyte. The dye was insoluble in ethanol and was filtered off, washed with fresh ethanol and dried at 50°C.

With the dyes which were synthesised, i.e. the trichloro, dichloro and 5-cyano-2,4-chloropyrimidinyl dyes, the inorganic salts were removed with dimethylformamide as above and the dye used in the salt free form in dyeing. A small quantity of each of these dyes was further purified by column chromatography, as they showed more than one spot when tested on thin layer chromatography and it was therefore necessary to purify them further for use in the calibration curves. Several diluents recommended for the T.L.C. of reactive dye[93] [94] were tried and it was found that the best one was n-butanol: n-propanol: ethyl acetate: water (20: 40: 10: 30). The chromatography column was

prepared by pouring into a glass column of $1\frac{1}{2}$" diameter and fitted with a glass wool plug at the bottom end, a slurry of silica gel G in the chosen diluent. Glass wool was again packed at the top and the column was well rinsed with the diluent before running in the dye. The dye solution obtained was then evaporated to dryness and any inorganic material present was removed by dissolving the dye in dimethylformamide in the manner already described. The dye was precipitated with acetone, washed with acetone, filtered and dried at 50°C.

The coloured impurity which was separated from the 5-cyano-2,4-chloropyrimidinyl dye was of an identical blue to the chromophore used in the final stage of the synthesis (XVI). In the case of the 2,4 dichloro and 2,4,5 trichloropyrimidinyl dyes the main coloured impurity which separated from the dyes was of a violet colour. It was a much weaker colour than the dye, which suggests very little conjugation. It was possibly the compound formed by the self coupling of the azo salt. There was also a very small amount of a blue impurity which is the chromophore XVI, mentioned above and is formed from the small amount of 1-amino-3,6-sulpho-8-hydroxy naphthalene, which was not possible to separate from the intermediate XX above. None of these coloured impurities contain the reactive ring and therefore have no affinity for the cellulose. This is confirmed by the fact that the dyes on the fibre have the same λ_{max} as the dyes used in the calibration.

2.4 Calibration curves of dyes

For the measurement of the concentration of dye on the fibre before the treatment, the optical density of the solutions of dye in sulphuric acid was measured. (See 2.6). However, for the measurement of the concentration of dye which broke away from the fibre due to hydrogen peroxide attack, the optical density of solutions of dye in dimethylformamide/water (50/50 proportions) was measured. (See 2.8). Hence it was necessary to plot curves of each dye, both in sulphuric acid solutions and in DMF/H_2O.

Calibration curves were drawn from optical density measurements of solutions of known concentration of the dyes tested in this work, with the exception of the Levafix P and the Procion H dyes, for reasons given later.

The concentration of sulphuric acid employed was 25% v/v because when a fabric was dissolved in concentrated sulphuric acid dilution to 25% still gave strong concentrations of dye and therefore the accuracy was good. Some dyes, however, were not soluble in a 25% strong solution and the dilution had to be increased until they dissolved. However, the results still proved to be satisfactory and this was the method followed.

Calibration in dimethylformamide/water did not present problems apart from the need to check the spectrophotometer cells for the presence of air bubbles. The cells were shaken or the solution changed when this happened. The optical density of the dye in either solvent was measured in a Pye Unicam SP600 spectrophotometer at the wavelength of maximum absorption (λ_{max}) which had previously been measured in a Pye Unicam SP -820 spectrophotometer. From the calibration curves and applying the Beer-Lambert Law the ratios of O.D./conc. of the dye in either solvent were calculated and were found to be as follows:

Table 1. Ratios of optical density/concentration of the dyes tested

Dye		Solvent	λmax (nm)	Ratio: O.D./Conc. (mg l^{-1})
I	Levafix Orange	10% H_2SO_4	485	0.0200
	E3GA	DMF/H_2O (50/50)	485	0.0186
II	Levafix Brilliant	10% H_2SO_4	520	0.0230
	Red E4BA	DMF/H_2O (50/50)	550	0.0240
III	Levafix Golden	25% H_2SO_4	430	0.0400
	Yellow E3GA	DMF/H_2O (50/50)	415	0.0260
IV	Levafix Blue	20% H_2SO_4	550	0.0193
	E3GLA	DMF/H_2O (50/50)	610	0.0280
V	Levafix Brilliant	25% H_2SO_4	520	0.0194
	Red E2B	DMF/H_2O (50/50)	545	0.0250
VI	Procion Red MX5B	10% H_2SO_4	510	0.0420
		DMF/H_2O (50/50)	545	0.0450
VIII	Dichloropyrimi	25% H_2SO_4	520	0.0350
	dinyl Red Dye	DMF/H_2O (50/50)	530	0.0450
IX	Trichloropyrimi	25% H_2SO_4	520	0.0380
	dinyl Red Dye	DMF/H_2O (50/50)	535	0.0410
X	5-Cyano-2,4-chloro	20% H_2SO_4	515	0.1730
	pyrimidinyl Red	DMF/H_2O (50/50)	555	0.0185
	Dye			

2.5 Dyeing methods

Of the commercial dyes, the Levafix EA, Levafix P and Procion MX dyes were applied by the 'pad-batch' method and Levafix E and Procion H dyes by the 'pad-bake' method. All the dyeings were prepared according to procedures recommended in the relevant pattern cards.

Of the dyes synthesised, the 5-cyano-2,4-chloropyrimidinyl dye was applied by the 'pad-bake' method in the same way as the Levafix E dyes, and the trichloropyrimidinyl and dichloropyrimidinyl dyes were applied by the 'pad-steam' method, as described in the pattern card for Drimarene R (Sandoz) dyes. Details of the methods are given below:

Pad-batch The pad liquor contained dye, urea and sodium carbonate. (See Table 2). The dry fabric was passed through the pad liquor in a laboratory Benz padding machine, wrapped in a polythene sheet to avoid evaporation and batched for over 20 hours. The unfixed dye was then washed off and the fabric was dried in a Werner Mathis laboratory machine, type DHe, at 110°C for 2 minutes.

Pad-bake The pad liquor again contained dye, urea and sodium carbonate, but in this method more urea was used. (See Table 2). The dry fabric was passed through the pad liquor as above and dried and fixed simultaneously by 3 minutes heating at 150°C in the Werner Mathis laboratory machine. The unfixed dye was washed off and the fabric was dried as before.

Pad-steam The pad liquor consisted of a solution of approximately the same quantities of dye, urea, soda ash and Glauber's salt. (See Table 2). The dry fabric was passed through the pad liquor as before, dried at 110°C for 2 minutes and steamed at 100-105°C for 10 minutes. The unfixed dye was washed off and the fabric was again dried as before.

Washing off Firstly the dyed fabric was rinsed thoroughly in cold water. Then it was rinsed in hot water. It was then boiled in a solution containing 1-2 parts of Lissapol ND per 1000 parts of water for at least 15 minutes. Finally, it was rinsed in hot, then in cold water.

Table 2. (overleaf)

Table 2. Dyeing method and dye liquor used for the different dyes tested

Dye	Dyeing method	Pad-liquor (g/l)	
Levafix EA dyes	Pad-batch	dye urea soda ash	30 50 30
Levafix Brilliant Red E2B	Pad-bake	dye urea soda ash	40 150 15
Procion Red MX5B	Pad-batch	dye urea soda ash	40 50 40
Procion Red H-8BN	Pad-bake	dye urea soda ash	40 200 20
Levafix Brilliant Red PNB	Pad-batch	dye urea soda ash	25 40 25
Trichloropyrimidinyl and Dichloropyrimidinyl dyes	Pad-steam	dye soda ash Glauber's salt	10 50 12
5-Cyano-2,4-chloro-pyrimidinyl dye	Pad-bake	dye urea soda ash	30 100 30

Procion Red MX5B and Levafix Brilliant Red E4BA were also applied by the exhaustion method as part of an experiment to find out the influence of the dyeing process on the breakdown. The procedure and the concentrations of common salt and soda ash were those recommended by the pattern cards and were the same for both dyes. The procedure was as follows:

Exhaustion dyeing Dyeing was carried out in a 1 litre beaker. The dyebath was set and maintained at 40°C by placing the beaker in a water bath with thermostat control. The cotton fabric was immersed and after 10 minutes common salt was added and the fabric was stirred at frequent intervals for 30 minutes. Soda ash was then added and the fabric was stirred in the dye solution for a further 10 minutes. Loose dye was then washed off in the same way as for the other dyeings.

2.6 Determination of the concentration of dye on the fibre.[95]

The dyed pieces of fabric were first dried in the oven at 70°C to constant weight. The dyed fabric was then cut up and dissolved in concentrated sulphuric acid at 0°C in the approximate proportion of 0.2 - 0.3g of fabric for 25cc of concentrated sulphuric acid. This took between 8 to 15 hours depending on the dye. Solutions were kept in an ice bath and were shaken regularly. When the fabric was completely dissolved, the solutions were diluted by pouring them slowly onto ice and diluted to 25% concentration. In the cases of dyes that do not dissolve in 25% sulphuric acid (see 2.3) the dyeings were dissolved in concentrated sulphuric acid and the solutions were diluted to less than 25% (same concentration as that used in the calibration of the respective dyes). The optical density of the solutions was measured using as a blank a solution of undyed fabric of the same concentration of sulphuric acid as the solution being tested. From the values of the slope (ratio O.D./conc.) of the calibration curves (Table 1) the amount of dye on the fabric was calculated. (Table 3).

Table 3. (overleaf)

* In these cases the concentrations of the solutions were halved to avoid errors in the optical density measurement.

Table 3. Concentrations of dyes on the fibre

	Dye	Solvent	Weight of fabric (g)	O.D.	Dye on fabric mg/g (ave.)
I	Levafix Orange E3GA (1st dyeing)	10% H_2SO_4 (25 in 250 cc)	0.253 0.230	0.30* 0.26*	29.0
	Levafix Orange E3GA (2nd dyeing)	10% H_2SO_4 (25 in 250 cc)	0.203 0.216	0.32 0.33	19.4
II	Levafix Brilliant Red E4BA (1st dye)	10% H_2SO_4 (25 in 250 cc)	0.265 0.254	0.22* 0.20*	17.6
	(2nd dyeing)		0.429	0.12	3.1
III	Levafix Golden Yellow E3GA	25% H_2SO_4 (25 in 100 cc)	0.228 0.227	0.3* 0.3*	6.6
IV	Levafix Blue E3GLA	20% H_2SO_4 (50 in 250 cc)	0.447 0.445	0.5 0.55	15.3
V	Levafix Brilliant Red E2B	25% H_2SO_4 (62.5 in 250cc)	0.442 0.432	0.57* 0.55*	33.0
VI	Procion Red MX5B	10% H_2SO_4 (25 in 250 cc)	0.250 0.240	0.32 0.35	8.0
VII	Dichloropyrimidinyl (Red)	25% H_2SO_4 (25 in 100 cc)	0.327 0.249	0.4 0.3	3.4
VIII IX	Trichloropyrimidinyl (Red)	25% H_2SO_4 (25 in 100 cc)	0.284 0.288	0.28 0.29	2.6
X	5-Cyano-2,4-chloropyrimidinyl(Red) (1st dyeing)	20% H_2SO_4 (50 in 250 cc)	0.407 0.404	0.28 0.3	10.3
	" (2nd dyeing)	20% H_2SO_4	0.370 0.408	0.07 0.07	2.6

2.7 Methods of testing

2.7.1 Reaction in solution of hydrogen peroxide

Solutions containing 5g/l of detergent and alkali were prepared as previous work on this field showed that this was the optimum concentration of detergent for the reaction.[2] The detergent used was the A.A.T.C.C. standard detergent without optical brightener (W.O.B.) and without perborate, and with the following composition:

Linear alkylate sulphonate-sodium salt (LAS)	- 14.0%
Alcohol ethoxylate	- 2.3%
Soap - high molecular mass	- 2.5%
Sodium tripolyphosphate	- 48.0%
Sodium silicate (SiO_2/Na_2O = 2)	- 9.7%
Sodium sulphate	- 15.5%
C.M.C (carboxymethylcellulose)	- 0.2%
Moisture	- 7.8%
	100%

The detergent had previously been tested for the presence of perborate and it was confirmed that it did not contain any.[1] The detergent was dissolved in 100cc of distilled water by warming it up to approximately 40°C with stirring. After cooling to room temperature (22°C ± 2°C) 0.4cc of hydrogen peroxide (100 volume) were added and the pH was adjusted to the required value with the addition of sodium hydroxide (2N solution) using a pH meter. The concentration of hydrogen peroxide chosen, 4 ml/1, had been found in previous work[1] in this field to have approximately the same effect on the dyeing as 5 g/1 of sodium perborate, which is quite a reasonable concentration for drawing comparisons with normal domestic laundering.

Samples of approximately 0.4g of dyed fabric were first dried at 70°C to constant weight and then soaked in 100cc of the prepared solution (liquor ratio 250:1) at room temperature (22°C ± 2°C) for 20 minutes (except when measuring rates of reaction when different soaking times were applied). It had been previously found by I.D. Rattee and K.F. So[1] that the reaction was almost complete after 20 minutes. All the dyeings were tested at pH 9.8 (± 01), which is the pH of the solution containing the A.A.T.C.C. standard detergent (5 g/1) and 0.4 of hydrogen peroxide (100 vol.), and at pH 11 (± 0.1). Some were also tested at pH 12 (± 0.1) The pH was increased to these values by the addition of a solution of 2N sodium hydroxide.

For every dyeing being tested a 'blank' test was carried out in a solution without hydrogen peroxide but also containing 5g/1 of detergent and at the same pH as the test solution, as it was observed that some dyeings underwent alkaline hydrolysis and colour was lost when the dyeing was subsequently rinsed with hot DMF/H_2O, 50/50. In some cases a very small amount of dye also came off just by rinsing the untreated dyeing with boiling DMF/H_2O, 50/50. This was unfixed dye that it was not possible to extract during the washing off process but which came off with the hot solvent. The value of the 'blank' was also assumed to include this value, corresponding to unfixed dye.

The samples of fabric were stirred occasionally during the soaking and were then squeeezed and dried. The pH of the solutions was measured at the end of the reaction and was observed to be the same as at the beginning.

2.7.2 Drying of samples

The samples were squeezed in a laboratory Benz padding machine at an expression of 75% and were dried under a flow of very hot air from a hair drier for approximately 1 minute. It was found that by drying some test samples in a Benz stenter at 90°C for 1 minute, as had been done in previous work[2], gave the same results. This was also a conclusion drawn by I.D. Rattee and K.F. So[1]. The hair dryer was therefore the method preferred for its simplicity from the beginning of this work.

2.7.3 Exposure of treated samples to heat and light source

The dried treated samples of fabric were exposed to a tungsten fluorescent lamp MBTF (240-250V, 500W) at a constant temperature of 40°C. The lamp had a cylindrical shield of aluminium sheet surrounding it, within which the samples were hung, (Figure 3) and the unit was enclosed in a small room, hardly bigger than the lamp and surrounding shield, so that the temperature was kept constant. The reproducibility of results when this lamp had been used previously for the same type of work[1] [2] was good so it was used again as a means of breaking down the dye on the fibre. The temperature was read from a thermometer specially fitted next to a sample.

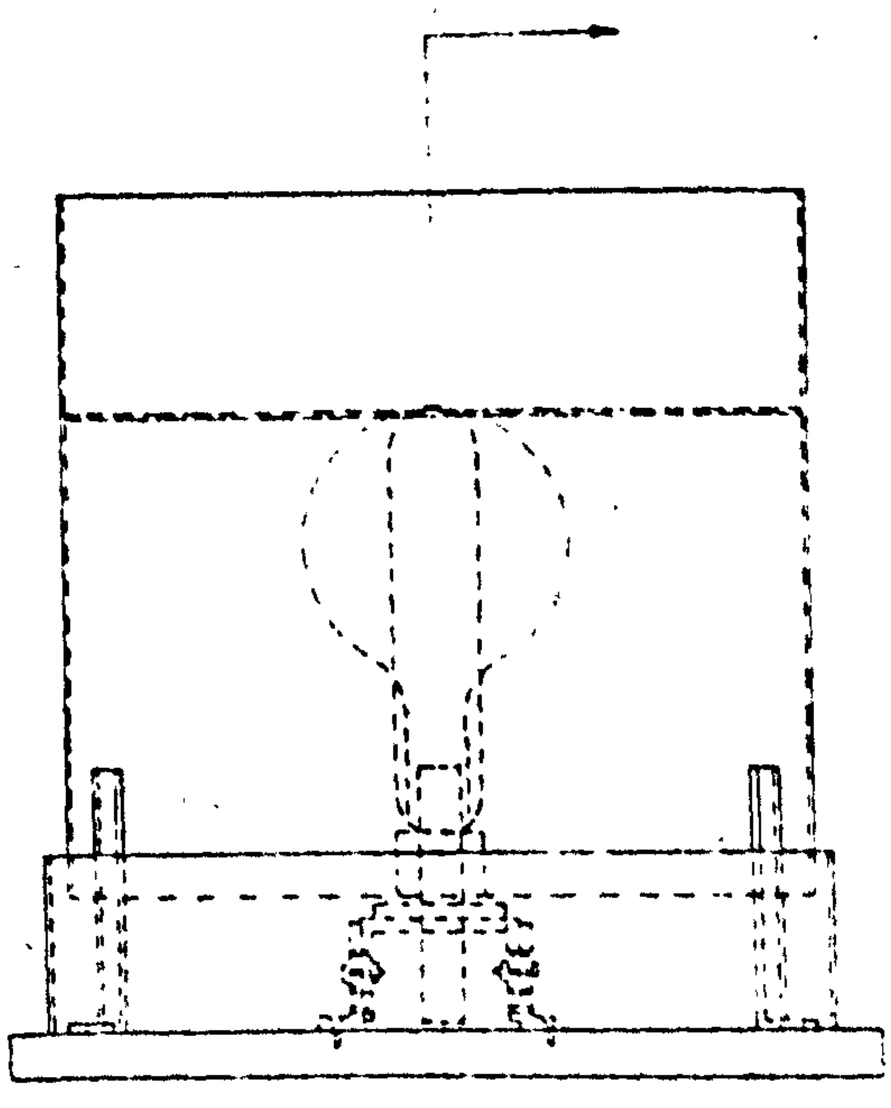


Figure 3. Heat and light source.

2.8 Extraction of breakdown product from the fibre and calculation of % breakdown.

The dye which was broken off from the fibre was extracted in a glass extractor of the type shown in Figure 4 . ('Novel extractor') as it had previously been found to be a very convenient apparatus to use when handling samples of fabric of the size used throughout this work, approximately 0.4g.(2) Much bigger samples would not fit, and fibre in other forms, i.e. loose fibre, would have to be handled in a soxhlet extractor, as the 'novel extractor' does not have a filter. The samples of fabric were placed in a centre bulb where the extracting solvent, a 50% solution of dimethylformamide in water, was raised to boiling point (105°C - 110°C) and forced out, carrying the dye with it. Some more fresh solution was dropped into the bulb and the procedure repeated until the solution did not carry any more dye with it. The bulb containing the fabric was heated by perchloro ethylene vapour which was continuously refluxed during the extraction. In order to avoid any reaction which could possibly occur due to the presence of any remaining hydrogen peroxide, the solvent was first passed cold through the fabric.

The wavelength of maximum absorption (λ_{max}) of the extracted dyes in the 50% dimethylformamide solution was measured and was found to be the same as the λ_{max} of the dye originally used in the dyeing and used in the calibration curve of the dye in DMF/water (50/50). One of the dyes tested, Levafix Brilliant Red PNB, was the exception, as the λ_{max} of the extracted dye was very different from that of the original dye, as shown later. No calibration curve was therefore plotted for this dye. The solutions of extracted dye were made up to 50ml with a fresh solution of 50% dimethylformamide in water, which was also used as a 'blank' and the optical density was measured in

a SP 600 UNICAM spectrophotometer at the wavelength of maximum absorption. In some cases the solutions were made up to 25ml and in one experiment 4 cm cells were used. Otherwise the results refer to solutions of 50 ml and cells of 1 cm thickness. From the value of the optical density and the value of the ratio O.D./conc. of the dye (Table 1) and applying Beer-Lambert's law, the quantity (mg.) of dye which comes off was calculated.

This quantity was converted to mg of dye which were lost by 1g of fabric, and by dividing this value by the values of the original amount of dye (mg.) in 1g of fabric (Table 3), the percentage breakdown was obtained.

The measurement of the loss of dye was attempted by measuring the dye on the fibre before and after the reaction, in the same manner as described in 2.5, avoiding in this way the calibration of the dyes which was difficult sometimes, and in the case of one dye, Levafix Brilliant Red PN-B, not possible as already mentioned (above). The errors were, however, large and this method was abandoned.

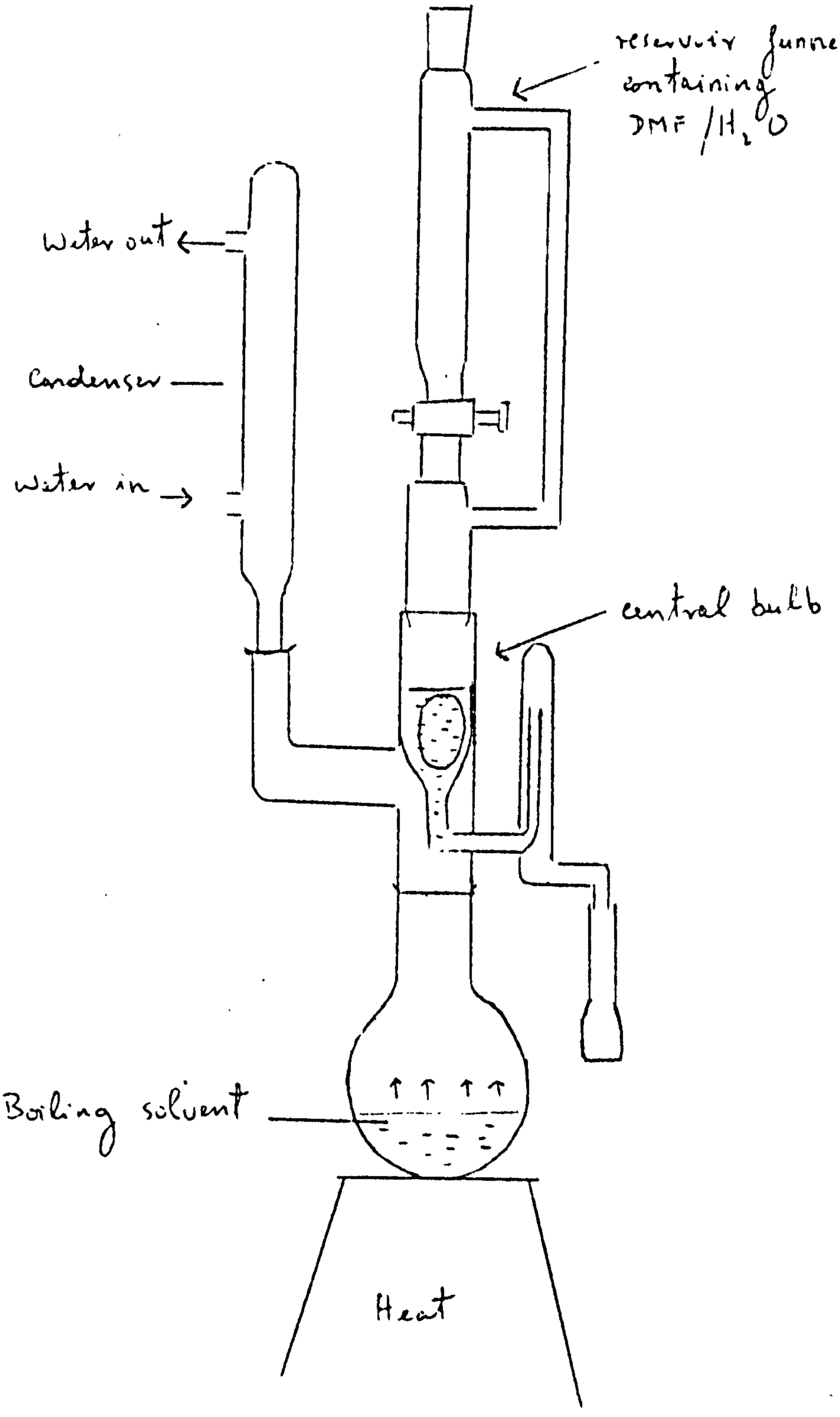


Figure 4. Apparatus for extraction of breakdown product.

2.9 Determination of the hydroperoxide content

The method used was developed from the method first used by Wagner, Smith and Peters[96] for the determination of organic peroxides and adapted by Carlsson and Wiles[98] for the determination of hydroperoxide on polypropylene films. Samples of approximately 0.4g of dyed fabric were rinsed thoroughly with cold water after the reaction in the hydrogen peroxide solution, and were squeezed and pressed between two sheets of absorbing paper. They could not be hot dried because of the risk of destroying the hydroperoxide formed. They were then acidified in a solution of 20ml of glacial acetic acid in 200ml of isopropyl alcohol and were refluxed in 50ml of a solution of 20% sodium iodide in isopropyl alcohol (w/v) for 30 minutes. During this time the iodide ions are oxidised by the hydroperoxide present on the dyeing to iodine, but the excess of iodide ions forms I_3^- ions with the iodine, as shown in the following equations (1,2).

(1) $R\text{-}O\text{-}OH + 2H^+ + 2I^- \longrightarrow I_2 + 2H_2O$

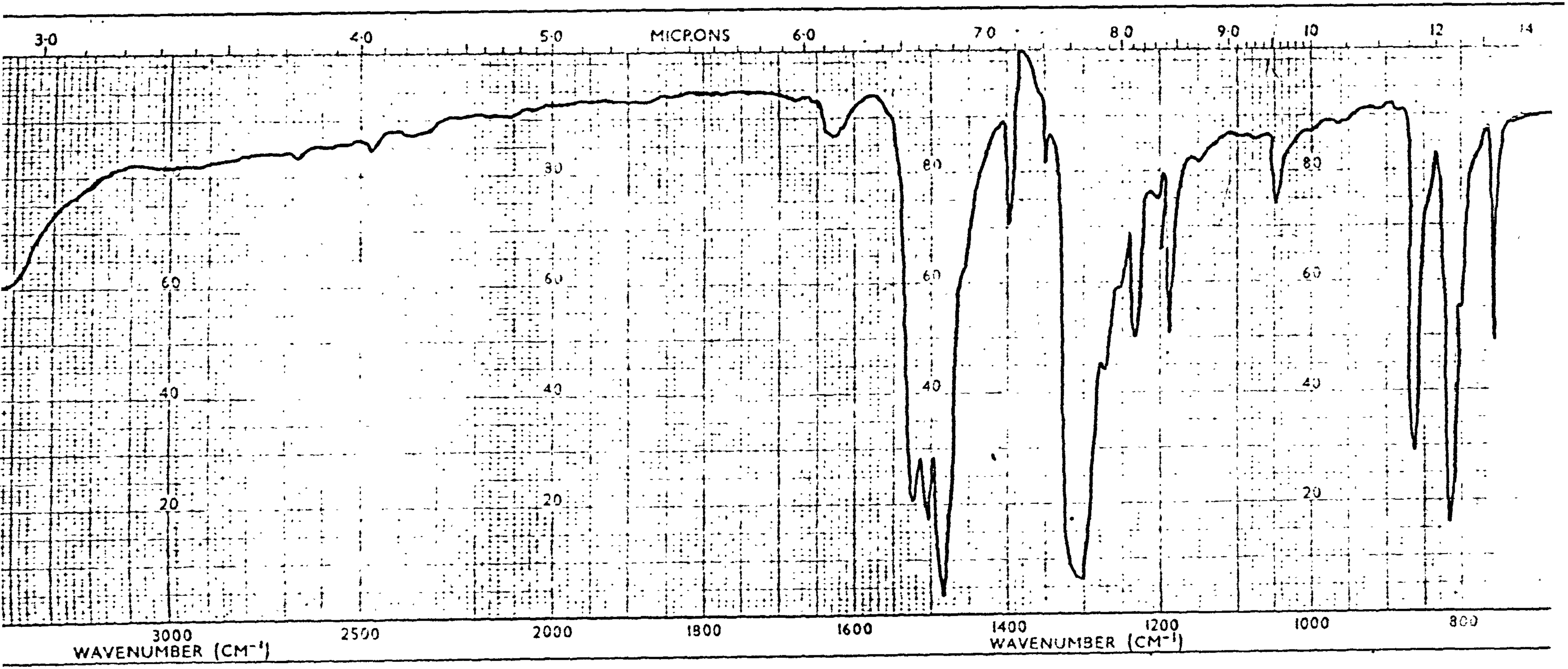
(2) $I_2 + I^- \rightleftharpoons I_3^-$

Shorter reflux times were tried but it was found that not all the hydroperoxide reacted. Light was found to catalyse, the reverse reaction (2) shown above, with the formation of iodine, confirmed by the loss of colour when adding sodium thiosulphate, and giving erroneous results. The reaction was therefore carried out in the dark. The 100cc reaction vesel was covered by aluminium foil and the reaction was carried out in a dark fume cupboard. The reaction solutions were cooled and poured into 50cc volumetric flasks which were inside suitable boxes to exclude light. The volume was made up to 50cc with a 20% solution of sodium iodide in isopropyl alcohol and

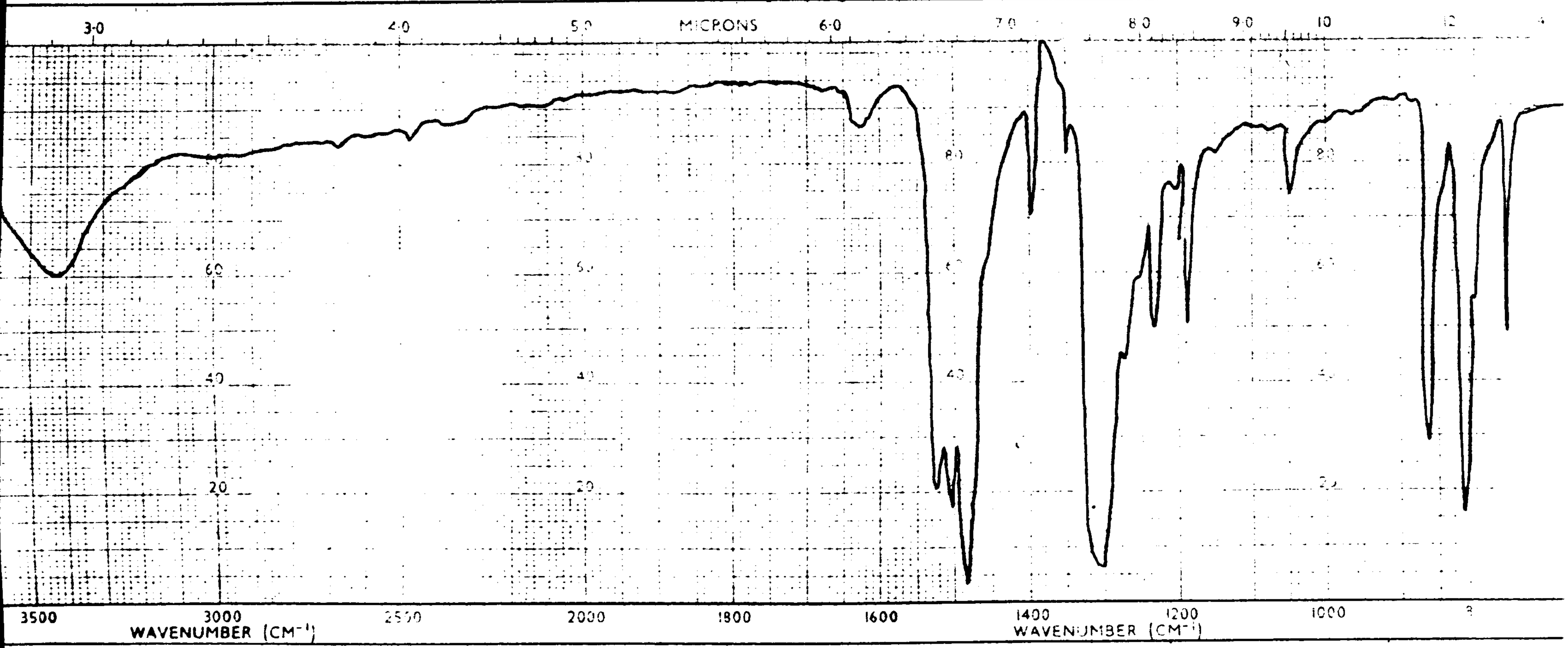
the optical density measured at 360nm (λ_{max} for I_3^- ions) in a Pye Unicam SP8-150 spectrophotometer, using 1cm quartz cells. Both these operations were done in an instrument room with only the red light on. The blank used was isopropyl alcohol which had been 'calibrated' in the following way: A solution obtained using an undyed sample of fabric (0.4g) was put through exactly the same treatment as the dyed samples being tested. This 'blank' treatment was repeated twice and the reading of the optical density at 360 nm, using isopropyl alcohol as a blank showed no significant variation. The average subtracted from the optical density values of the test samples which were obtained using isopropyl alcohol as a blank. (O.D. of blank = 0.04).

For the calculation of the concentration of hydroperoxide the molar extinction coefficient of 25000 M^{-1} cm^{-1} for I_3^- given by Carlson and Wiles[97] was used.

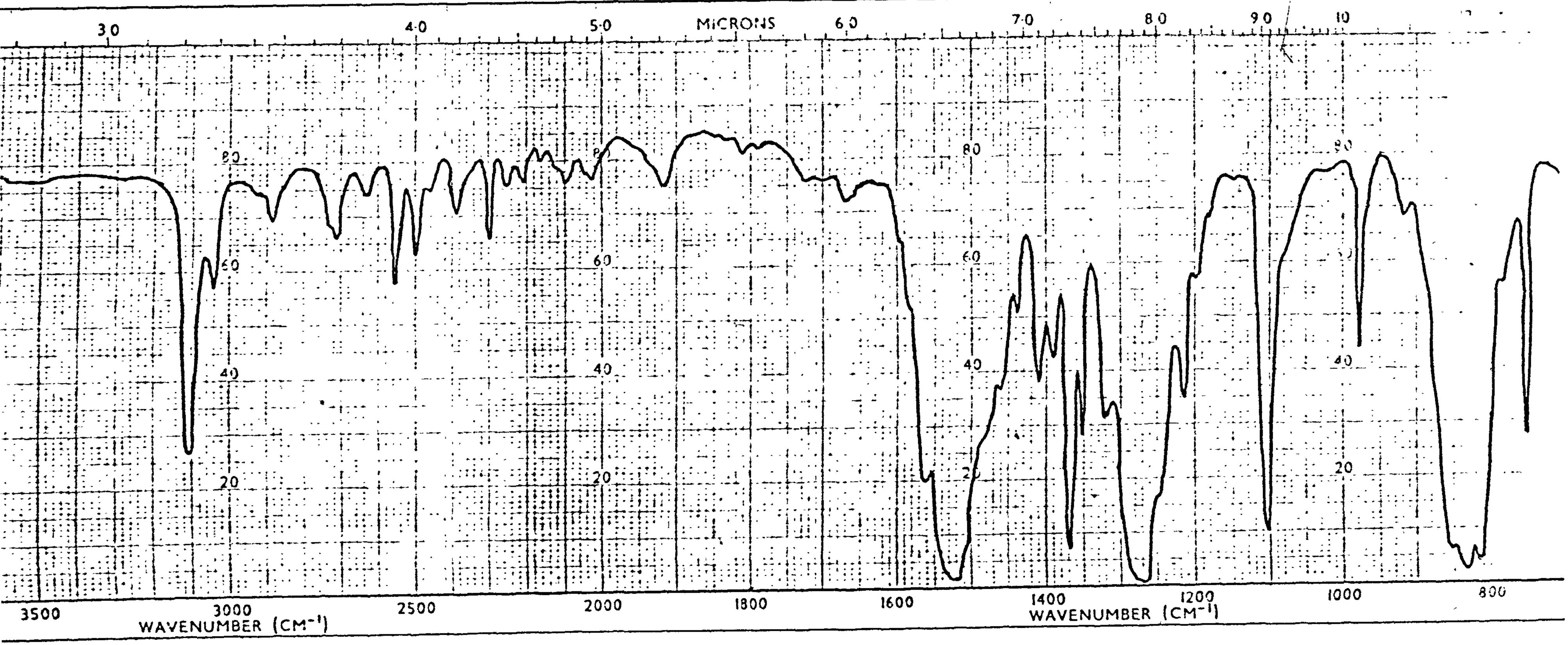
With the above procedure it is possible to take advantage of the oxidative stability of iodide ions in isopropyl alcohol (obviating the need for nitrogen blanketing) and the high sensitivity and convenience of a spectrophotometric method.



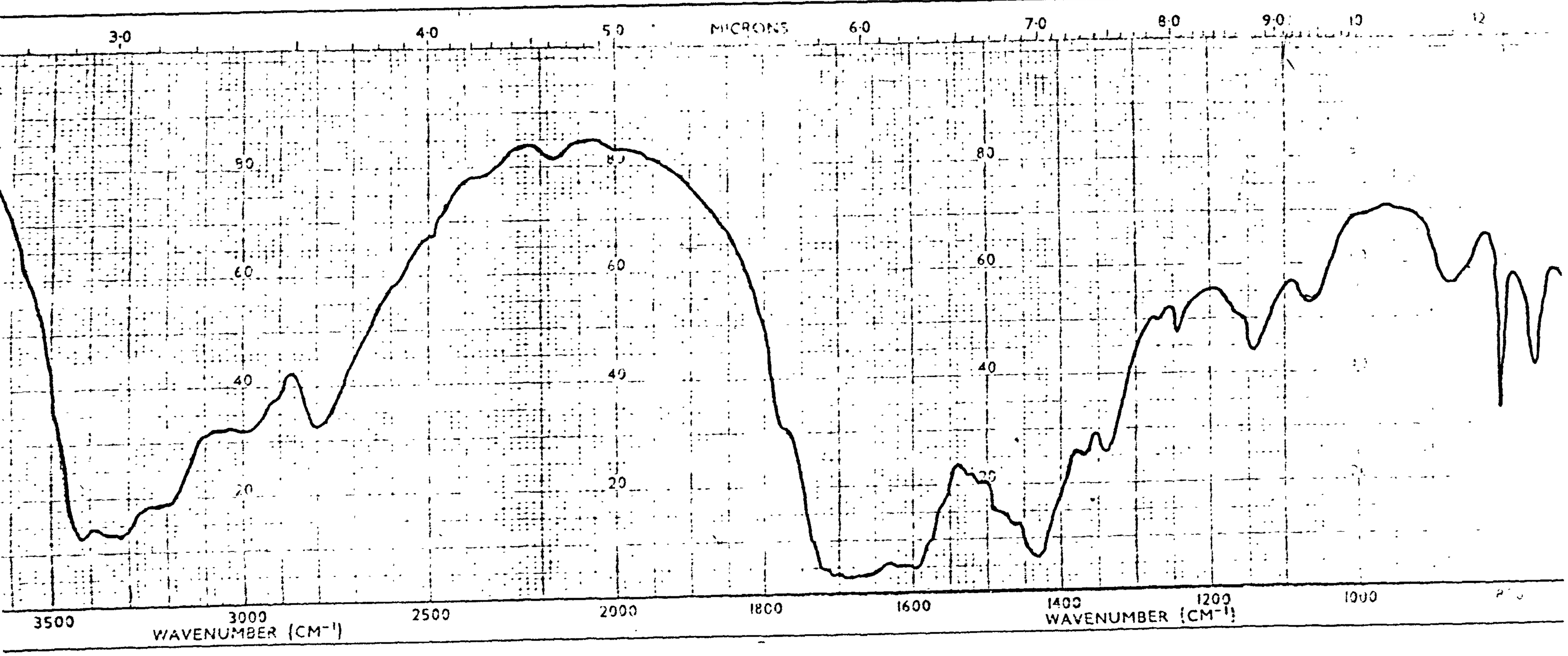
I.R. 1 Tetrachloropyrimidine



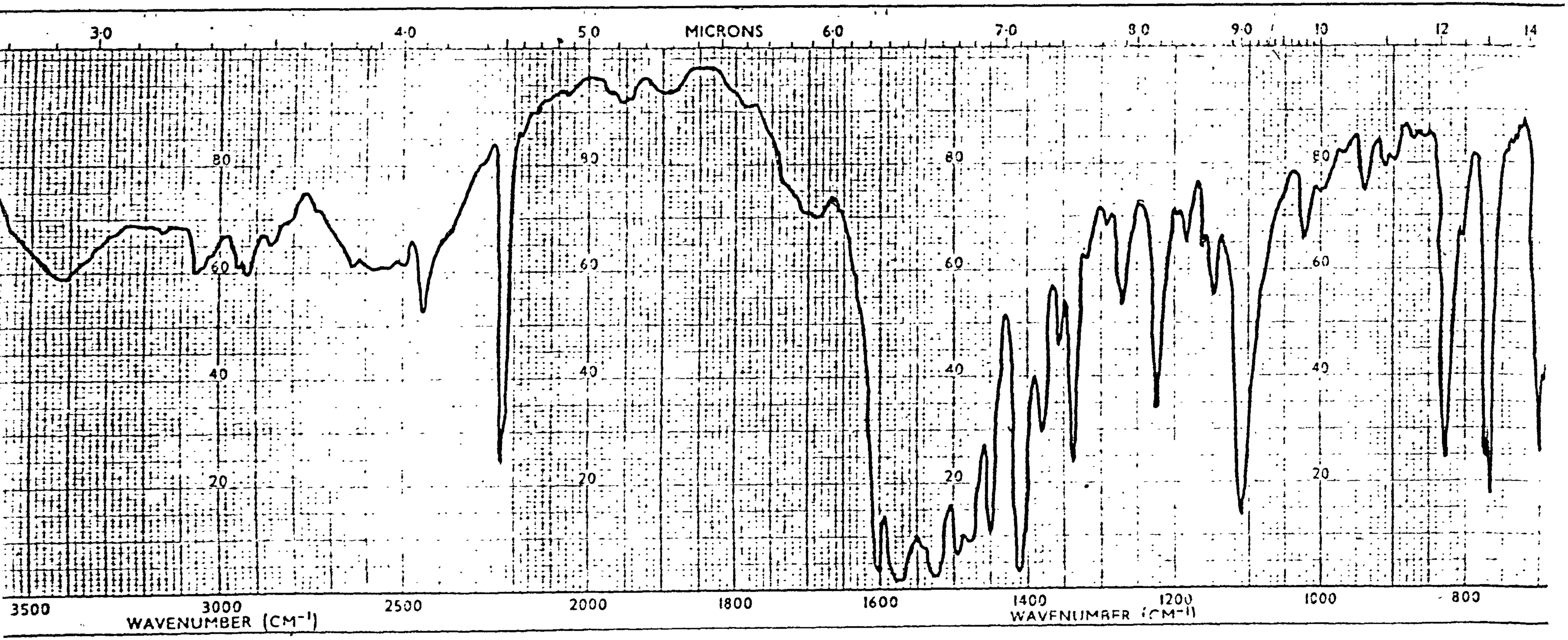
I.R. 1 Tetrachloropyrimidine



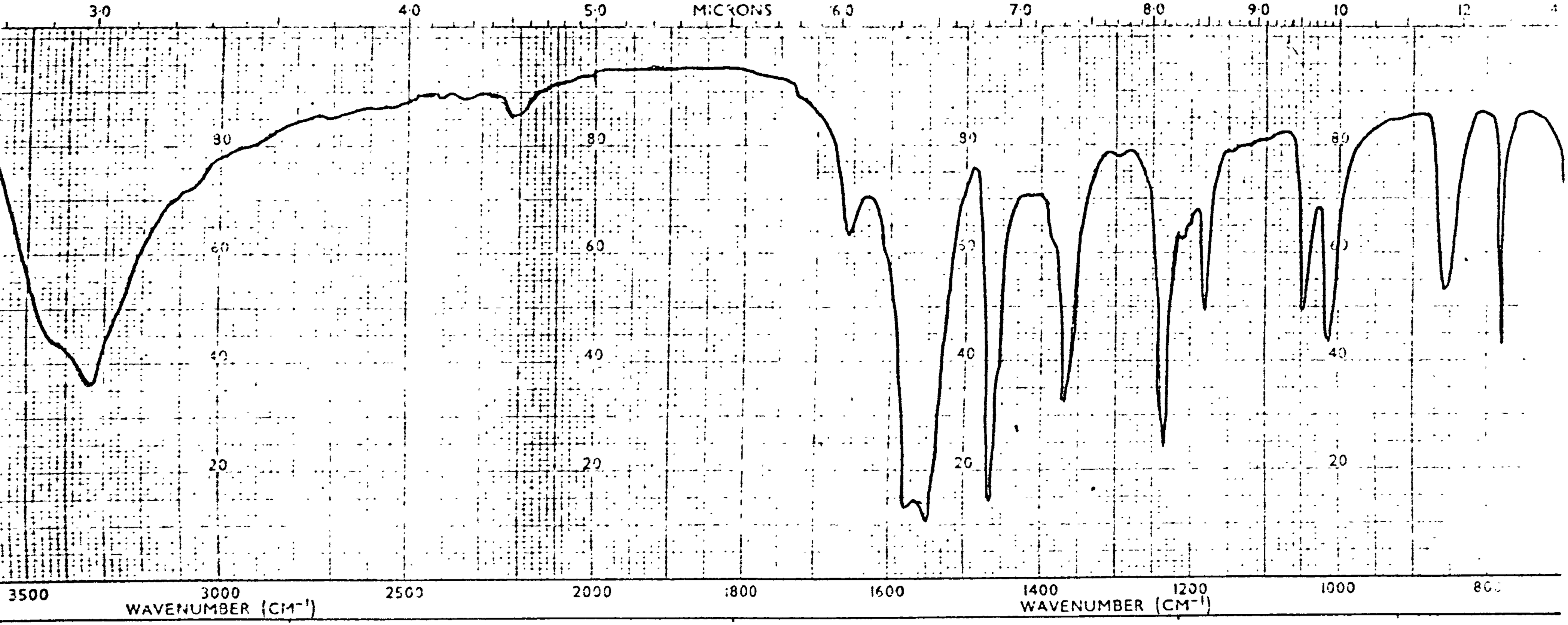
I.R. 2 Trichloropyrimidine



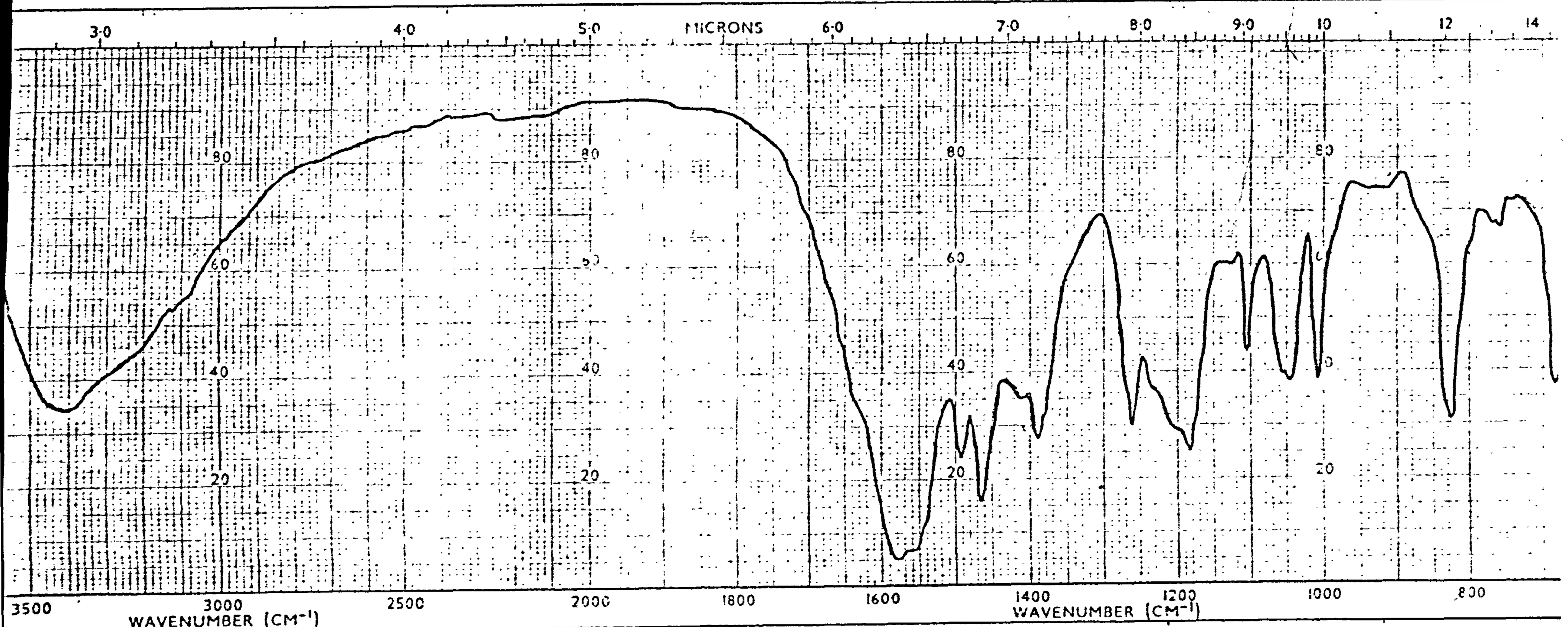
I.R. 3 5-Carbamoyl barbituric acid.



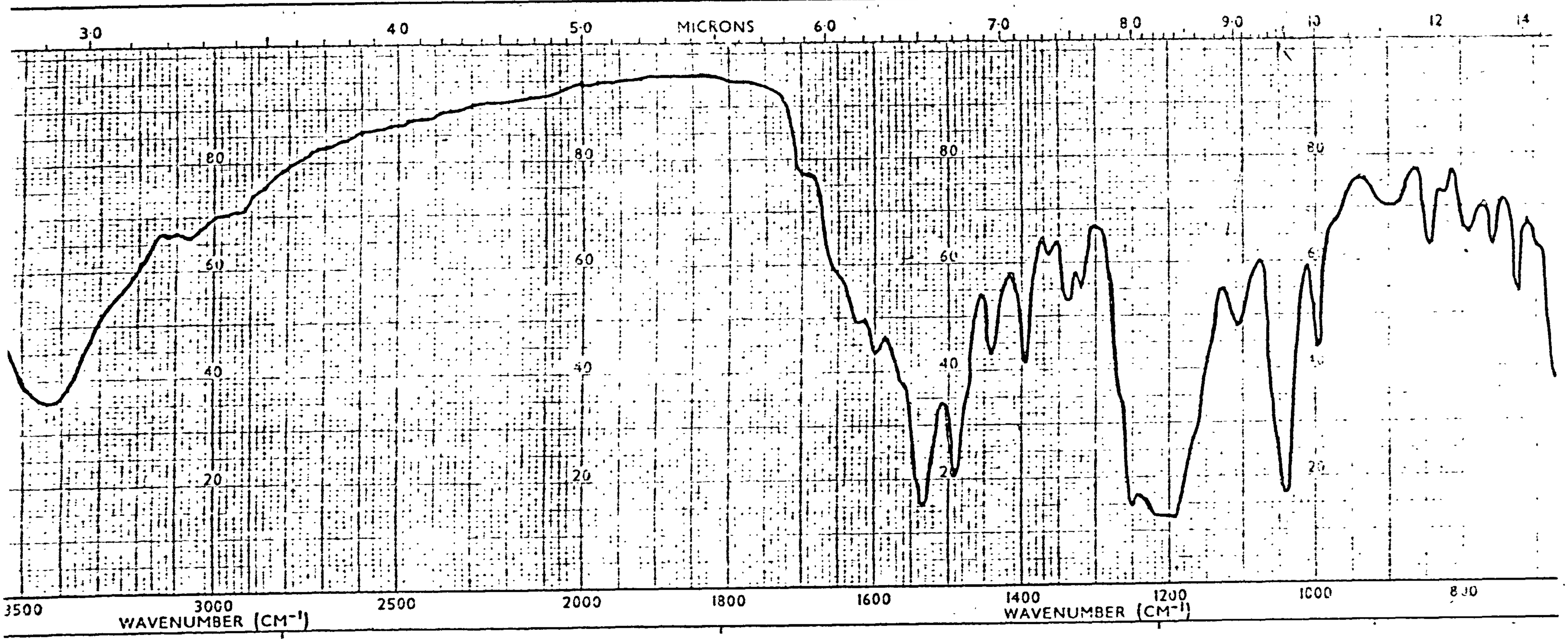
I.R. 4 2,4,5-chloro-5-cyanopyrimidine.



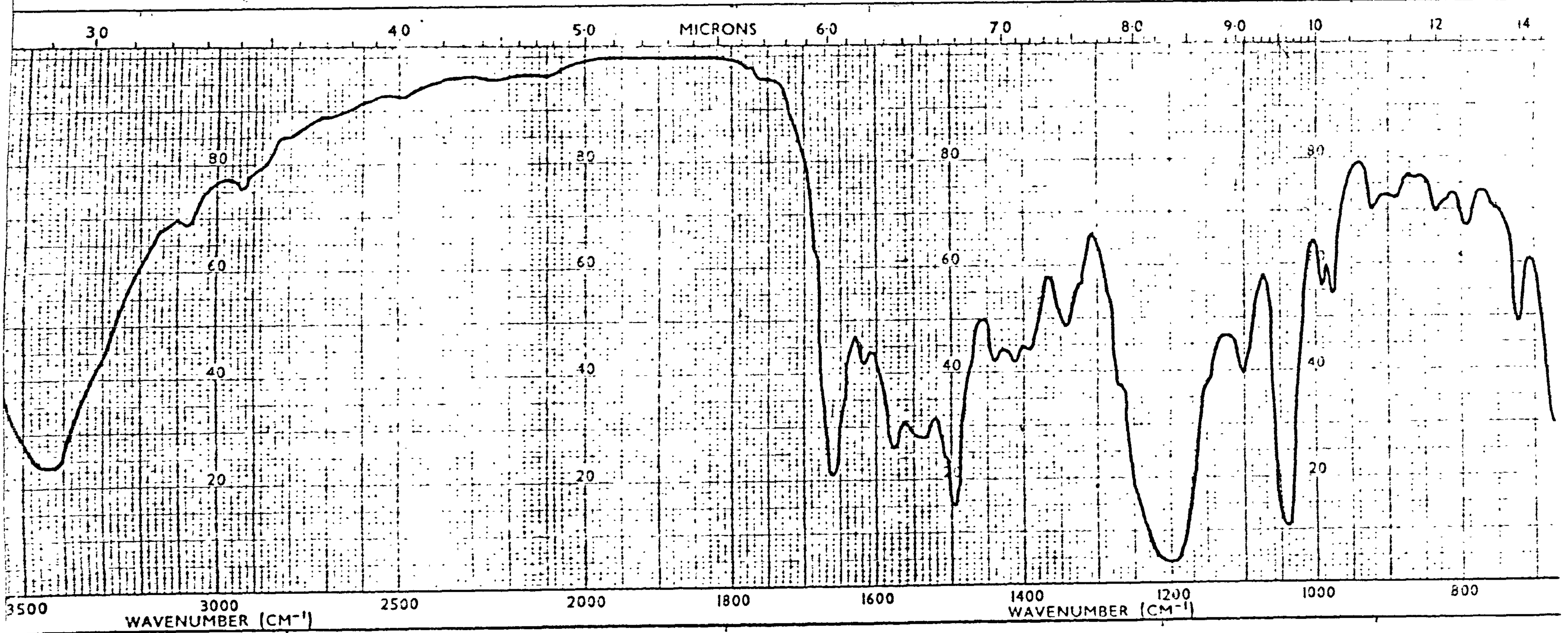
I.R. 5 2,4,5-trichloropyrimidin-6-yl-H acid



I.R. 6 2,4-dichloropyrimidin-6-yl-H acid

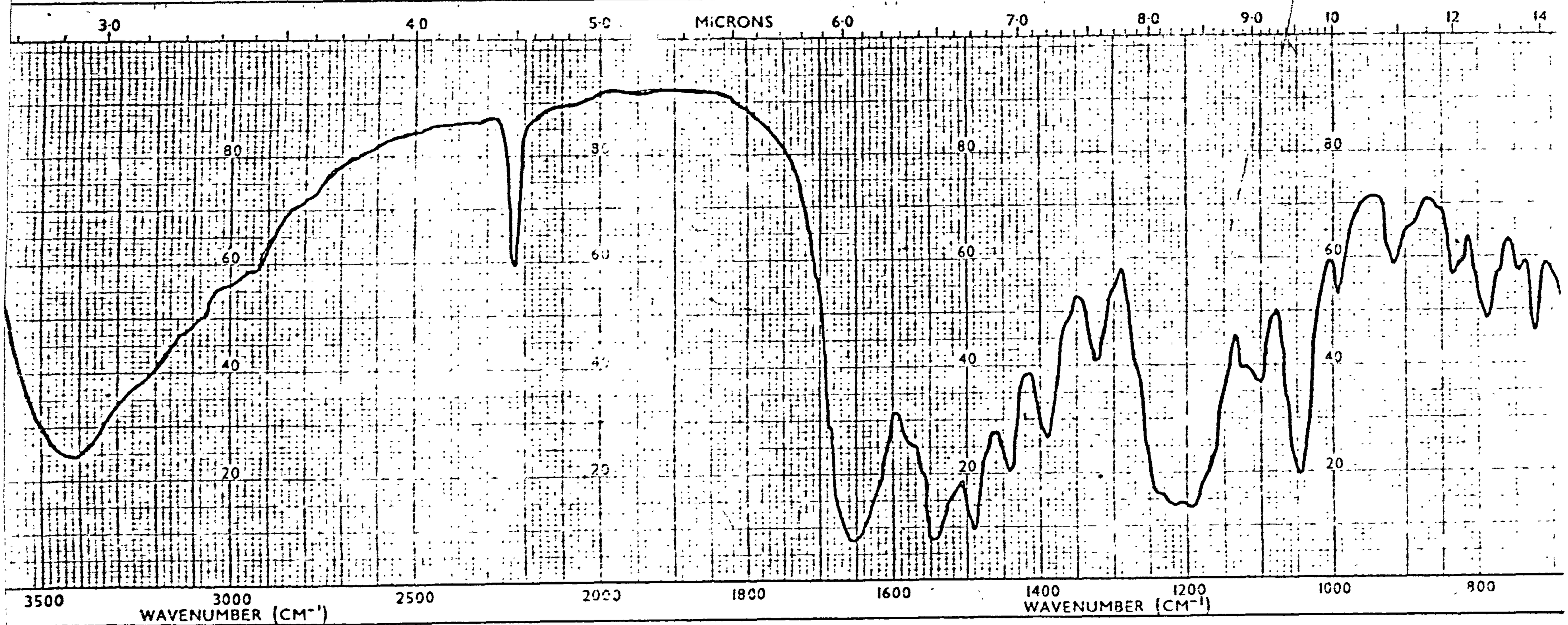


I.R. 7 Metanilic acid → 2,4,5-trichloropyrimidin-6-yl-H acid.
(Dye IX)



I.R. 8 Metanilic acid → 2,4-dichloropyrimidin-6-yl-H acid.

(Dye VIII)



I.R. 9 Metanilic acid → 2,4-chloro-5-cyanopyrimidin-6-yl-H acid.
(Dye X)

CHAPTER III

RESULTS AND DISCUSSION

3.1 Breakdown of different reactive dyeings tested in hydrogen peroxide solutions.

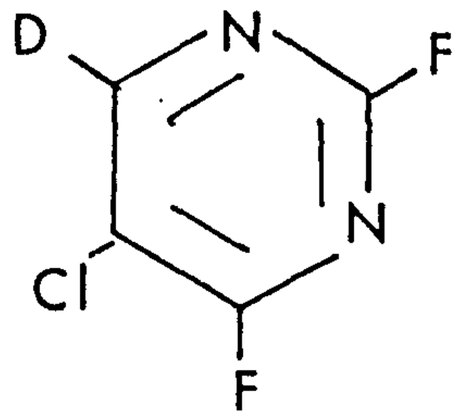
3.1.1 Different chromophores

All previous published work on the breakdown of dyes by perborate or hydrogen peroxide had been done on the Levafix Orange E3GA dye.[1] [2]

First, in order to establish the influence of the chromophore on the breakdown of the dye, other Levafix EA dyes were tested in the same way. The dyeings were treated in test solutions as described in 2.7.1, were squeezed and dried as described in 2.7.2. and exposed to heat and light (see 2.7.3.) for 30 minutes. The breakdown was determined as described in 2.8. and the results are shown in the table below. (Table 4.)

Table 4.
Breakdown of 2,4-fluoro-5-chloropyrimidinyl dyeings with different chromophores.

Reactive system D = chromophore



Dye No.	Commercial name	pH (±0.1)		Weight of fabric (g)	O.D.	Mg dye/ g. fabric	% break pH 9.8	% break pH11
I	Levafix Orange E3GA (1st dyeing)	9.8	Treated	0.434	0.056	0.346		
			Blank	0.422	—	—	1.2	
		11	Treated	0.397	0.245	1.650		
			Blank	0.431	—	—		5.7
II	Levafix Brilliant Red E4BA (1st dyeing)	9.8	Treated	0.406	0.050	0.256		
			Blank	0.407	—	—	1.5	
		11	Treated	0.387	0.120	0.656		
			Blank	0.422				3.7
III	Levafix Golden Yellow E3GA	9.8	Treated	0.422	0.055	0.250		
			Blank	0.410	0.020	0.093	2.3	
		9.8	Treated	0.439	0.140	0.673		
			Blank	0.443	0.060	0.260		5.3
IV	Levafix Blue E3GLA	9.8	Treated	0.415	0.057	0.240		
			Blank	0.411	0.017	0.076	1.1	
		11	Treated	0.410	0.140	0.600		
			Blank	0.411	0.017	0.076		4.5

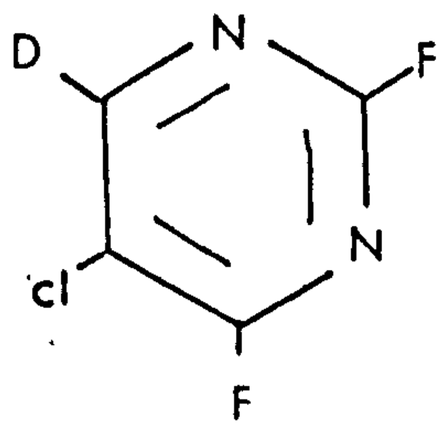
3.1.2 Breakdown of dyeings with different reactive groups

The different dyes tested were all based on the same chromophore so as to eliminate any substituent effect due to the colour system. The dye was treated in test solutions as described in 2.7.1., squeezed, dried, and exposed to heat and light for 30 minutes, as before. The breakdown was determined as described in 2.8

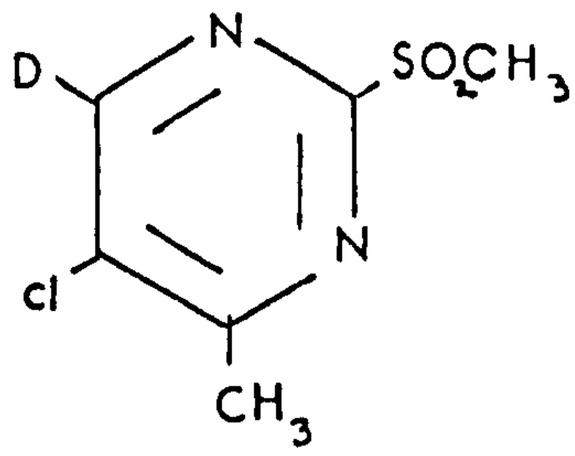
The structures of the dyes can be represented as below and the results are shown on Table 5 (overleaf).

Reactive Group

Substituted pyrimidine ring

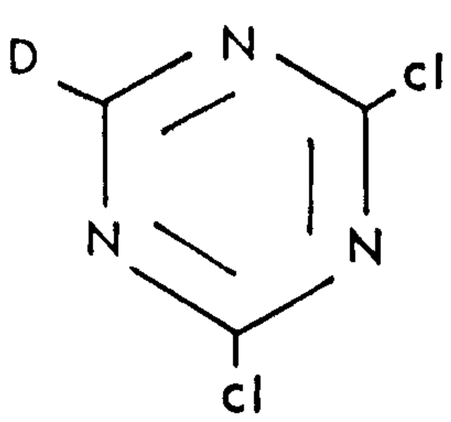


Dye II

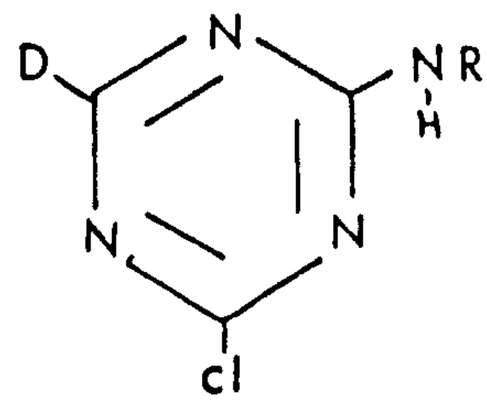


Dye XI

Substituted triazine ring

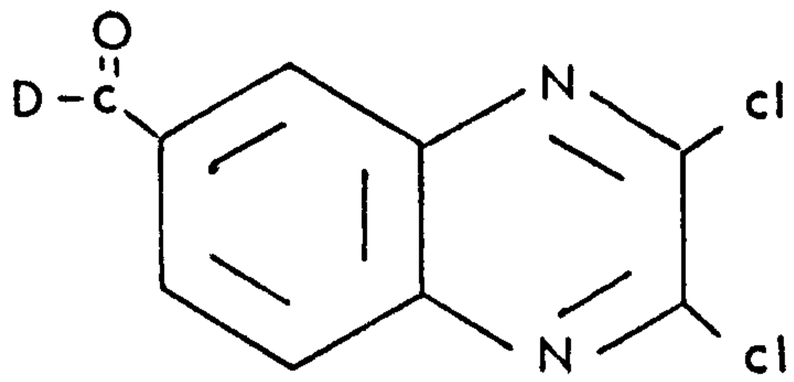


Dye VI



Dye VII

dichloro quinoxaline ring



Dye V

D = Chromophore

Table 5. Breakdown of dyeings with different reactive groups.

Dye No.	Commercial Name	pH (±0.1)		Weight of fabric (g)	O.D.	Mg Dye/ g. fabric	% break pH 9.8	% break pH11
*			Treated	0.406	0.500	0.256		
II	Levafix Brilliant	9.8	Blank	0.407			1.5	
	Red E4BA		Treated	0.381	0.120	0.656		3.7
		11	Blank	0.422				
			Treated	0.430	0.065	0.307		
V	Levafix Brilliant	9.8	Blank	0.431	0.040	0.185	0.35	
	Red E2B		Treated	0.425	0.240	1.13		
		11	Blank	0.440	0.050	0.227		2.7
			Treated	0.386	0.045	0.129		
		9.8	Blank	0.392	0.035	0.099	0.37	
VI	Procion Red MX5B		Treated	0.425	0.055	0.143		
		11	Blank	0.389	0.040	0.144		0.36
			Treated	0.429	0.090	negligible		
		9.8	Blank	0.409	0.090			
VII	Procion H		Treated	0.435	0.105	negligible		
		11	Blank	0.443	0.090			
	**		Treated	0.416	0.045			
XI	Levafix Brilliant	9.8	Blank	0.406	0.020		0.5	
	Red PN-B		Treated	0.419	0.085			
		11	Break	0.390	0.035			1.5

* Values transferred from Table 4 for comparison.

** Breakdown calculated from the ratio of its optical density to that of Levafix Brilliant Red E4BA (as shown above).

3.1.3 Studies in lability of the chlorine in the 5-position of the pyrimidine ring

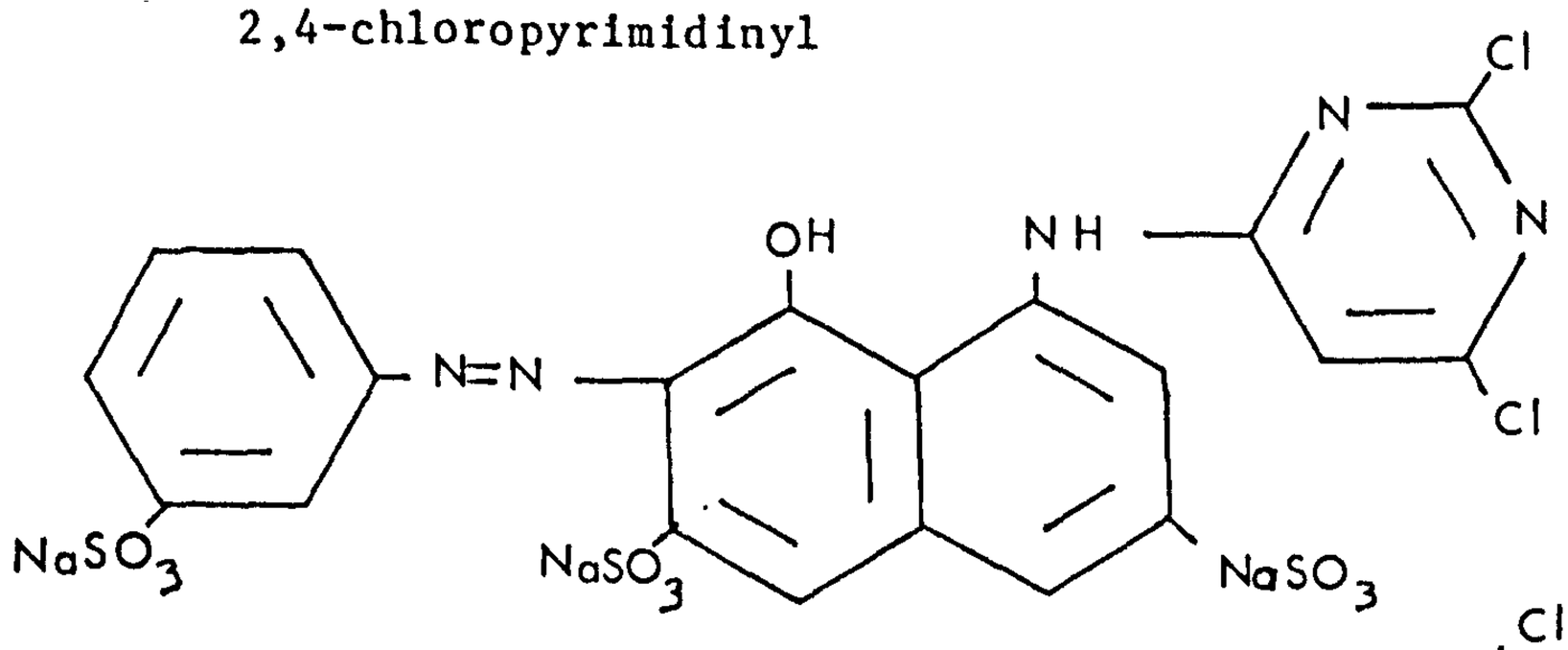
Previous work[2] showed that the reaction of 2,4-fluoro 5-chloropyrimidine dyeings in solution with hydrogen peroxide involved nucleophilic substitution on the ring. It was suggested that the 5 position in the pyrimidine ring is also attacked and that the resulting hydroperoxidegroup at the ortho position to the cellulose was the cause of the breakdown. The result now obtained with two other dyes (Table 5) seemed to agree with this theory. Hence the higher breakdown of the 2,4-fluoro-5-chloropyrimidine and the quinoxaline dyes as compared to the dichlorotriazine dye.

To test the dyeing for lability of the 5-chloro would be difficult as the quantity of dye on the fabric is comparitively small. The dyestuff however could be tested in any amount and 1g of Levafix Orange E3GA dye was therefore tested instead. The inorganic salts present in this dye were extracted using dimethylformamide in the manner described. This procedure was repeated and the remaining chloride ions were precipitated from a solution of the dye as described in Ref. 99. The precipitate was discarded and the 'chloride free' solution was set at pH 11. To half of the solution was then added 0.4ml of 100V hydrogen peroxide and the solution was left to stand for approximately 20 minutes at room temperature. It was then tested with silver nitrate as described in Ref. 99 and a white precipitate was obtained indicating the presence of chloride ions. The other solution without hydrogen peroxide, but at the same pH, was also tested but no precipitate was obtained. To ensure that it was not the hydrogen peroxide by itself that reacted with the silver nitrate solution, the test was carried out on a solution of hydrogen peroxide of the same concentration and at the same pH (11). No precipitate was obtained.

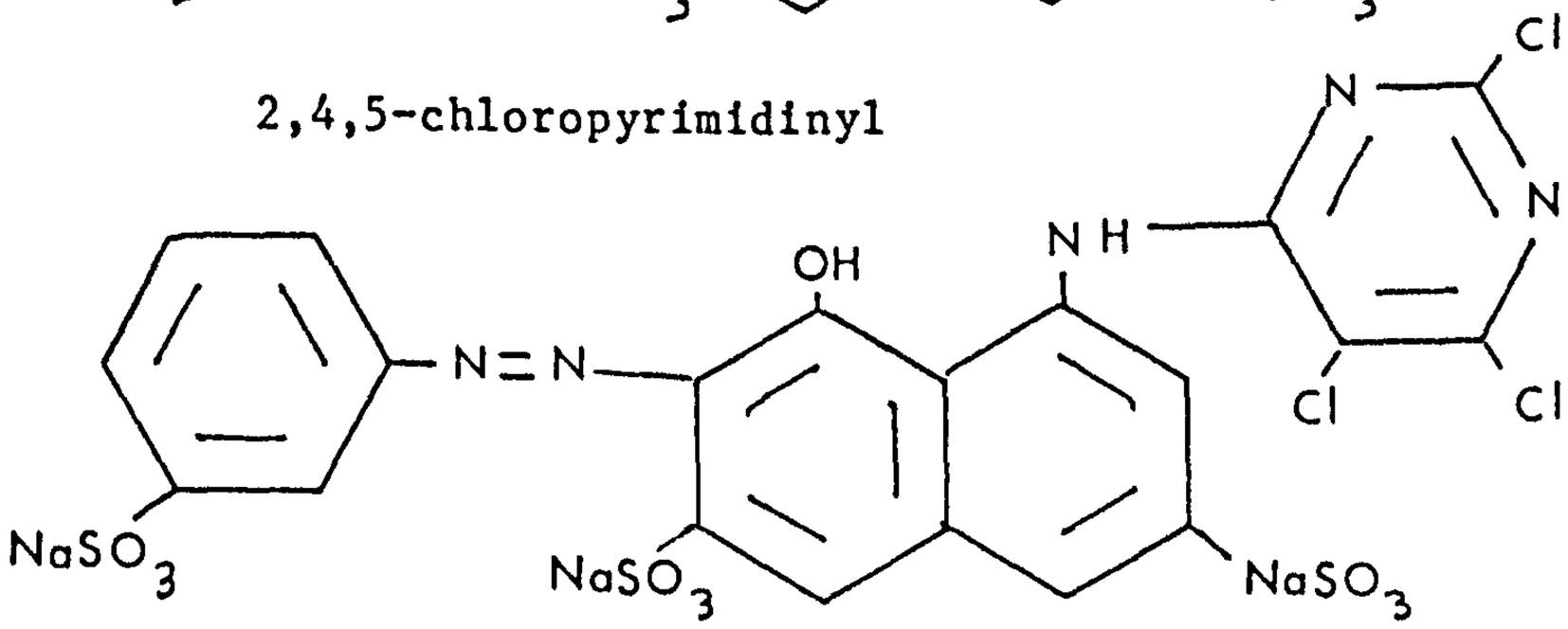
3.1.4 Breakdown of 2,4-chloropyrimidinyl dyeings with different substituents in the 5-position of the ring.

When considering the results of the preceding experiments, a nucleophilic attack on the 5 position of the pyrimidine ring seemed to be a possible decisive factor on the breakdown of pyrimidinyl dyes. In such a case an electron withdrawing group in this position should increase the breakdown. Consequently, two chloropyrimidinyl dyes were initially prepared which were identical except that one had an extra chloro in the 5 position of the ring, and their dyeings on cellulose were tested for breakdown as before. The structure of these two dyes are as follows:

Dye VIII 2,4-chloropyrimidinyl



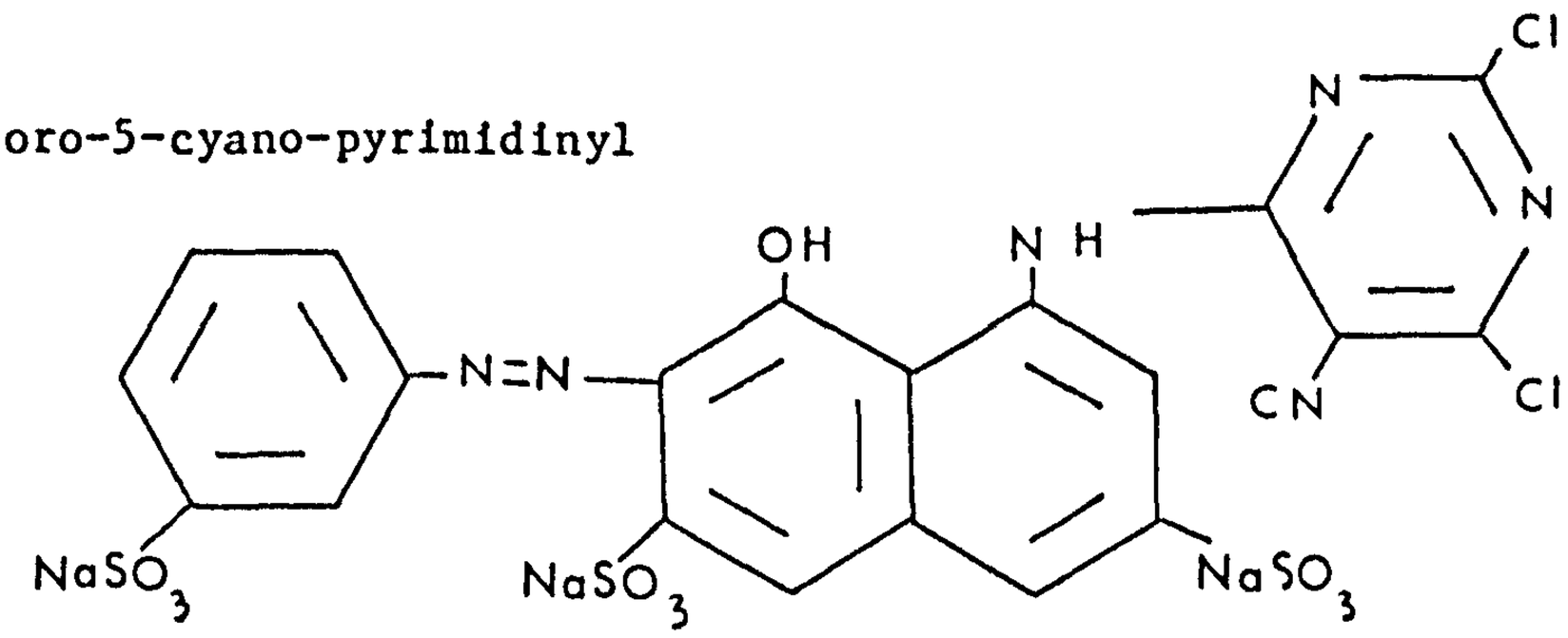
Dye IX 2,4,5-chloropyrimidinyl



These dyeings were treated in the test solutions as described in 2.7.1 and were squeezed and dried and exposed to heat and light for 30 minutes, as before. There was no appreciable difference in their breakdown at the pH value of 9.8 and 11, so the pH was raised to 12. The other reaction conditions were kept the same. The results are on Table 6.

In order to further establish the significance of the substituent in the position of the ring, another dye was prepared with an even stronger electron withdrawing group in this position: a cyano group. The rest of the structure was identical to the dyes above.

Dye X 2,4-chloro-5-cyano-pyrimidinyl



The dyeing obtained from this dye was tested as before at the pH values of 9.8 and 11. The results are also on Table 6.

Table 6. Breakdown of 2,4-chloropyrimidinyl dyeings with different substituents in the 5-position of the ring.

Dye		pH		weight of fabric	O.D.	mg dye /g fabric	% break		
No.	Reactive Group X	(± 0.1)					pH 9.8	pH 11	pH 12
VI	2,4-dichloro-pyrimidine	9.8	Treated	0.440	0.028*	0.035			
			Blank	0.449	0.016*	0.020	0.44		
		11	Treated	0.440	0.052*	0.066			
			Blank	0.435	0.014*	0.021		1.3	
		12	Treated	0.353	0.020	0.062			
			Blank	0.380	0.016*	0.023			1.1
IX	2,45-trichloro-pyrimidine	9.8	Treated	0.450	0.025*	0.034			
			Blank	0.460	0.015*	0.020	0.53		
		11	Treated	0.452	0.052*	0.070			
			Blank	0.420	0.013*	0.020		1.9	
		12	Treated	0.339	0.045	0.160			
			Blank	0.370	0.015*	0.020			5.4
X	2,4-chloro-5-cyanopyrimidine (2nd dyeing)	9.8	Treated	0.436*	0.015	0.093			
			Break	0.450	0.012	0.040	2.0		
		11	Treated	0.520	0.030	0.156			
			Blank	0.475	0.010	0.057		3.8	
II	2,4-Fluoro-5-chloropyrimidine	9.8					**7.5	**	
		11						3.7	
		12	Blank	0.417	0.01	0.05			11.6
			Treated	0.425	0.43	2.10			

* 25 ml solutions, others are 50 ml

** values transferred from Table 4, for comparison.

3.2 Effect of variation of labile group content on breakdown.

As only dyeings with labile groups have been shown in the preceding tests to exhibit bond breakdown with hydrogen peroxide, various experiments were carried out to study how a variation in the labile group content affected the breakdown. The labile group can be lost during the process of dyeing or it can be substituted by reacting the dyeing with alkali or with another base such as an amine.

3.2.1 The effect of different dyeing conditions on the breakdown.

Work done on this field has shown that in the dyeing of cotton with dichlorotriazinyl dyes, 3 different types of dyeings are produced (see 1.4) and only one type has still a labile chlorine remaining in the triazine ring. A dye of this class, Procion Red MX5B (Dye VI) was therefore the first one to be tested by applying it to cotton using different dyeing procedures and measuring the breakdown, since the proportion of these three types of dyeings varies with the methods used. The methods of dyeing are described in 2.5 and the conditions for testing breakdown were the same as before; the dyeings were treated in test solutions as described in 2.7.1 and were squeezed and dried, and exposed to heat and light for 30 minutes. The tests were only done at one pH value (pH=11)as it had been shown that with this dye the breakdown does not increase with pH (see Table 5). The breakdown was determined as before and the results are on Table 7.

Table 7. The effect of different dye conditions on the breakdown of dichlorotriazinyl dyeings.

Dye = Procion Red MX5B (Dye VI)

Dyeing Method	Dye in Fabric (mg/g)	Test No.		Weight of Fabric (g)	O.D.	mg dye/g fabric	% break	Average % break
Exhaustion	5.08	1	Treated	0.410	0.040	0.108		0.1
			Blank	0.430	0.040	0.103	0.099	
		2	Treated	0.412	0.040	0.107		
			Blank	0.433	0.040	0.102	0.103	
Pad dry	11.26	1	Treated	0.422	0.070	0.184		0.39
			Blank	0.418	0.060	0.159	0.22	
		2	Treated	0.427	0.090	0.234		
			Blank	0.421	0.065	0.171	0.56	
Pad-dry-steam	12.21	1	Treated	0.429	0.085	0.220		0.49
			Blank	0.427	0.065	0.169	0.4	
		2	Treated	0.454	0.090	0.220		
			Blank	0.410	0.055	0.149	0.58	
* Pad-batch	8.0		Treated	0.386	0.045	0.129		0.37
			Blank	0.392	0.035	0.099		

* Values transferred from Table 5 for comparison.

The effect of different dyeing conditions on the breakdown of 2,4-fluoro-5-chloropyrimidinyl dyeings.

2,4-Fluoro-5-chloro pyrimidinyl dyes have similar reactivity to dichlorotriazinyl dyes and therefore are expected also to lose some of their labile groups during the dyeing. The method of dyeing which showed most loss of labile groups in the dichlorotriazinyl dyeing was the exhaustion method as can be seen from Table 7, above. It was therefore this method which was used for comparison with the pad-batch method which had been used in previous dyeings. The method of dyeing is described in 2.5 and the conditions for testing breakdown were identical to those used for the dichlorotriazinyl dyeings (see above).

The results are shown in the table below. (table 8)

Table 8. The effect of different dyeing conditions on the breakdown of 2,4-fluoro-5-chloropyrimidinyl dyeings.

Dye: Levafix Brilliant Red E4BA (Dye II)

Dyeing method	Dye in fabric (g)	pH		Weight of fabric (g)	O.D.	mg dye/ g fabric	% break pH 9.8	pH11
Exhaustion	10.5	9.8	Treated	0.416	0.030	0.150	1.4	
			Blank	0.420	0	-		
		11	Treated	0.448	0.065	0.302		2.9
			Blank	0.399	0	-		
		9.8		0.406	0.050	0.256	1.5	
*Pad-batch	17.6	11		0.381	0.720	0.656		3.7

* Values transferred from Table 4 for comparison.

3.2.2. Breakdown of pyrimidinyl dyeings pretreated in alkaline solutions.

The three pyrimidinyl dyeings which showed a significant breakdown when tested with hydrogen peroxide were first soaked, with stirring, in an alkaline solution (pH 12.5) containing 5 g/l of detergent but no hydrogen peroxide, at 40°C, for 20 minutes, and after rinsing were treated in test solutions as described in 2.7.1, at pH 11. The dyeings were then squeezed, dried and exposed to heat and light for 30 minutes, as before. The breakdown was determined as previously and the results are shown in the table below. (table 9)

Table 9. Breakdown of pyrimidinyl dyeings pretreated in alkaline solutions.

Dye		Dye in fabric (mg/g)		Weight of dyed fabric (a)	O.D.	Break mg dye/ g Fabric	% Break
No.	Class						
II	2,4-Fluoro-5-chloropyrimidinyl***	10.5	Treated	0.445	0.105	0.492	
			Blank	0.478	0.025	0.109	3.6
IX	2,4,5-chloro-pyrimidinyl	2.6	Treated	0.349	0.020	0.069	
			Blank	0.370	0.030*	0.025	1.75
X	2,4-chloro-5-cyanopyrimidinyl	2.6	Treated	0.564	0.015	0.072	
			Blank**	0.475	0.010	0.057	0.57

* 4cm cell

** Transfered from Table 6 for comparison

*** Exhaustion dyeing (Table 8.)

3.2.3. Breakdown of pyrimidinyl dyeings pretreated in ammonia.

Dyeings of the same dyes which had been tested for breakdown after pretreatment with alkali (Table 9), were refluxed in 100cc of a 1.5% solution of ammonia for 30 minutes. After rinsing with water they were also tested for breakdown as bove. The pH they were tested at was also 11 except for the 2,4,5-chloropyrimidnyl dyeing which was tested at pH12. The results are shown in the table below. (table 10)

Table 10. Breakdown of pyrimidinyl dyeings pretreated in ammonia

Dye		Dye in fabric (mg/g)		Weight of fabric (g)	O.D.	Break mg dye/ g fabric	% Break
No.	Class						
II	2,4-Fluoro-5-chloropyrimidinyl**	10.5	Treated	0.360	0.065	0.370	
			Blank	0.472	0.020	0.088	2.7
IX	2,4,5-chloro-pyrimidinyl	2.6	Treated	0.399	0.020	0.060	
			Blank*			0.020	1.5
X	2,4-chloro-5-cyanopyrimidinyl	2.6	Treated	0.461	0.020	0.117	
			Blank*			0.057	2.3

* transferred from Table 6 for comparison.
** Exhaustion dyeing (Table 8)

3.2.4 Breakdown of a 2,4-fluoro-5-chloropyrimidinyl dyeing pretreated with a tertiary amine.

As can be seen from the table above, of the 3 dyeings tested, the 2,4-fluoro-5-chloropyrimidinyl was the only one which did not improve its resistance to breakdown after treatment with ammonia. A tertiary amine, Diazabicyclo (2.2.2) octane, DABCO (XXIX) which is a stronger nucleophile than ammonia, was therefore tried as a means of elimination of remaining labile groups.

The dyeing was first soaked, with stirring, in a solution of 5 g/l DABCO at 80°C for 20 minutes. After rinsing it was tested for breakdown as above. The results are shown in the table below. (table 11)

Table 11. Breakdown of a 2,4-fluoro-5-chloropyrimidinyl dyeing pretreated with a tertiary amine.

Dye: Levafix Orange E3GA, conc. of dye in fabric = 29 mg/g.

	Weight of fabric (g)	O.D.	Break mg dye/g fabric	% Break
No pretreatment *				5.7
Pretreatment	0.406	0.15	0.993	3.4

* see Table 4

3.3 Studies on the intermediate dyeing-peroxide product.

Experiments done previously on Levafix Orange E3GA[1] showed that even after rinsing the dyeing with cold water at the end of the reaction with hydrogen peroxide, there was breakdown of the dye-fibre bond. This implied that an intermediate product was formed from the reaction of the dyeing with hydrogen peroxide. In order to study the nature of this intermediate product and how it was related to the breakdown, the experiments that follow were carried out on dyeings which were treated with hydrogen peroxide and were then rinsed with cold water.

3.3.1 Stability to alkaline hydrolysis

The intermediate dyeing-peroxide product was formed as described in 2.7.1 and the dyeings were then rinsed with cold water and soaked in alkaline solutions (pH 12) containing 10 g/l of sodiumchloride, at room temperature, for different intervals of time. A 'blank' treatment was carried out on a dyeing which was not treated with hydrogen peroxide and which was soaked in an identical solution at the same pH and for the same length of time as each test sample.

The dyeings were rinsed at the end of the reaction, dried as before and exposed to heat and light (see 2.7.3.) for 3 hours, and the optical density of the solution containing the dye that broke down was measured as before.

The results are on Table 12 (overleaf)

Table 12. Stability of the dyeing-peroxide product to alkaline hydrolysis

Dye: Levafix Orange E3GA (1st dyeing)

Time of reaction (mins)		Weight of fabric (g)	O.D.	Total break mg dye/g fabric	Peroxide break mg/g fabric	% Break
* 0		0.414	0.21	1.36	1.36	4.7
30	Treated	0.425	0.23	1.45		
	Blank	0.410	0.03	0.196	1.18	4.1
60	Treated	0.479	0.15	0.994		
	Blank	0.390	0.04	0.269	0.725	2.5
90	Treated	0.399	0.10	0.673		
	Blank	0.408	0.04	0.263	0.41	1.4

* Treated fabric was rinsed and immersed in a pH7 buffer solution for 90 minutes.

3.3.2 Analysis and identification of the intermediate dyeing-peroxide product

The results from the preceding experiment confirmed the presence of a new group on the pyrimidine ring of the dye which could be hydrolysed like any other substituent. It had been shown in previous work[2] that the reaction of the dyeing with hydrogen peroxide was a nucleophilic reaction where the anion was most probably the perhydroxyl anion HO_2^-, in which case the new substituent on the ring would be a hydroperoxide group. In order to check this possibility, a test to detect the hydroperoxide groups was carried out as described in 2.9. An absorption curve of the sodium iodide test solution was obtained in a u.v. spectrophotometer and it showed a maximum absorption peak at 360 nm, which was an indication of the presence of hydroperoxide groups. If the temperature of the hydrogenperoxide solution was raised above 35°C, no peak was detected, showing that the hydroperoxide groups are destroyed above this temperature. The value for the 'blank' was obtained as described in 2.9.

A further test to check that the hydroperoxide was formed by the alkaline hydrogen peroxide only, was done by testing a Levafix Orange E3GA dyeing in a detergent solution at pH 11, but without hydrogen peroxide. The result obtained was the same as for the 'blank'.

Once the method was established as being reproducible, it was used for the measurement of hydroperoxide content of the other dyeings, which had been tested for breakdown. The conditions the dyeings were submitted to were the same used for the measurement of breakdown, except that in this experiment the dyeings were rinsed in water after the reaction with hydrogen peroxide. The hydroperoxide content measured would therefore be expected to cause lower breakdowns than if the dyeings were not rinsed. The rinsing was, however, necessary because if any hydrogen peroxide was left on the dyeings the results obtained would not be accurate.

3.4 Hydroperoxide content of different reactive dyeings tested in hydrogen peroxide solutions.

3.4.1. Different Chromophores

As can be seen on Table 4, dyeings of 2,4-fluoro-5-chloropyrimidinyl dyes based on different chromophores show different breakdown levels, especially at the higher pH of 11. They were therefore tested for hydroperoxide content at pH 11 in order to establish whether there was any correlation between this factor and bond breakdown. The reaction in the solution of hydrogen peroxide was carried out as described in 2.7.1., the dyeings were then rinsed and tested for hydroperoxide content as described in 2.9.

The results are shown in the table below. (table 13)

Table 13. Hydroperoxide content of 2,4-fluoro-5-chloropyrimidinyl dyeings with different chromophores.

Dye		Dye in fabric (mg/g)	wt. fabric (g)	Dye in fabric (mg)	O.D. *(minus Blank)	Moles OOH/mg dye ($\times 10^{-7}$)
I	Levafix Orange E3GA	19.4	0.364	7.06	0.290	0.821
II	Leafix B Red E4BA	17.6	0.432	7.60	0.170	0.447
III	Levafix Golden Yellow E3GA	6.6	0.443	2.92	0.245	1.680
IV	Levafix Blue E3GLA	15.5	0.420	6.57	0.510	1.560

* O.D. of Blank = 0.04

3.4.2 Hydroperoxide content of dyeings with different reactive groups

The other commercial dyes with different reactive groups which had been tested for breakdown (Table 5) were also tested for the presence and quantity of hydroperoxide groups in the same way. The dyeings were treated in test solutions as described in 2.7.1. were rinsed with cold water and were tested for hydroperoxide content as described in 2.9. The results are shown in the table below.

Table 14. Hydroperoxide content of dyeings with different reactive groups

Dye			Weight of fabric (g)	Conc. of dye (mg)	pH (±0.1)	O.D. *(minus Blank)	Moles OOH/mg ($x10^{-7}$)
No.	Commercial name	Reactive group					
II	Levafix B Red E4BA (1st dyeing)	2,4-Fluoro-5-chloro-Pyrimidine	0.458	8.06	9.8	0.093	0.230
			0.432	7.60	11	0.170	0.447
			0.438	7.71	12	0.770	2.010
V	Levafix B Red E2B	Dichloro-quinoxaline	0.378	12.47	9.8	0.060	0.096
			0.422	13.90	11	0.140	0.201
VI	Procion Red MX5B	Dichloro-triazine	0.427	3.42	9.8	0.170	0.994
			0.434	3.47	11	0.530	3.050
VII	Procion H 3B	Monochloro-triazine	0.416	6.24	11	0.002	-
	Levafix Brilliant Red PN-B	2-methyl-sulphonyl pyrimidine			11	0.073	*0.18

* O.D. of Blank = 0.04

3.4.3 Hydroperoxide content of 2,4-chloro pyrimidinyl dyeings with different substituents in the 5-position of the ring.

These dyeings, which had previously been tested for breakdown with hydrogen peroxide (Table 6), were also tested for hydroperoxide content. As before, the dyeings were treated in test solutions as described in 2.7.1., were rinsed with cold water and were tested for hydroperoxide content as described in 2.9. The results are shown in the table below. (table 15)

Table 15. Hydroperoxide content of 2,4-chloro pyrimidinyl dyeings with different substituents in the 5-position of the ring.

Dye		Weight of fabric (g)	Conc. of dye (mg)	pH (± 0.1)	O.D. * (minus Blank)	Moles OOH/mg dye ($\times 10^{-8}$)
No.	Reactive Group X					
VIII	2,4-chloro-pyrimidine	0.443	1.40	11	0.037	5.30
IX	2,4,5-chloro-pyrimidine	0.444	1.15	11	0.047	8.17
		0.345	0.90	12	0.034	7.55
X	5-cyano-2,4 chloro-pyrimidine	0.254	2.60	9.8	0.064	4.90
		0.245	2.50	11	0.072	5.76

* O.D. of Blank = 0.04

3.4.4 Hydroperoxide content of dyeings after different times of reaction with hydrogen peroxide.

A dichlorotriazinyl, a 2,4-fluoro-5-chloropyrimidinyl and a dichloroquinoxalinyl dyeing were treated in test solutions as described in 2.7.1., at pH 11, and were rinsed with cold water and tested for hydroperoxide content as before. The results are shown in the table below.

Table 16. Hydroperoxide content of dyeings after different times of reaction with hydrogen peroxide.

Time of Reaction (mins)		Dye		
		II	V	VI
1	Weight of Fabric (g)	0.437		0.402
	Conc. of dye (mg)	7.69		3.21
	*O.D. (minus Blank)	0.06		0.184
	Moles OOH/mg dye (10^{-7})	0.156		1.14
2	Weight of Fabric (g)	0.420	0.454	0.422
	Conc. of dye (mg)	7.39	15.0	3.37
	*O.D. (minus Blank)	0.06	0.050	0.24
	Moles OOH/mg dye (10^{-7})	0.16	0.067	1.42
5	Weight of Fabric (g)	0.455	0.453	0.424
	Conc. of dye (mg)	8.0	14.9	3.39
	O.D. (minus Blank)	0.11	0.077	0.38
	Moles OOH/mg dye (10^{-7})	0.275	0.103	2.24
**20	Moles OOH/mg dye (10^{-7})	0.447	0.201	3.05

* O.D. of Blank = 0.04

** The results were transferred from Table 14 for comparison.

3.4.5 Formation of hydroperoxide in the dark.

This method of analysis of hydroperoxide was also used to test whether light had any influence on the reaction of formation of the hydroperoxide.[100][101]

For this purpose the dyeing which forms hydroperoxide most easily, dichlorotriazinyl, was tested in the dark. Even though the reaction of a dichlorotriazinyl dyeing with hydrogen peroxide without protection from the standard lighting conditions used in the laboratory had been done before, (Table 14), it was nevertheless repeated, so as the check the first result obtained with possibly slightly different lighting conditions. The other reaction conditions were the same; the dyeings were treated in test solutions as described in 2.7.1., at pH 11 and were rinsed in cold water and tested for hydroperoxide content as before. The results are shown in the table below.

Table 17. Formation of hydroperoxide in the dark

Dye: Procion Red MX5B (Dye VI)

	Weight of fabric (g)	Conc. of dye (mg)	O.D. (minus Blank)	Moles OOH/mg dye ($\times 10^{-7}$)
In light	0.445	3.56	0.55	3.08
In dark	0.424	3.39	0.58	3.42

3.5 Formation of hydroperoxide from the reaction of a 2,4-fluoro-5-chloro-pyrimidinyl dyeing with sodium perborate.

So far in this work hydrogen peroxide has been used instead of sodium perborate since it was assumed that sodium perborate formed hydrogen peroxide in solution (see 1.5). The similar amount of breakdown obtained with hydrogen (1) peroxide as with sodium perborate agreed with this theory. In order to further confirm this theory the sodium iodide test was done on a dyeing treated with a concentration of sodium perborate which had previously been calculated to form in solution the same amount of hydrogen peroxide as that used in testing of the dyeings up to now (4ml/l H_2O_2). The other reaction conditions were the same. Thus, the dyeing was treated in a solution containing 5g/l of detergent and 5g/l of sodium perborate, at pH 11, and at room temperature ($22^{o} \pm 2^{o}C$) for 20 minutes. It was then rinsed in cold water and tested for hydroperoxide as before. The results are shown in the table below.

Table 18. Formation of hydroperoxide from the reaction of a 2,4-fluoro-5-chloropyrimidinyl dyeing with sodium perborate.

Dye: Levafix Brilliant Red E4BA (Dye II)

Reagent	Weight of fabric (g)	Conc. of dye (mg)	O.D. ** (minus Blank)	Moles OOH/mg dye ($\times 10^{-7}$)
Sodium perborate	0.3932	6.92	0.117	0.338
*Hydrogen peroxide	0.4320	7.60	0.170	0.447

* Values transferred from Table 13 for comparison.

** O.D. of Blank = 0.04

3.6. Preliminary studies of the radical mechanism of the breakdown of 2,4-fluoro-5-chloropyrimidinyl dyeings.

A series of experiments were carried out to determine whether, as the results from the preceding experiments suggest, the breakdown of 2,4-fluoro-5-chloropyrimidine dyeings involved possible decomposition of the hydroperoxide groups into free radicals.

3.6.1 Breakdown of a treated dyeing containing only hydrogen peroxide during exposure to heat and light.

One possible source of free radicals would be the hydrogen peroxide left on the fabric. This possiblity was tested in the following way:

A 2,4-fluoro-5-chloropyrimidinyl dyeing was treated as before in a test solution as described in 2.7.1., at pH 11 and was then rinsed in cold water. It was then soaked in a neutral solution of hydrogen peroxide of the same concentration as above (4 ml/l), without detergent, for another 20 minutes, at room temperature ($22^{o} \pm 2^{o}C$). It was dried, squeezed and exposed to heat and light for 30 minutes, as before. The breakdown was determined as before and the results are shown in the table below (Table 19). A 'blank' reading was taken from a dyeing which was exposed to heat and light immediately after being treated in the test solution and rinsed, without the intermediate soaking in a neutral hydrogen peroxide solution.

Table 19. Breakdown of treated dyeing containing only hydrogen peroxide during exposure to heat and light. Dye: Levafix Orange E3GA (1st dyeing)

	Weight of fabric (g)	O.D.	Break mg dye/g fabric	% Break
Blank	0.395	0.085	0.578	2.0
Treated	0.401	0.095	0.637	2.2

3.6.2 Breakdown of a treated dyeing containing only detergent during exposure to heat and light.

When the fabric is exposed to heat and light without rinsing, besides hydrogen peroxide there is detergent present. In some cases, the breakdown of dyes and polymers is due to absorption of u.v. light (Ref.102) and as detergents also absorb u.v. light, it could possibly enhance this effect and thus increase the breakdown. In an experiment to check this possibility, a dyeing treated in the usual way in a test solution as described in 2.7.1., was rinsed and soaked in a solution containing only 5 g/l of detergent (pH 10.2), for another 20 minutes at room temperature ($22^{o} \pm 2^{o}C$). It was then squeezed dried and exposed to heat and light (2 hours), as before. The breakdown was determined as before and the results are shown in the table below.
A 'blank' reading was obtained from an equally treated dyeing which was not soaked in a detergent solution prior to exposure to heat and light. The rest of the reaction conditions were identical.

Table 20. Breakdown of a treated dyeing containing only detergent during exposure to heat and light. Dye: Levafix Orange E3GA (1st dyeing)

	Weight of fabric (g)	O.D.	Break mg dye/g fabric	% Break
Blank	0.418	0.18	1.16	4.00
Treated	0.433	0.74	1.18	4.07

3.6.3 The effect of raising the temperature of the test solution, without subsequent exposure to light, on the breakdown of the dyeings.

It was clear from the results of the two previous experiments that none of the products present on the fabric when it was exposed to heat and light were responsible on their own for the enhancement in breakdown. Together, however, they did enhance the breakdown which implied that the nucleophilic reaction which took place in solution, may carry on during the exposure to heat and light, even though the fabric was apparently dry. So as to obtain some evidence for this theory, an experiment ws done in which a dyeing which had been tested in a hydrogen peroxide solution at pH 11 in the usual manner (see 2.7.1), was dried, without having been rinsed, and was re-immersed in the same solution but at 40°C. Some breakdown dye was lost into the solution at this stage and its quantity was estimated using an identical detergent solution as a 'blank' when measuring the optical density. The rest of the breakdown was extracted from the fabric as before and its optical density was measured. The results are shown in the table below.

Table 21. The effect of raising the temperature of the test solution, without subsequent exposure to light, on the breakdown of the dyeings.

Dye: Levafix Orange E3GA (1st dyeing)

	Weight of fabric (g)	O.D. (50ml) of extracted dye	O.D. (100ml) of dye in soln.	Break (mg dye/g fab.)	% Break
**Blank					5.7
Treated	0.409	0.16	*0.11	2.50	8.6

* Result not accurate as solution was cloudy due to detergent.

** Values transferred from Table 4 for comparison.

3.6.4 The effect of DABCO on the breakdown.

When the effect of DABCO was tested previously (Table 11), the dyeing was rinsed after the reaction and before exposing it to heat and light. However, even in very small quantities DABCO works as a singlet oxygen quencher (103)

To check that the decrease in breakdown was not caused by DABCO acting as a singlet oxygen quencher, the following experiment was carried out:

The dyeing was treated in a solution of hydrogen peroxide as described in 2.7.1., at pH 11, rinsed, and after soaking in a solution only containing DABCO (5 g/l), it was squeezed, dried and exposed to heat and light for 3 hours, as before. The breakdown was determined as before and the results are shown in the table below. (table 22)

A 'blank' reading was taken of an equally treated dyeing but was not soaked in a DABCO solution after rinsing.

Table 22. The effect of DABCO on the breakdown.

Dye: Levafix Brilliant Red E43A (2nd dyeing)

	Weight of fabric (g)	O.D. (4cm cell)	Break (mg dye/g Fabric)	% Break
Blank	0.406	0.140	0.179	5.7
Treated	0.414	0.135	0.170	5.5

3.6.5 The effect of copper sulphate on the breakdown

Some metal ions such as Cu^{2+} are known to catalyse peroxide free radical reactions.[65] The results so far suggest that the reaction of breakdown of 2,4-fluoro-5-chloro-pyrimidinyl dyeing, is of this type. A series of experiments with copper sulphate were therefore carried out to determine the effects of cupric ions on the breakdown of these dyeings. These experiments were as for the previous tests for breakdown with the difference that besides detergent (5 g/l) and hydrogen peroxide (4 ml/l) these test solutions also contained 10 mg/l of copper sulphate. After soaking in the test solutions for 20 minutes at room temperature (22 ± 2°C) the dyeings were squeezed, dried and exposed to heat and light for 30 minutes, as before. A 'blank' treatment was also carried out by not including copper sulphate in the test solution. The breakdown was determined as before and the results are shown in the table below. (table 23)

Table 23. The effect of copper sulphate on the breakdown

Dye: Levafix Orange E3GA (1st dyeing)

pH (+ 0.1)		Weight of fibre (g)	O.D.	Break mg dye/g fabric	% Break
9.8	Treated	0.372	0.11	0.795	2.7
	*Blank				2.0
11	Treated	0.393	0.32	2.19	7.5
	Blank	0.391	0.24	1.65	5.7

* Values transferred from Table 19 for comparison

3.6.6 Breakdown in the presence of antioxidants

Several antioxidants of different types were tested so as to obtain furthe evidence of a free radical reaction and as an attempt in establishing which free radicals are involved.

The dyeings were first treated in hydrogen peroxide solutions as described in 2.7.1., at pH 11, and after rinsing were soaked in 50cc solutions of antioxidant (4% wt of fibre). They were then squeezed, dried and exposed to heat and light as before. The dyeings were first exposed to heat and light for 30 minutes, but except for one antioxidant, 2 hydroxy-5-methyl phenyl-methylketOXIME, the difference between the treated and the blank was not very noticeable, so the times of exposure were increased.

The breakdown was determined as before and the results are shown on Table 24.(overleaf).

Blank readings were taken of dyeings which were tested exactly in the same way but which were not soaked in solutions of antioxidants prior to exposing to heat and light.

Table 24. Breakdown in the presence of antioxidants

Dye: Levafix Orange E3GA

Time in light (hours)	Antioxidant	Conc. of dye in fabric (mg/g)	Solvent for antioxidant	Weight of fabric (g)	O.D.	Break mg dye/g Fabric	% Break
½	Nickel complex of 2-hydroxy-5-methyl phenyl methylketOXIME	29.0	Toluene	0.425	0.35	2.214	7.6
	* Blank						2.0
	2266 tetra methylpipiredine	29.0	Water	0.424	0.28	1.775	6.1
2	2 hydroxy-4-methoxy benzophenone 5 sulphonic acid	29.0	Water	0.435	0.28	1.136	4.2
	Ni-oxime	29.0	Toluene	0.347	0.11	0.852	2.9
	Blank	29.0		0.440	0.20	1.220	4.2
	Carbon tetrabromide	19.4	DMF	0.457	0.18	1.050	5.4
3	2,6-di-tertiary butylphenol	19.4	DMF	0.437	0.12	0.738	3.8
	Blank	19.4		0.429	0.21	1.379	6.8

* Values transferred from Table 19 for comprison

3.7. Visual assessment of dyeings from different dyes, after a wash fastness test with a detergent containing sodium perborate.

The first dyeing that was tested was Levafix Orange E3GA which was submitted to a test where the conditions were the same as for the ISO 3 test, but a commercial detergent containing sodium perborate (PERSIL) was used instead of the standard products. The dyeing (2g) was immersed in 100cc of distilled water (L:R = 50:1) containing 5 g/l of PERSIL, and the container with the solution was placed in the wash wheel which ran for 30 minutes at 60°C. The dyeings were rinsed with water and dried.

The results showed a very marked decrease in the brightness of the dyeing as can be seen from the mounted samples 1 and 2 in Appendix 1. Some dye was also lost into the test solution as expected, but assessment with the grey scales was not possible due to the change in brightness of the dyeing.

A standard commercial laundering test, test no. C_2 of ISO C06, was also carried out using a Levafix Orange E3GA dyeing. The testing conditions were the same as above, (ISO 3) but the detergent used for testing were: 4 g/l of the AATCC standard detergent used throughout this work and 1 g/l of sodium perborate. The result (Appendix 1 - sample 3) showed less shade change than was obtained with commercial detergent, as above, which infers that the products used in this test do not therefore reproduce faithfully the composition of commercial detergents. The test with the commercial detergent itself, PERSIL, was therefore preferred for testing the remaining dyeings which had been tested for breakdown throughout this work. The tested samples are shown in Appendix 1.

3.8 Effect of pretreatment of a 2,4-fluoro-5-chloropyrimidinyl dyeing with a tertiary amine on its appearance after testing with a commercial detergent containing sodium perborate.

A tertiary amine, DABCO, had already successfully been used in reducing the breakdown (see 3.6.1)and was now also tried as a means of reducing the change in brightness caused by washing with PERSIL. As it had been concluded previously that DABCO acted as a nucleophile when reacting with the dyeing (see 1.4) detergent was also included in the pretreatment solution since it contains electrolytes, alkali and surface active agents, all known to promote such types of reactions with dyes on fibres. Thus, the dyeing was treated in a solution containing 5 g/l of the AATCC detergent, and DABCO (3% on wt. of fibre) for 15 minutes at the boil. It was then rinsed and tested with PERSIL as above.

A 'blank' test was done on the dyeing by not pretreating it with DABCO and submitting it to an identical test with PERSIL. At the end of the testing, the dyeings were rinsed and dried. The tested samples are shown in Appendix II.

Both the pretreated and the 'blank' dyeing were submitted to a second identical treatment with PERSIL. They were again rinsed and dried. The tested samples areshown in Appendix II.

CHAPTER IV

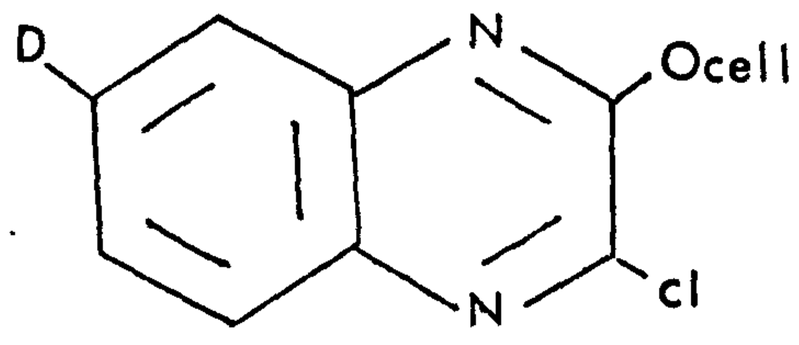
GENERAL DISCUSSION

4.1 Relationship between breakdown and hydroperoxide content

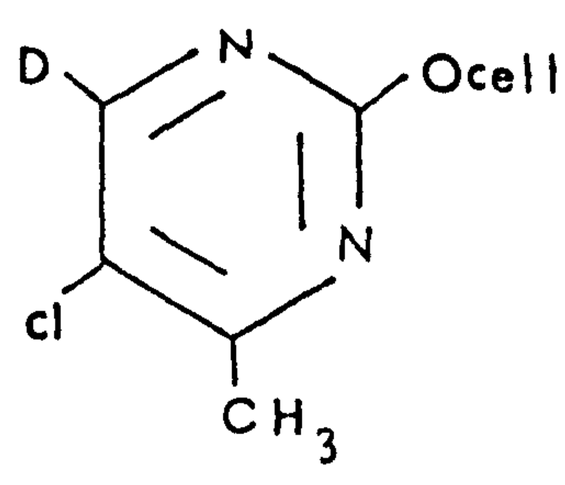
Of the dyeings tested it was observed that only those containing a pyrimidinyl or a quinoxaline ring showed significant breakdown (Table 5) when treated in a hydrogen peroxide solution. However, not all pyrimidinyl dyeings showed significant breakdown e.g. the 2,4-dichloro-pyrimidinyl dyeing did not show significant breakdown even at pH 12. Dichlorotriazinyl dyeings did not show significant breakdown either and monochlorotriazinyl dyeing did not show any breakdown whatsoever.

A hydroperoxide group was detected in all the dyeings (Tables 13, 14, 15) mentioned above after they were treated in the hydrogen peroxide solution, except in the case of monochlorotriazinyl dyeing. Thus it seemed that the formation of hydroperoxide was related to the breakdown of some of the dyeings. Thus, the dichloro-quinoxalinyl dyeingwhich showed lower breakdown than a 2,4-fluoro-5-chloropyrimidinyl dyeing with a similar chromophore (Table 5) also forms hydroperoxide more slowly. (Table 16, graph 1). On the other hand a dichlorotriazinyl dyeing forms hydroperoxide much faster than a 2,4-fluoro-5-chloropyrimidinyl dyeing (with a similar chromophore) but Table 5 shows that the same dichlorotriazinyl dyeing does not show any significant breakdown when treated with a hydrogen peroxide solution, by comparison with the 2,4-fluoro-5-chloropyrimidinyl dyeing. This difference in behaviour was taken as indicative that the hydroperoxide group has to be in the ortho or para

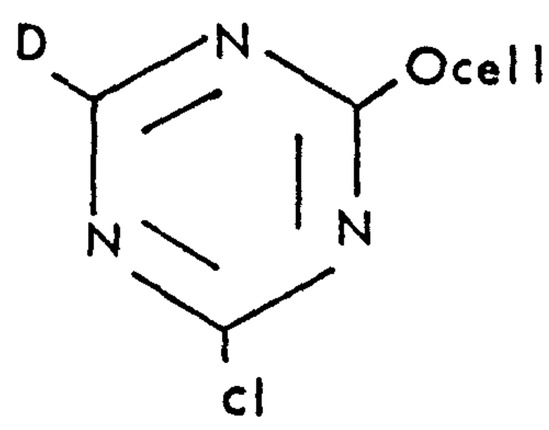
position of the ring, relative to the dye-fibre bond in order to cause the breakdown of the dye-cellulose bond. Thus, assuming that the reaction between the hydrogen peroxide and the dyes tested is a nucleophilic reaction (see Ref. 2 and Section 3.32) and considering the positions in the ring which still remain labile, it can be seen how the hydroperoxide group can only be in the para position relative to the cellulose in the 2-methylsulphonyl-4-methyl-5-chloropyrimidinyl dyeing (XLIII) and ortho to the cellulose in the dichloroquinoxaline dyeing (XLII). On the other hand, in the dichlorotriazinyl dyeing (XLIV) the hydroperoxide group can only be in the meta position of the ring relative to the cellulose. The 2,4-dichloropyrimidinyl (XLV) dyeing can also only form hydro-peroxide at a position in the ring meta to the cellulose, and it does not shown significant breakdown either, as already pointed out. This is illustrated below:-



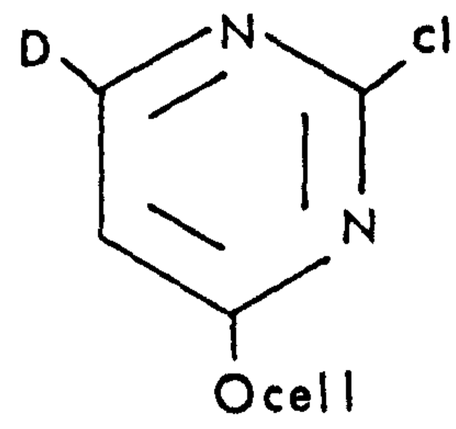
XLII



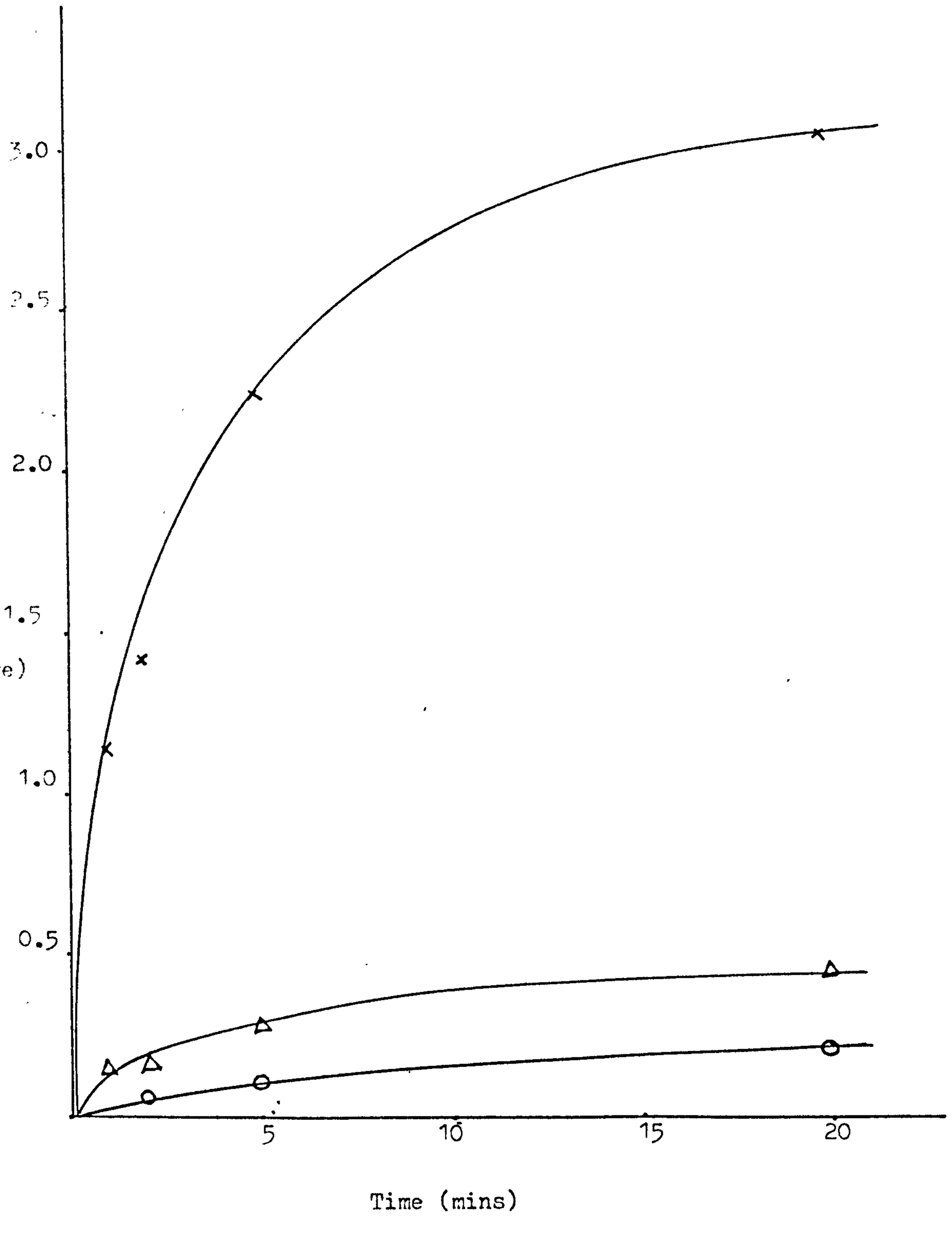
XLIII



XLIV



XLV



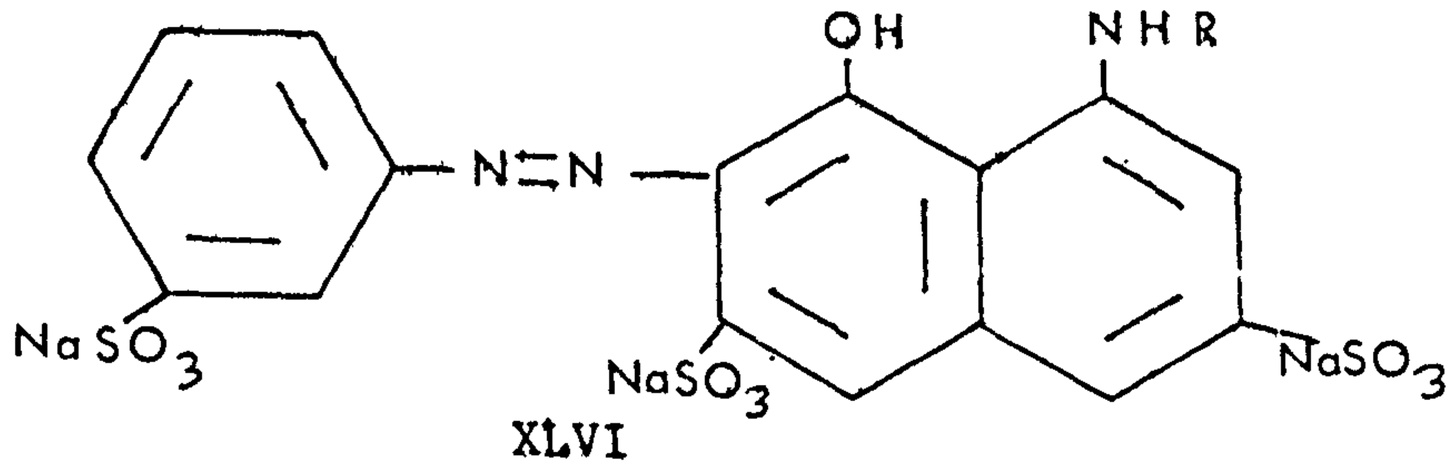
Graph 1. Hydroperoxide formation of dyeings after different times of reaction with hydrogen peroxide.

Δ dye II (2,4-fluoro-5-chloropyrimidinyl)

O dye V (dichloroquinoxalinyl)

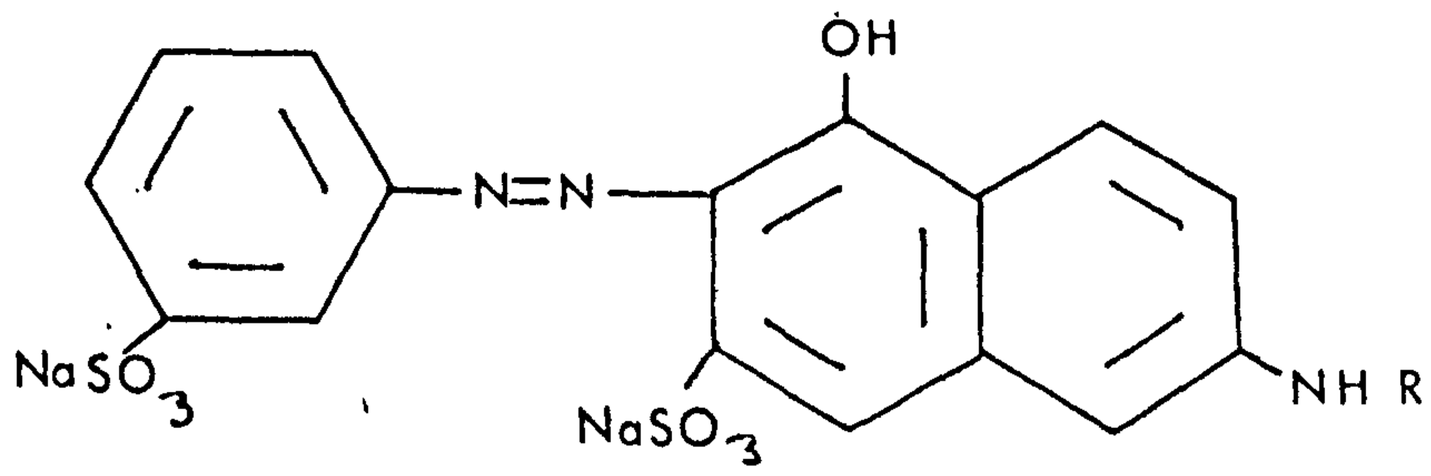
× dye VI (dichlorotriazinyl)

If a graph is plotted for the pyrimidinyl dyeings (except 2,4-dichloropyrimidinyl) of the values for % breakdown (Table 6) vs. hydroperoxide formation(Table 15) it is clearly show that the breakdown increases with hydroperoxide content, even if not all the points fall on a straight line (Table 25 and graph 2). Not all the dyes on the graph have the same chromophore. Thus, only two of the dyes, the 2,4,5-tri chloro and the 2,4-chloro-5-cyano pyrimidinyl dyes (dyes IXand X) have the same chromophore. The structure of the chromophore, which is red, is as follows:-



XLVI

The other dye on the graph is the Levafix Orange E3GA, which has a 2,4-fluoro-5-chloropyrimidine as the reactive group. The formula of the chromophore is not known, but usually orange azo dyes are based on J-acid (6-aminonaphthol-3-sulphonic acid), as follows:-



However if the results from Table 25 referring to the dyes containing the red chromophore XLVI are plotted separately from the results referring to Levafix Orange EGA, two straight lines are obtained. (Graphs 3 and 4 respectively).

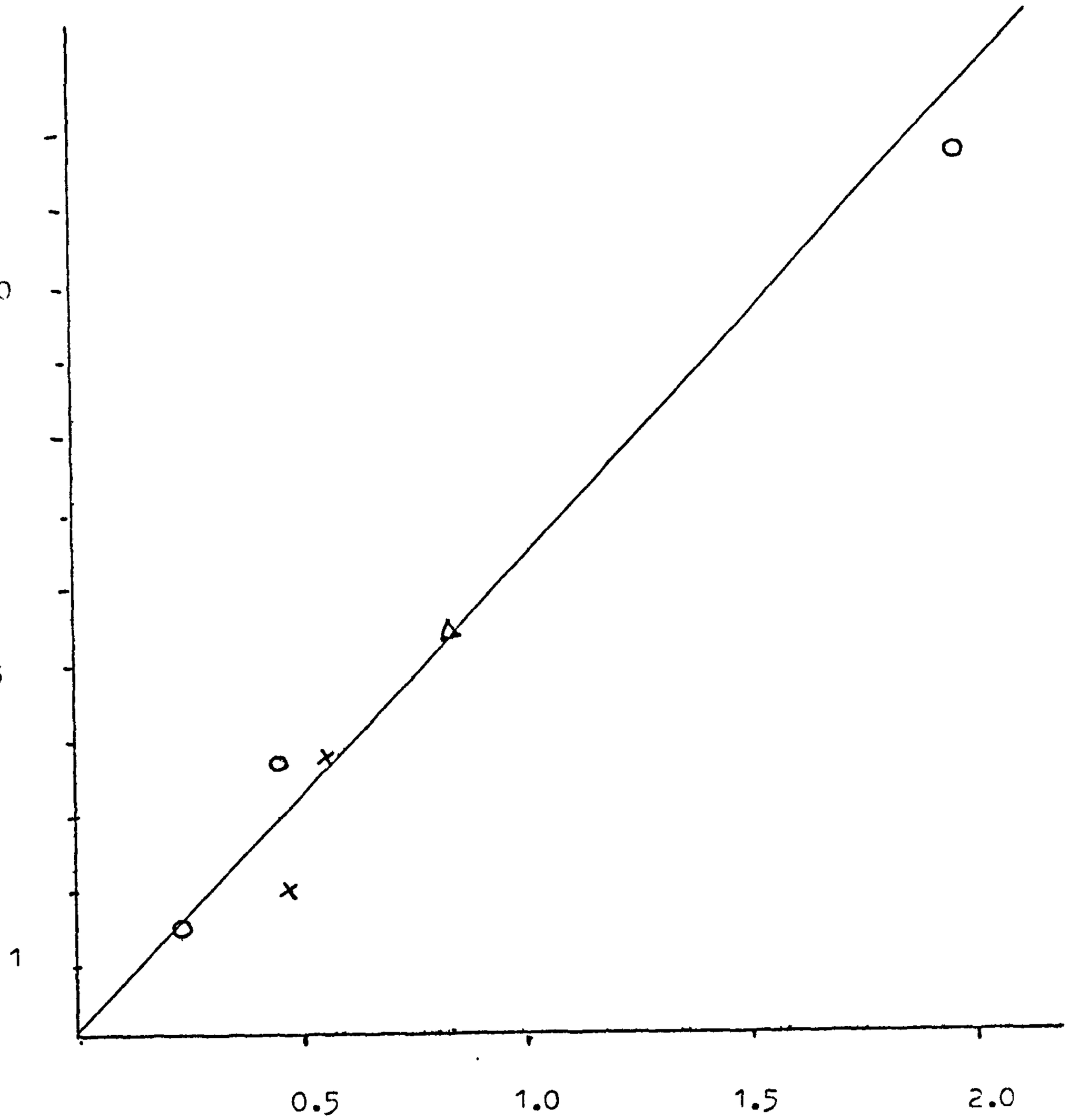
The influence of the chromophore on the results can be clearly seen in Graph 5 plotted from the results on Tables 4 and 13, corresponding to the % breakdown and to the hydroperoxide formation (moles - OOH/mg dye), respectively, of 2,4-fluoro-5-chloropyrimidinyl dyeings with different chromophores. The points on this graph are scattered. This probably arises from the fact that where the chromophore is large the number of moles of dye would be less in 1mg of dye than for a smaller chromophore and therefore the corresponding true hydroperoxide content is higher than indicated. For the points to fall on a straight line in a graph of % breadown vs. hydroperoxide content, when testing dyeings containing different chromophores, the hydroperoxide content would have to be expressed in 'moles of hydroperoxide/moles of dye'. This is not however possible with the commercial dyes tested, since the formulae of the different chromophores have not been disclosed.

These graphs are only useful as a means of showing that the breakdown of pyrimidinyl dyeings increases with hydroperoxide content, but cannot for example be used to establish an empirical relationship between them, since the experimental conditions used in the formation of the hydroperoxide were different.

Thus, for the measurement of the hydroperoxide content, the dyeing was rinsed after the reaction with hydrogen peroxide (see 2.9), but for the measurement of the breakdown it was not rinsed (see 2.7.2). The breakdown of the dyeings is much less when the cloth is rinsed after the reaction with hydrogen peroxide, and these values were not measured instead, because the errors when measuring such small values would be considerable.

Table 25. Relationship between % breakdown and hydroperoxide formation of pyrimidinyl dyeings.

	Dye	pH of H_2O_2 Soln.	Moles OOH/mg dye ($x10^{-7}$)	% Break
II	Levafix Brilliant Red E4BA	9.8	0.230	1.5
		11	0.447	3.7
		12	2.010	11.6
IX	2,4,5-trichloro-pyrimidinyl	12	0.755	5.4
X	2,4-chloro-5-cyanopyrimidinyl	9.8	0.490	2.0
		11	0.576	3.8

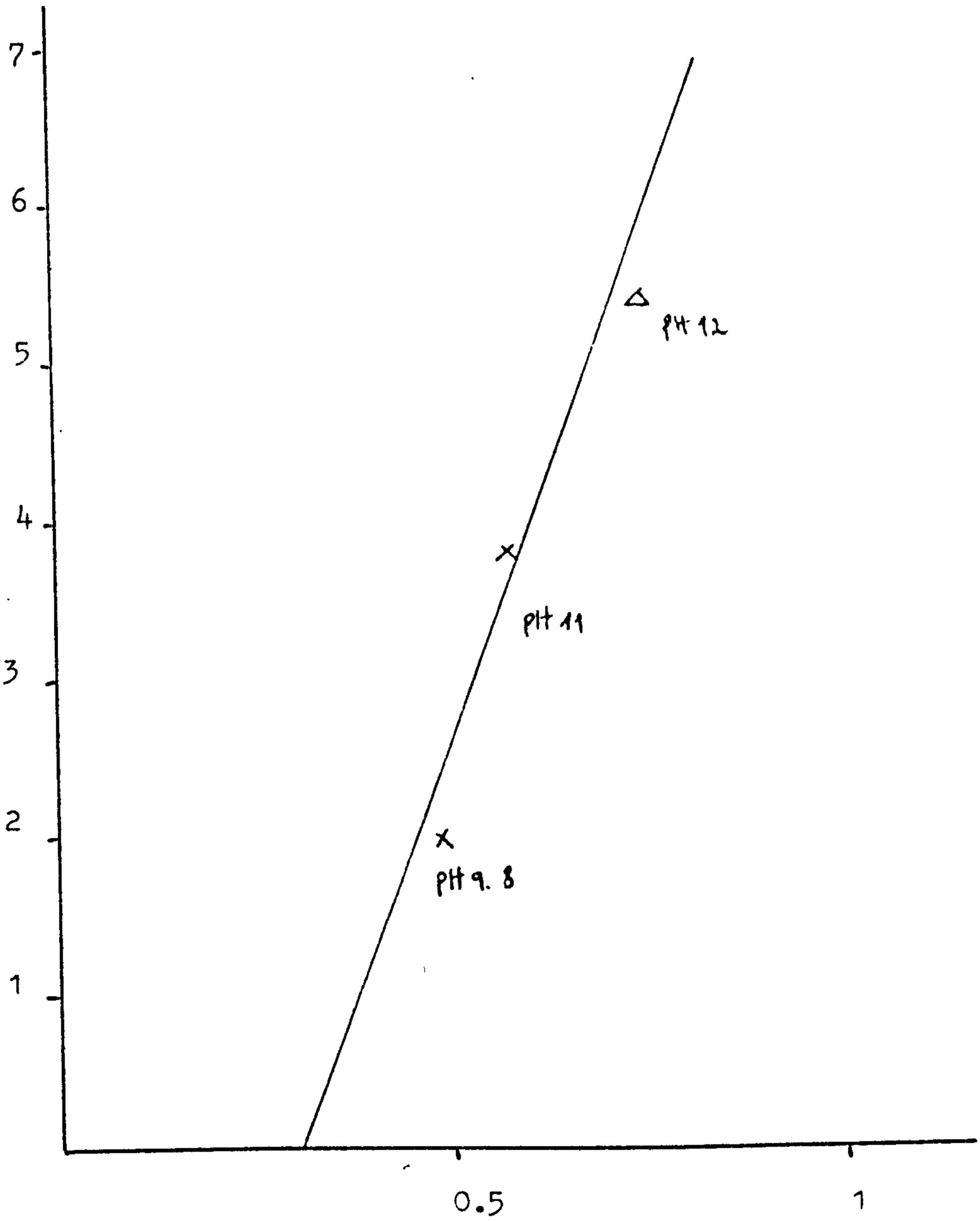


Graph 2. Plot of % breakdown vs. hydroperoxide content of different pyrimidinyl dyeings.

O dye II (2,4-fluoro-5-chloropyrimidinyl

Δ dye IX (2,4,5-trichloropyrimidinyl)

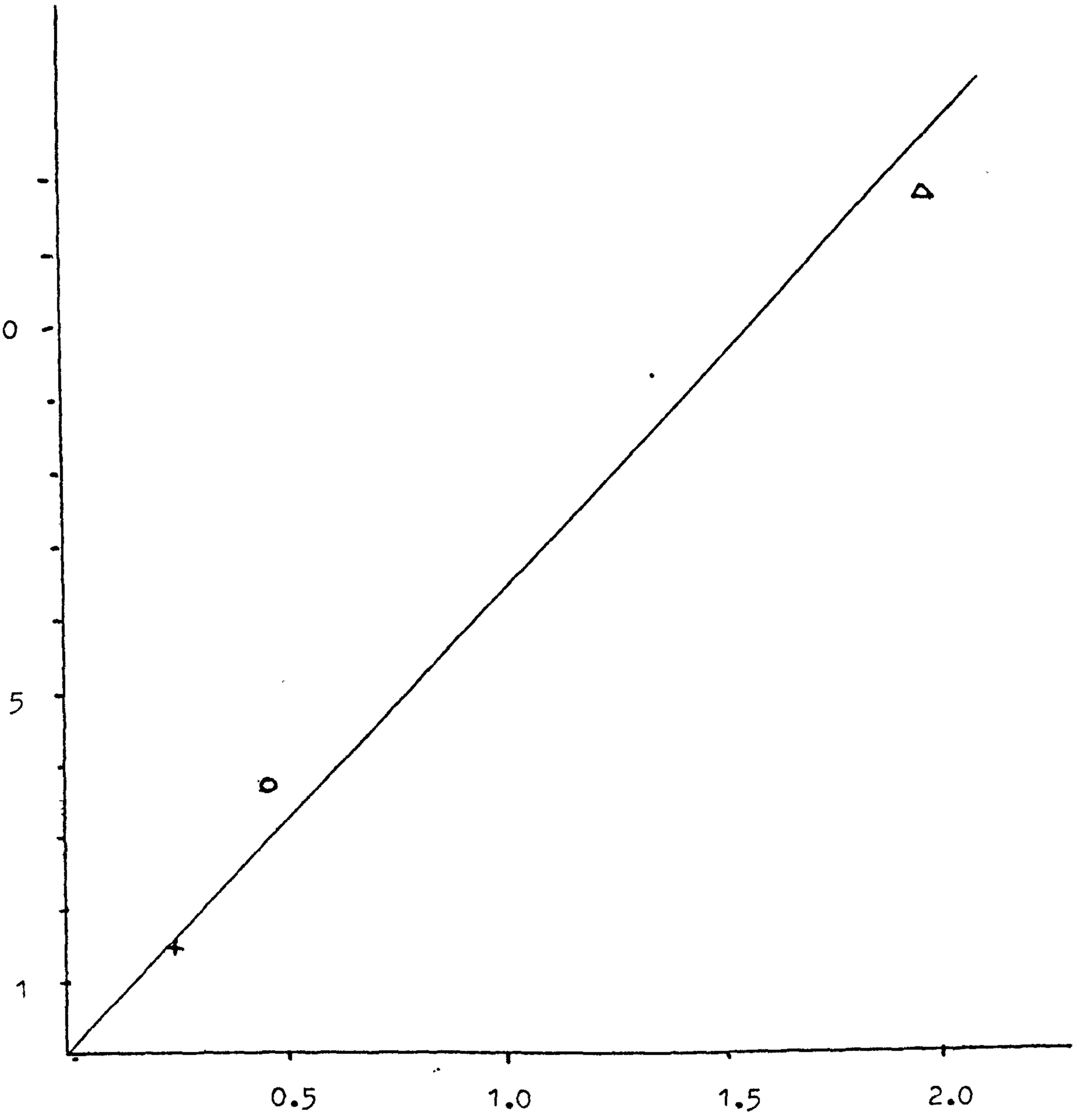
X dye X (2,4-chloro-5-cyanopyrimidinyl)



Graph 3. Plot of % breakdown vs. hydroperoxide content of pyrimidinyl dyeings with the same chromophore.

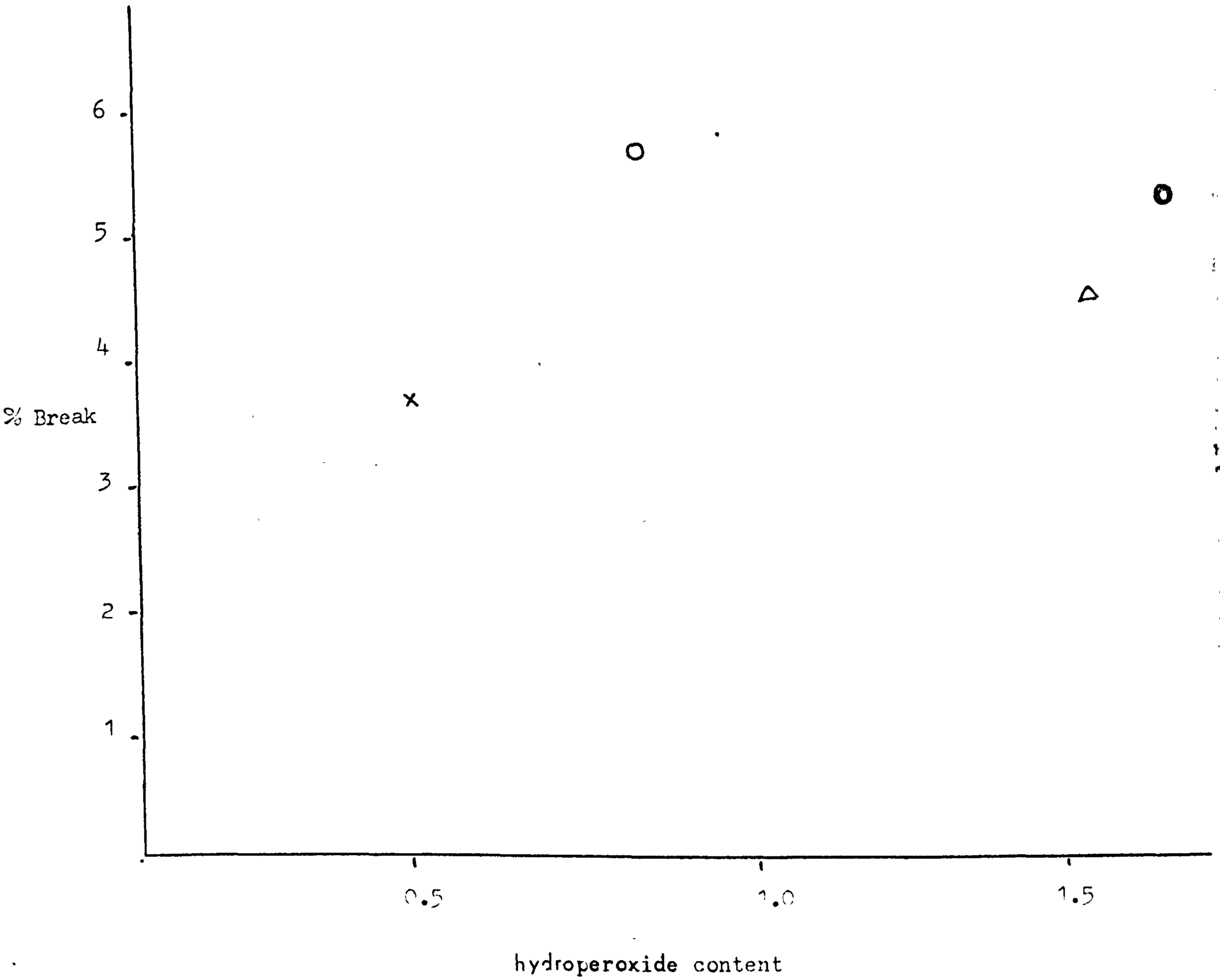
Δ Dye IX (2,4,5- trichloropyrimidinyl)

X Dye X (2,4-5-cyan opyrimidinyl)



Graph 4. Plot of % breakdown vs. hydroperoxide content of a 2,4 fluoro-5-chloropyrimidinyl) dyeing (Dye II) tested at diferent pH values.

Reaction with H_2O_2 at pH 9.8 (X), pH 11 (o) and pH 12 (Δ).



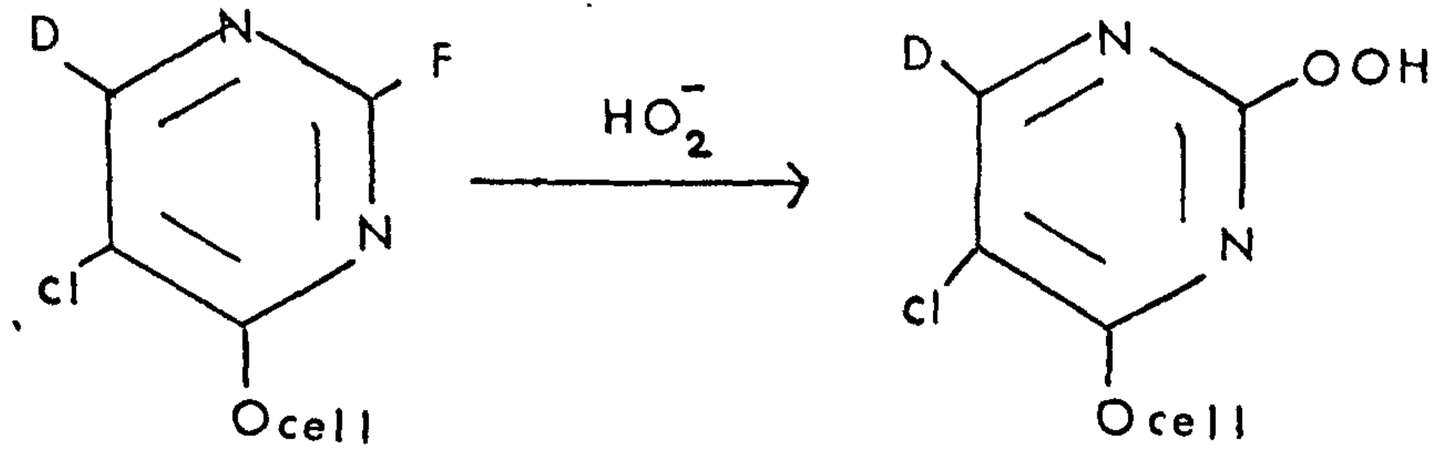
Graph 5. Plot of % breakdown vs. hydroperoxide content of 2,4-fluoro-5-chloropyrimidinyl dyeings with different chromophores.

O Dye I (Orange); X Dye II (Red) O Dye III (yellow)

Δ Dye IV (Blue)

4.2 Structure of the hydroperoxide which causes the breakdown of the bond between the 2,4-fluoro-5-chloropyrimidinyl dye and the cellulose

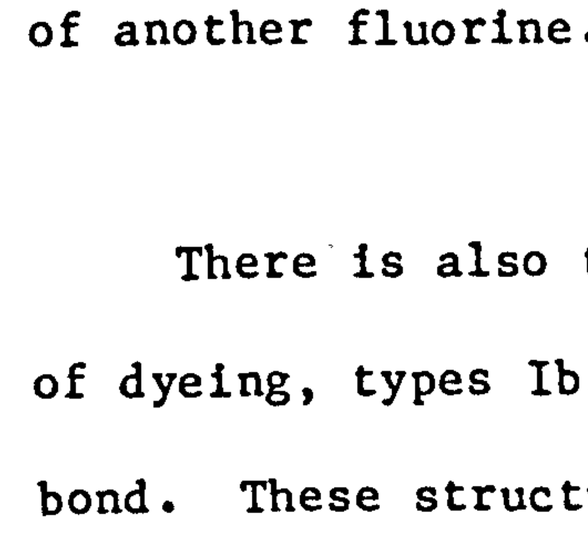
During the dyeing of cellulose with a 2,4-fluoro-5-chloro-pyrimidinyl dyeing the cellulosate ion can attack at the 2 or 4 position of the ring. It has already been discussed how in similar pyrimidinyl compounds the nucleophile prefers to attack at the 4 position (see 1.3), and the configuration of the dyeing with the cellulose at the 4 position of the ring is therefore considered first. Assuming that the reaction of the dyeing with the hydrogen peroxide is a nucleophilic reaction where the perhydroxyl anion HO_2^- is the nucleophile (see Ref.2 and section 3.32), there are two positions where the HO_2^- can attack, i.e. the 2 and 5 positions of the ring. For breakdown to occur the hydroperoxide has to be at the ortho or para position to the cellulose, as already argued in the previous section. This means that the attack by the perhydroxyl anion would have to take place at the 5 position. However, the 2 position is much more activated and attack would be expected here first:



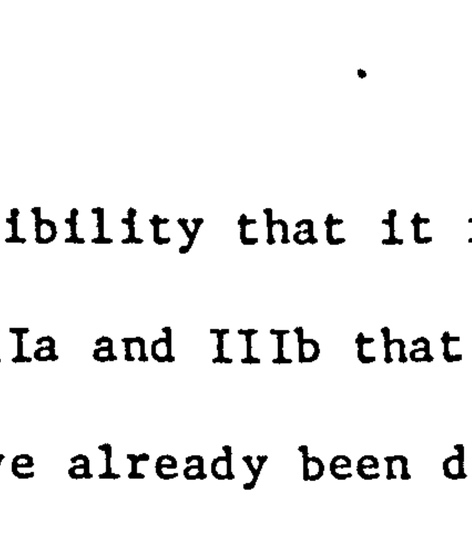
D = chromophore

The 5 position would not be expected to be any more activated due to the presence of a hydroperoxide group para to it. On the other hand the possiblity of a nucleophilic attack taking place first at the 5 position of the ring seems remote since a fluorine in the para position is non-activating (Hammet value $\sigma = 0.06$) and it has actually been shown to be deactivating with regard to nucleophilic substitution of another fluorine.

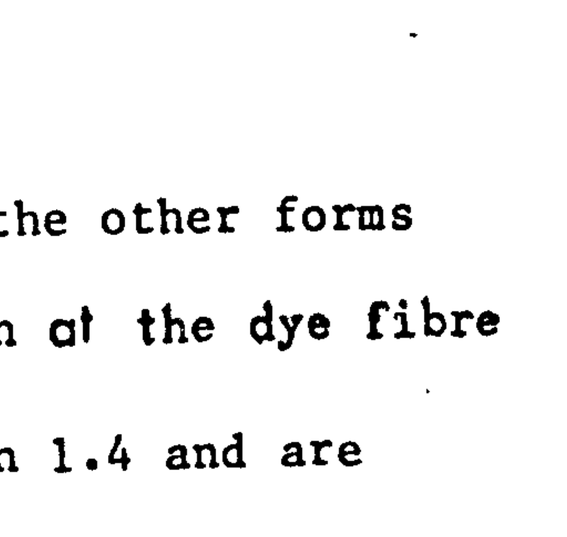
There is also the possibility that it is one of the other forms of dyeing, types Ib, II, IIIa and IIIb that break down at the dye fibre bond. These structures have already been discussed in 1.4 and are reproduced below (the dyeing above already considered, is type Ia).



Ia

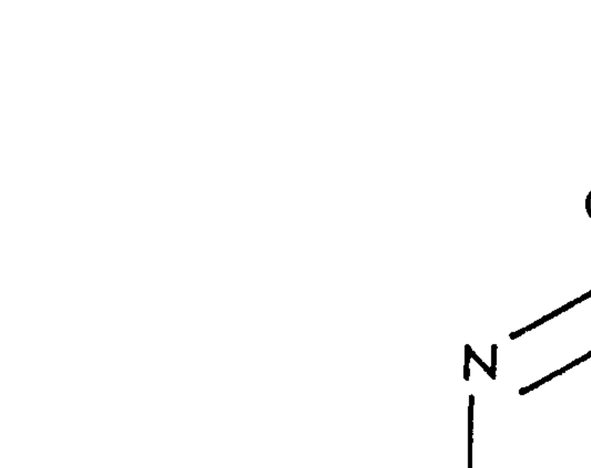


Ib



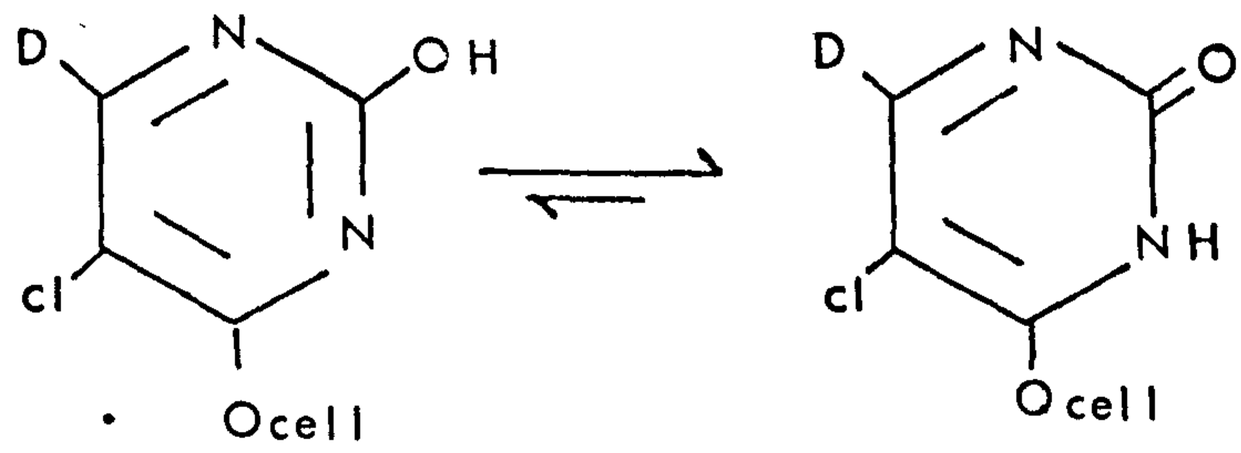
II

IIIa



IIIb

Type II would not be expected to break down since there are two links with the cellulose. The results in Table 8 show a lower breakdown for the exhaustion than for the pad-batch dyeing which seems to confirm that Type II dyeing does not break down, since the more severe conditions of hot exhaustion dyeing are expected to form more Type II. (For example, Preston and Fern[50] found that exhaustion dyeing of dichlorotriazinyl dyes produced more Type II than cold pad-batch dyeing). Type III dyeings can exist in two forms (see 1.3 and Fig. 1) the enol (XLVII) and the oxo form (XLVIII) represented below.



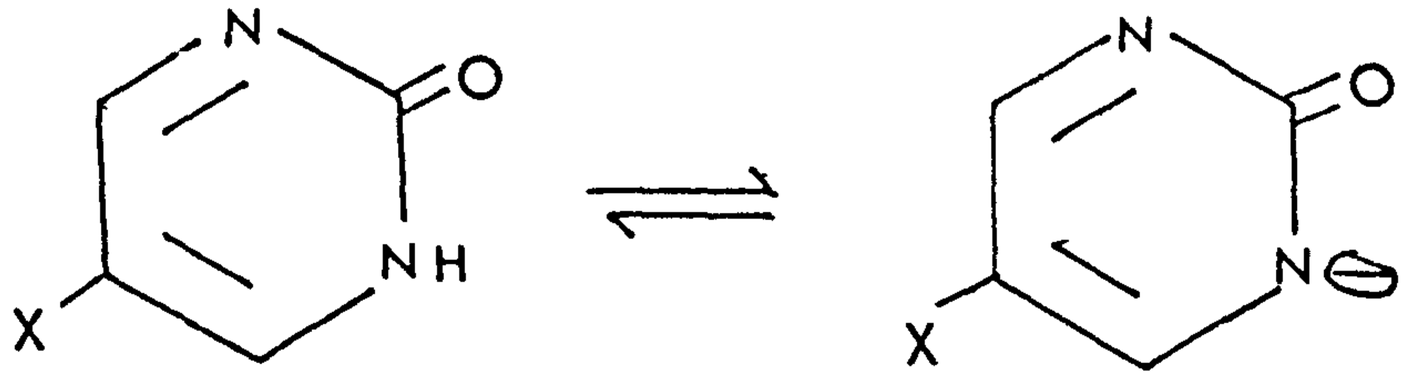
XLVII XLVIII

The Type III represented above is Type IIIb.

The enol form of Type III dyeing would be less susceptible to nucleophilic attack at the 5 position than Type Ia since the hydroxyl group is electron donating. However evidence from similar compounds (see Fig. 1) suggests that the oxo form is the predominant one. It is very likely that this form is more reactive at the 5 position than is Type Ia. For example, Hannout[39] found that 2-chloro-5-bromopyrimidine slowly hydrolysed to 2,5-dihydroxypyrimidine when treated with solutions of sodium hydroxide in 20% dioxan-water at 20°C and that the amount formed increased as the concentration of sodium hydroxide was increased from 0.05 to 0.2 molar.

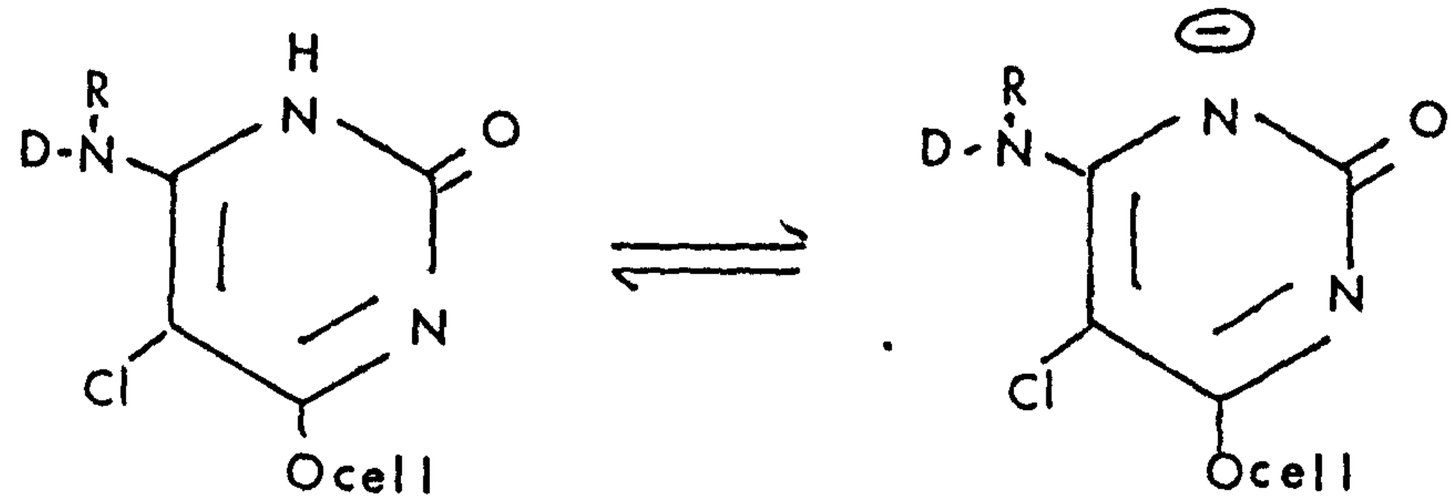
The possiblity of hydrolysis occuring first at the 2 position was checked by treating the authentic 2-hydroxy-5-bromo-pyrimidine under the same conditions as the 2-chloro-5-bromo-pyrimidine but no hydrolysis at the 5 position was observed, not even after several hours. However, 2,4-dihydroxy-5-bromo-pyrimidine had been reported by Wang to form 2,4,5-hydroxypyrimidine with sodium bicarbonate. Hannout therefore attempted to hydrolyse 2-hydroxy-5-bromo-pyrimidine by refluxing with 0.1M sodium bicarbonate. He confirmed that the 5 position is hydrolysed under these conditions and suggested that under mildly alkaline conditions the 5 position can be hydrolysed but that with sodium hydroxide the 2-hydroxy-5-bromopyrimidine is largely ionised (pK_A = 7.35) and therefore the ring is strongly deactivated against hydrolysis with hydroxide ion. Sodium hydroxide had also been found not to hydrolyse 2,4 dihydroxy-5-bromopyrimidine by Wang.

Hannout found good agreement with σ_M values for the ionisation of 2-hydroxypyrimidines with different substituents at the 5 position which suggested ionisation of the oxo form, as represented below:-



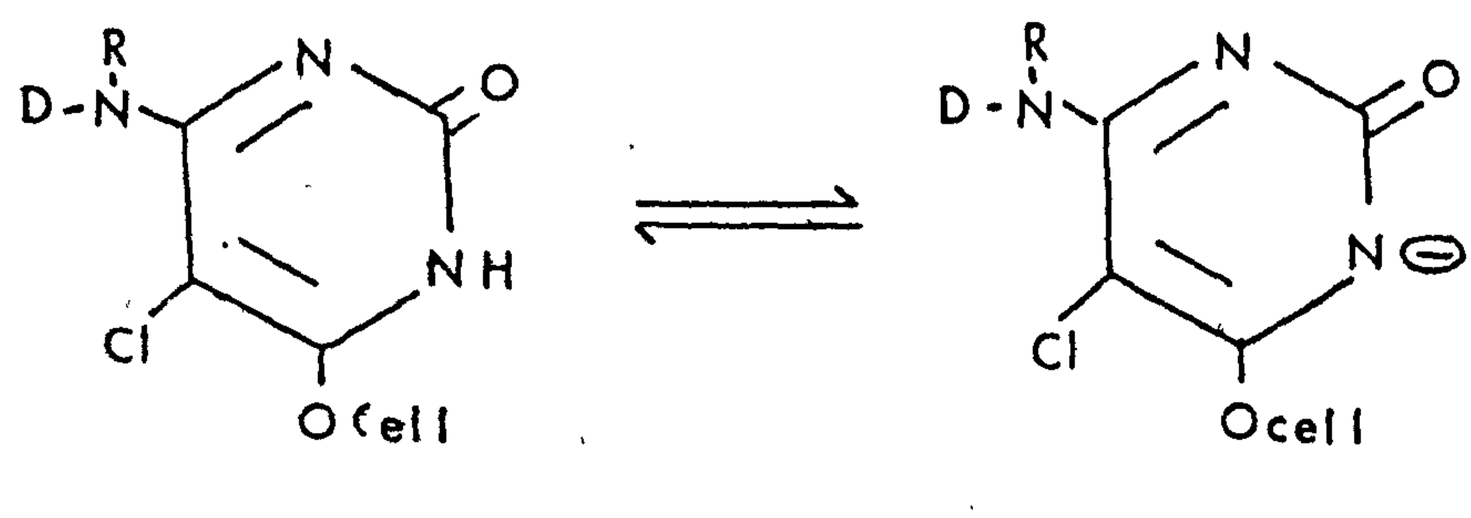
If the analogous oxo form of Type III dyeing is ionised similarly it can take one of two resonance forms (same structure)

1)



L

2)



XLIX

If a $-NH_2$ group para to the charge is considered as having approximately the same influence as the -NRD substituent in XLIX, where R is a hydrogen atom or an alkyl group and D is the chromophore, then since for $-NH_2$ the Hammet value $\sigma_p = -0.66$ and for chlorine $\sigma_M = +0.37$, by applying the additivity principle for these two substituents (see 1.2):

$$\sigma\ (NH_2+Cl) = -0.29$$

The ρ value for this reaction is $\rho = +4.5$, and log Ko = -9.05. Then from Hammet's equation (1.3):

$$\log \frac{K}{K_o} = \sigma\rho = -1.3$$

where Ko is the rate of ionisation of 2-hydroxypyrimidine. From the equation above:

log K = -10.3 and pK_A = 10.3

This will be a minimum value for thepK_A of form XLIX since the effect of the ortho electron donating substituent has not been considered. σ values of substituents in the ortho substitution are unreliable as already discussed in 1.2 and $\sigma_o$for cellulose would be difficult to predict from the σ_p value since it is a very bulky molecule. Form L of the ionised dyeing has the cellulose in the para position to the charge. If a $-OC_2H_5$ substituent para to the charge is considered as having a similar influence (as compared with a cellulose molecule), then we can consider the $\sigma_p$value for cellulose as being approximately σ_p = -0.24. We can also assume that for ortho $-NH_2$ the value of σ_o will not be smaller than that of σp and therefore we can safely assign a value of σ = -0.66 again. If these two values are added to the σ_p value for chlorine, the total value will be

σ_{total} = -0.24 - 0.66 + 0.37 = 0.53 and from Hammet's equation (1.3) pK_A = 11.4

There will be errors in these predictions, not least the error in the additivity which will be caused by the proximity of the substituents to each other, but one can assume that the true value for pK_A of ionisation of this dyeing will be between 10.3 and 11.4, i.e. the minimum and the maximum values calculated above.

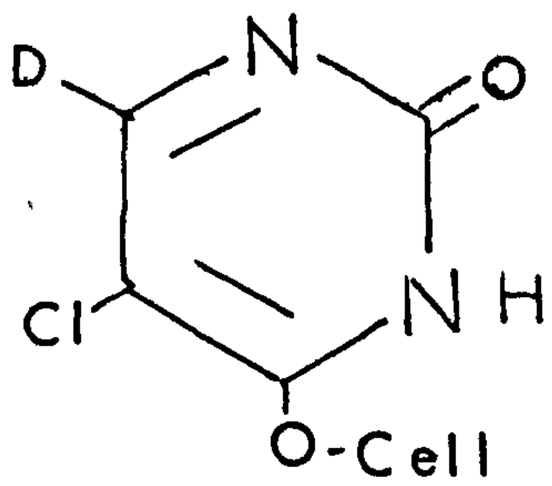
In order to find out whether the dyeing would be largely ionised or not under the conditions of the reaction with hydrogen peroxide, the internal pH would have to be known (see 1.4). Accordingly, the internal pH was calculated using the computer program prepared in previous work.[2] At the pH values at which the reactions were carried out, 9.8, 11 and 12, the calculated internal pH values were respectively 8.1, 9.35 and 10.4. These values are well below the maximum pK_A value above (11.4) and only one value is slightly higher than the minimum value for pK_A of 10.3. It can therefore be assumed that Type III dyeings of 2,4-fluoro-5-chloropyrimidine remain largely unionised during the reaction with hydrogen peroxide.

However, the electron donatingeffect of the amino and of the cellulose substituent also result in the deterioration of position 5 of the ring towards nucleophilic attack and presumably the peroxide anion HO_2^- attacks it only because it is a very strongnucleophile. This is supported by the results of an experiment carried out in previous work on the same dye,[2] whereby the dye was treated with 0.4 V hydrogen peroxide before it was applied to the cloth. It was observed that the dye did not fix into fabric, whereas another portion of the dye which had not been treated with hydrogen peroxide but had been treated in an alkaline solution at the same pH, did. This implied that the labile substituents of the ring were replaced by HO_2^- ions prior to dyeing but not by OH^- ions.

One type of dyeing obtained from the same dye which would have position 5 more activated than the dyeing above would be a Type Ia dyeing formed as a result of an attack by the cellulose at the 2 position. This is not likely, as already mentioned (see also section 1.3), but if even a small amount of it is formed it could account for the small values of breakdown being discussed. This possiblity is considered on Table 26 alongside the possibility of TypeIIIb dyeing, as the form of dyeing which is responsible for the breakdown. The experiments which give support to either theory are listed in the table.

The structures of the dyeings considered in the table are illustrated below and the table is on the next page.

Type IIIb



Type Ib

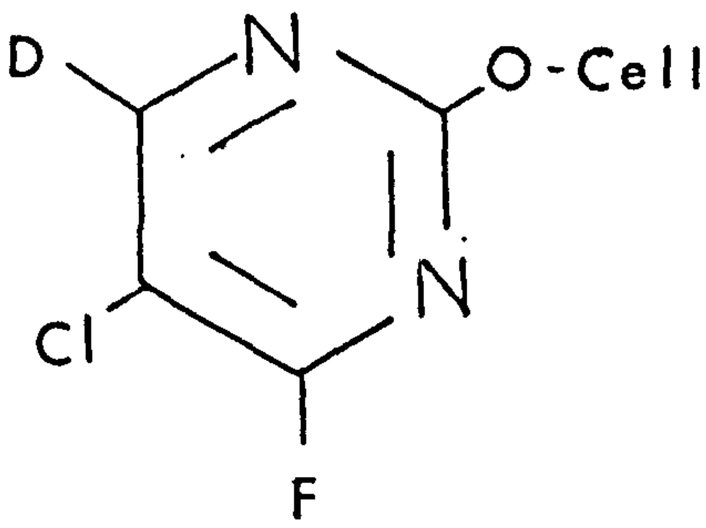


Table 26. Structures of 2,4-fluoro-5-chloropyrimidinyl dyeings consistent with results obtained on tests on breakdown

Test	Test	Observations on breakdown	Structure responsible for breakdown
1	Breakdown by H_2O_2 (Table 4)	Preferential attack at 5 position of ring	Type IIIb
2	Different dyeing conditions (Table 8)	Exhaustion dyeing shows less bond breakdown than pad batch dyeing	Type IIIb or Ib
3	Pretreatment in alkaline solutions (Table 9)	Slightly higher breakdown	Type IIIb
4	Pretreatment in ammonia (Table 10)	No difference	Type IIIb

The conditions leading to Table 26 are listed below:-

Test No. 1 - For dyeing Ib to show breakdown with hydrogen peroxide due to the presence of a hydroperoxide group in position 5 of the ring, this position should be attacked by a perhydroxyl anion preferentially to position 4. If position 4 is attacked first, then position 5 would be expected to be less activated than in Type Ib dyeing, since a hydroperoxide group would not be electron withdrawing as in fluorine.

A perhydroxyl anion, HO_2^- would be expected to be a hard nucleophile, and there would therefore be no reason why it should not attack the more activated 4 position with a hard fluorine rather than the 5 position with the chlorine. Fluorine is also replaced

preferentially when in an activated position,[8] [9] [10] and this is the case since the two nitrogen hetero atoms activate the ring. The solvent might also influence the mobility order of halogens, as discussed in 1.1,[20] [21] and a polar protic solvent like water favours a fluorine replacement.

With the Type IIIb dyeing there is no argument as to where the chlorine will attack, since position 6 of the ring has got a strongly electron donating imino group on it, and position 4 is not attacked since all the evidence points to the dye-cellulose being broken only after the formation of a hydroperoxide when it is exposed to heat and light.

Test No. 2 - The exhaustion dyeing is expected to form more Type II dyeing than pad batch dyeing, as already mentioned and this would mean proportionally less Type III and Type I dyeings.

Test No. 3 - Pretreatment with alkali prior to testing would form more Type IIIb dyeing from Type Ib dyeing, therefore there would be an increase in Type IIIb dyeing and a decrease in Type Ib dyeing. Since there is an increase in the breakdown, the dyeing responsible for the breakdown must be of the Type IIIb.

Considering the relatively mild conditions used (pH 12.5, 40°C) the chlorine at the 5 position would not be expected to be replaced in either type of dyeing.

Test No.4 - Ammonia would not be expected to replace the chlorine in the 5 position of Type IIIb dyeing since it is not a strong enough nucleophile. However, it would be expected to replace fluorine from the highly activated 4 position of Type Ib dyeing since it is a hard base and the electrophilic centre at the carbon atom attached to the fluorine atom is also 'hard'. This would mean that there would be a decrease in breakdown if this was the type of dyeing responsible for the breakdown. But since there is no difference, it is not this type but Type IIIb which is responsible.

The results shown in Table 2.6 therefore suggest that it is the Type III dyeing of the 2,4-fluoro-5-chloro pyrimidinyl dye that is attacked at the 5 position of the pyrimidine ring by a perhydroxyl anion (HO_2^-).

4.3 Studies of the structures of the hydroperoxides of 2,4,5-trichloro and 2,4-chloro-5-cyano pyrimidinyl dyeings which cause the breakdown of the dye-cellulose bond.

With 2,4,5-trichloropyrimidinyl dyes, Type III dyeings are not expected to be formed to any great extent during the dyeing process since the chlorine on the ring is less labile than fluorine, for reasons already discussed.

A 2,4,5-trichloropyrimidinyl dyeing was put through the same tests as the 2,4-fluoro-5-chloropyrimidinyl dyeing, in order to find out which structure was responsible for the breakdown. The results are summarised in the Table below:

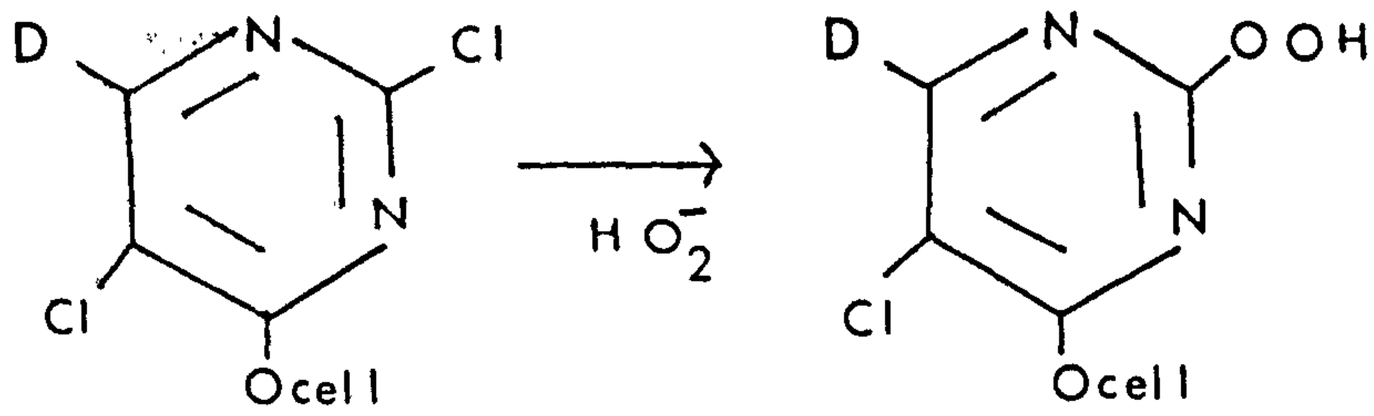
Table 27. Results of test on breakdown of 2,4,5-trichloropyrimidinyl dyeings

Test No	Test	Observation on break by H_2O_2
1	Breakdown by H_2O_2 (Table 4)	No significant breakdown by H_2O_2 solutions at pH 9.8 and 11 but significant breakdown at pH 12.
2	Pretreatment in alkaline solution (Table 9)	Slightly higher breakdown
3	Pretreatment in ammonia (Table 10)	Less breakdown

From the results of the table above (Table 27), the following conclusions can be drawn.

Test no. 1 - Even though there is no breakdown when 2,4,5-trichloro-pyrimidinyl dyeings are treated in hydrogen peroxide solutions at pH 9.8 and 11, Table 15 shows that there is hydroperoxide formation under these conditions. This suggests that the hydroperoxide group is in a position where it cannot cause breakdown of the dye-cellulose bond, i.e. meta to the cellulose substituent. Only Type I can form a hydroperoxide meta to the cellulose (equation 4.1 below). As already discussed, the cellulose is more likely to be at the 4 position of the ring and therefore Type Ia is considered first. The reaction of Type Ia with the perhydroxyl ion can be represented as follows:

(4.1)



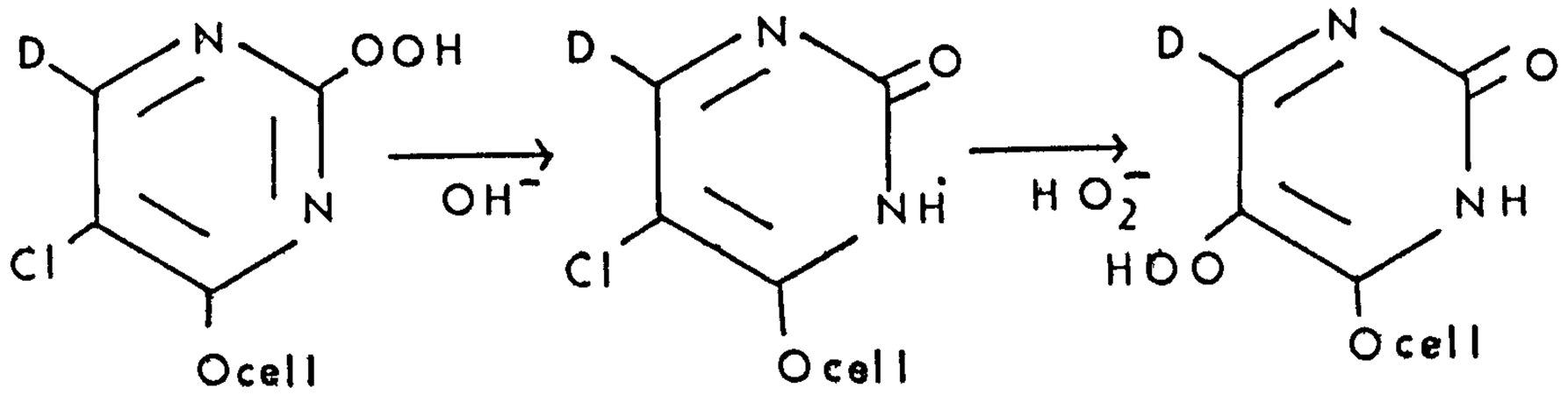
L I

D = chromophore

When the pH of the hydrogen peroxide solution is raised to pH = 12, the dyeing shows loss of dye caused by the breakdown of the dye-cellulose bond. It is unlikely that there is any Type I dyeing left at this pH value, since it should all have been converted to the hydroperoxide LI. However, hydroperoxide LI would not be expected to be more susceptible to attack at the 5 position of the ring than Type I dyeing, since the hydroperoxide group would be more electron donating than chlorine. Furthermore, evidence discussed in the previous section (4.2) suggests that Type IIIb dyeing of 2,4-fluoro-5-chloropyrimidinyl dye (identical to Type IIIb dyeing of 2,4,5-trichloropyrimidinyl dye) is attacked at the 5 position of the ring.

It is therefore possible that Type III dyeing is formed from hydroperoxide at pH 12, and that once it is formed it is attacked at the 5 position by a perhydroxyl anion as represented below:

(4.2)

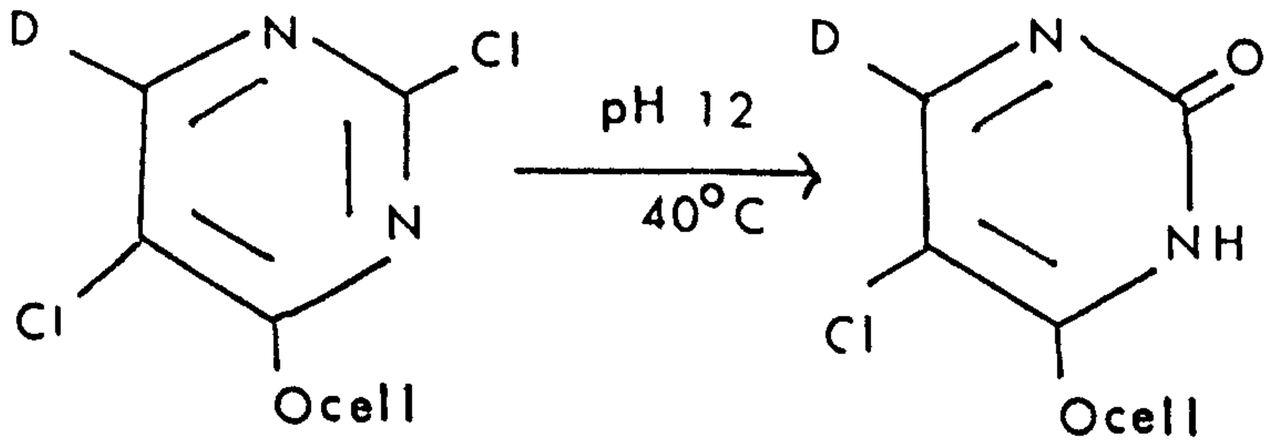


D = chromophore

As supporting evidence for this reaction there is the fact that a hydroperoxide group on a 2,4-fluoro-5-chloropyrimidinyl dyeing has been shown to be hydrolysed at pH 12 (Table 12). In this case the hydroperoxide group is in the 5 position of the pyrimidine ring since the breakdown decreases with hydrolysis.

Test No. 2 Just as with the 2,4-fluoro-5-chloropyrimidinyl dyeing there is a slight increase in breakdown after pretreatment with alkali. This could be explained by the formation of some Type III dyeing from Type I, as shown below:

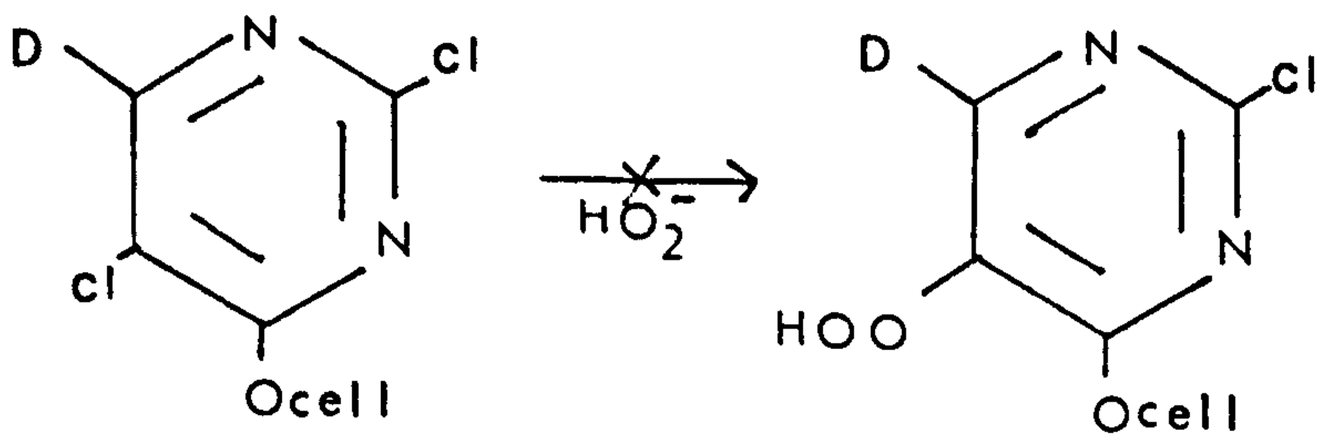
(4.3)

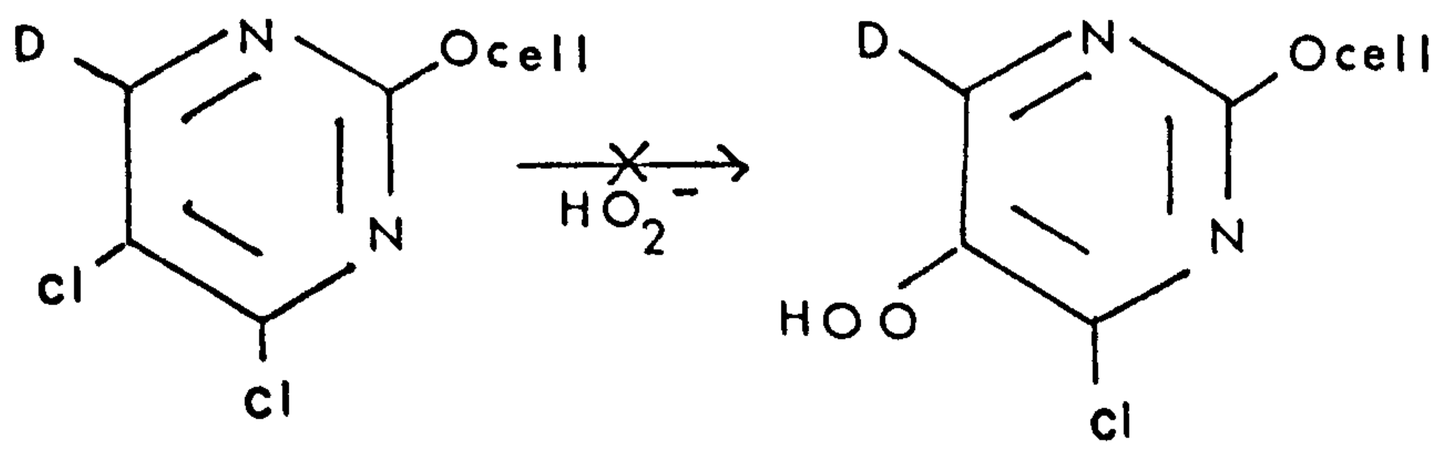


Type III dyeing would then be attacked by the perhydroxyl anion at the 5 position of the ring as shown above (equation 4.2).

Test No.3 The pretreatment in ammonia causes a decrease in breakdown, which is consistent with reactions 4.2 and 4.3 above. Thus ammonia replaces the chloro substituent at the 2 position, preventing the subsequent attack at the 2 position by the perhydroxyl or the hydroxyl ions.

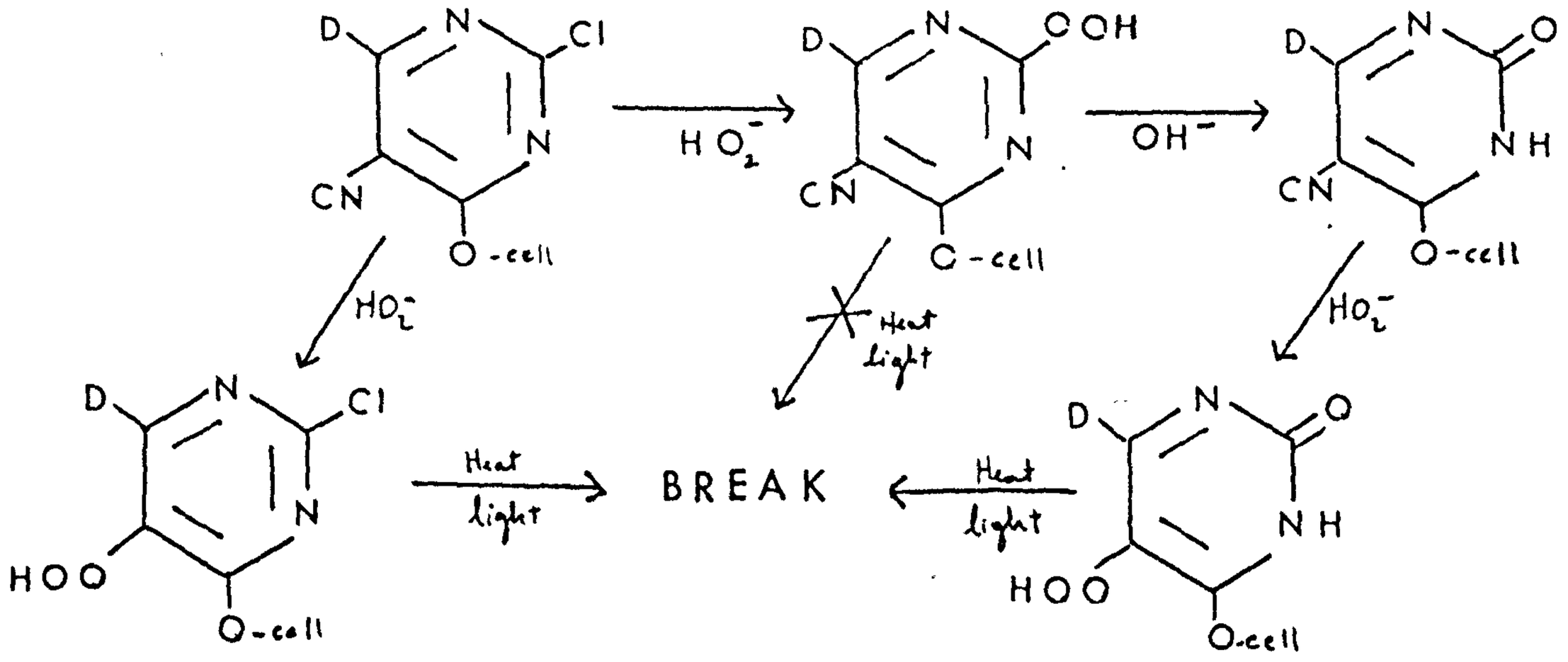
The other possibilities of a hydroperoxide formation on carbon 5 of the ring, are via an attack by the perhydroxyl ion at the 5 position of Type Ia or Ib. Since this position is much less activated than positions 2 or 4 respectively, this is unlikely to happen. This is illustrated below:





D = chromophore

The 2,4-chloro-5-cyanopyrimidinyl dyeing shows a breakdown with hydrogen peroxide to a degree similar to that of a 2,4-fluoro-5-chloro-pyrimidinyl dyeing. Since the cyano group is very electron withdrawing an attack on the 5 position of the ring might be possible both with Type IIIb and Type Ia. Both the pretreatment in ammonia and in alkali reduce the breakdown and this could mean an attack by both these bases on the 5 position either on Type IIIb or Type Ia, thereby reducing the breakdown. Therefore these tests do not in the case of this dye, determine which type of dyeing is responsible for the breakdown. However, in the graph of the hydroperoxide formed by 2,4-chloro-5-cyano and 2,4,5-trichloropyrimidine dyeings vs. breakdown, the points on the graph fall on a straight line (Tables 6 and 15, graph 3). This suggests that only Type III dyeing is attacked at the 5 position. This type of dyeing could have been formed during dyeing or during the treatment with hydrogen peroxide, as shown below (equation 4.4). With Type Ia dyeing, some attack at the 2 position by the perhydroxyl anion HO_2^- would be expected and this would give a higher value for hydroperoxide content than expected from the graph of hydro-peroxide content vs. breakdown, since a hydroperoxide group at the 2 position of the ring does not cause breakdown. The same can be argued for the 2,4,5-trichloropyrimidinyl dyeing. These reactions can be represented as follows:



4.4 The reaction of 2,4-fluoro-5-chloropyrimidinyl dyeings with hydrogen peroxide in an alkaline medium

It has already been suggested in previous work[2] that the reaction between hydrogen peroxide and a 2,4-fluoro-5-chloro pyrimidinyl dyeing is a nucleophilic reaction. This was supported on the evidence that breakdown increased with pH of the hydrogen peroxide solutions. In a nucleophilic reaction where the perhydroxyl anion is the nucleophile this would be expected (section 1.6, equation 1.13).

All dyes were tested at least at two different pH values in order to confirm the effect the pH had on the breakdown, and those dyes which showed significant breakdown were indeed found to show a higher breakdown with higher pH values of the hydrogen peroxide solution (Tables 4,5 and 6). The same dyes were tested for hydroperoxide formation at different pH values and it was found that thehydroperoxide content also increased with increasing pH of the test solution (Tables 14 and 15). The breakdown is proportional to the hydroperoxide content in the dyes that show the effect, as seen in a previous section (4.1) and therefore the increase in both the breakdown and the hydroperoxide content with increasing pH of the test solution, seems to confirm the attack on the dyeings by a perhydroxyl anion HO_2^-. As more evidence for a nucleophilic attack by a perhydroxyl anion on these dyes, there is the fact that the greater the electrophilicity of the ring, the higher the hydroperoxide content after the reaction with hydrogen peroxide. Thus, the formation of hydroperoxide in the dyeings follows the order of the dyes : dichlorotriazine$>$2,4-fluoro-5-chloropyrimidine$\simeq$ 2,4-chloro-5-cyanopyrimidine$>$dichloroquinoxaline$\simeq$2 methylsulphonyl-4-methyl-5-chloropyrimidine$>$ 2,4,5-trichloropyrimidine (Tables 14, 15).

This is also the general order of reactivity of these dyes with the cellulosate ion during the dyeing of the cellulose.

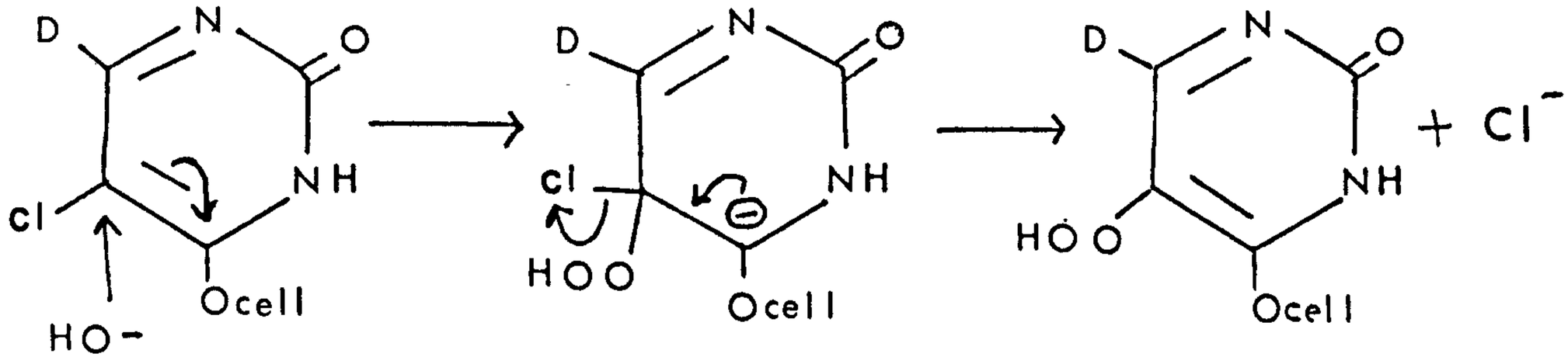
There can also be differences in the formation of hydroperoxide within the same dye class. Thus the results of Table 13 show that the red 2,4-fluoro-5-chloropyrimidinyl dyeing forms less hydroperoxide than the other colours. This result agrees with the lower breakdown of the red dye, compared with the other colours (Table 4). It is possible that the chromophore of the red dye influences the reactivity of the ring to a higher degree than the other chromophores, by being a stronger electron donating substituent on the ring, thereby making it less susceptible to nucleophilic attack. However, it is more likely that the lower breakdown is due to the influence the chromophore has on the surface potential of the fibre. Thus a higher number of negative charges or a higher acidity of the sulphonic acid groups in the chromophore, would lower the internal pH (see 1.4), with less formation of perhydroxyl ions, and/or would repulse the perhydroxyl anions. In either case, the hydroperoxide formation would be less.

It has been discussed how almost all nucleophilic substitution reations at an activated aromatic ring follow second order kinetics (see 1.1). So and Rattee[1] had found that the breakdown of the 2,4-fluoro-5-chloropyrimidinyl dyeing Levafix Orange E3GA by sodium perborate increased proportionally with the dye concentration. However sodium perborate was shown to form hydroperoxide through the formation of hydrogen peroxide (section 3.5 and Table 18) and it can therefore be inferred from So and Rattee's results that the formation of hydroperoxide is also proportional to the dye concentration.

On the other hand, as mentioned above, the hydroperoxide content of a 2,4-fluoro-5-chloropyrimidinyl dyeing is proportional to the concentration of perhydroxyl ions. Therefore, the reaction of formation of hydroperoxide must be an SN_2 type reaction.

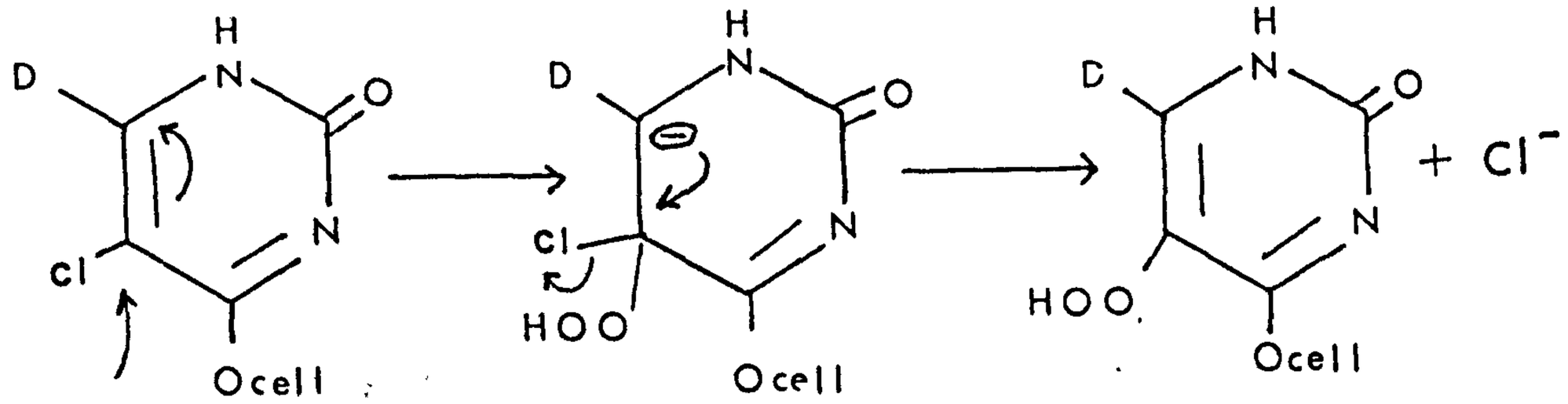
It has been shown in 4.1 that the hydroperoxide is formed at the 5 position of the ring, and in 4.2 that the dyeing attacked is the oxo form of Type IIIb dyeing.

The reason why the 5 position of the oxo form of Type IIIb dyeing is attacked by a nucleophile, whereas the other forms of dyeing are not, must be due to the 5 position being less aromatic than in the other forms of dyeing. The reaction can then proceed in a similar way to other SN_2 reactions typical of unsaturated compounds and can be represented as follows:



LII LIII

The intermediate complex LII will be stabilized by the electron withdrawing oxygen of the cellulose substituent (-I). The other resonance form of Type III, dyeing LIV, would form a carbanion on C_6 where the chromophore is located LV. This reaction can be represented as follows:

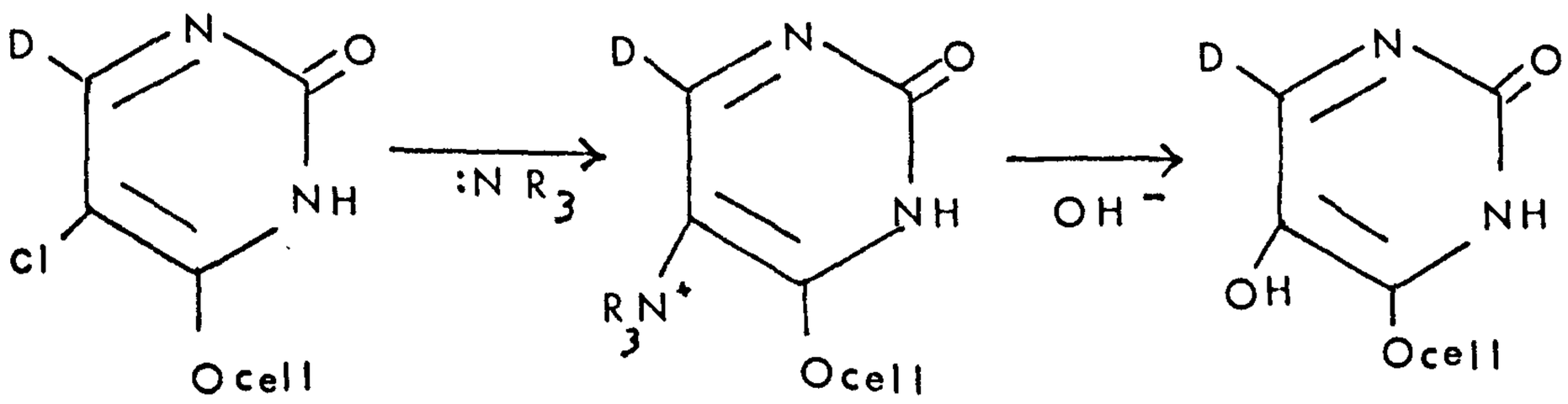


HO_2^-

LIV LV LVI

It has also been shown that position 5 of the ring is only attacked by strong nucleophiles or by using more vigorous conditions of reaction. Thus, besides the perhydroxyl anion HO_2^-, the tertiary amine 1,4 Diaza-2:2:2 bicyclooctane (DABCO) has also been shown to attack at the 5 position of the ring, reducing in this way the proportions of dyeing with a labile chlorine in the 5 position. The reaction would proceed in a similar way to reaction 1.11, as discussed in 1.4 and can be represented as shown below:

(4.5)



LVII

Compound LVII would not be attacked at the 5 position by a perhydroxyl anion and would not therefore show breakdown of the dye-cellulose bond. This is confirmed by the results in Table 11.

The possibility that the reaction of formation of the hydroperoxide is via photochemical nucleophilic substitution (see for example Refs.100 and 101) can be ruled out since this reaction was carried out with a similar dye, dichlorotriazinyl dye, in the dark and in the presence of light, and the amount of hydroperoxide formed in both cases was the same (Table 17).

4.5 Possible mechanism of the reaction of breakdown of the bond between the 2,4-fluoro-5-chloropyrimidinyl dye and the cellulose

It has already been discussed how hydrogen peroxide does not decompose into radicals unless under very specific conditions, such as a very high pH (>12) and the presence of certain metals (section 1.8). Table 19 confirms that it is not the decomposition of the hydrogen peroxide itself into radicals that causes the breakdown of the dye-fibre bond. On the other hand, Table 22 also shows that singlet oxygen, which could originate from the decomposition of hydrogen peroxide, is not responsible for the breakdown of the dye-fibre bond either, since a singlet oxygen quencher has no effect. However, when copper sulphate is present in the hydrogen peroxide solution, there is an increase in breakdown of the dye-celullose bond (Table 23). Since during the bleaching of cellulose copper has the same damaging effect on the cellulose as iron (section 1.6), it can be inferred that Cu^{+2} produces hydroxyl radicals from hydrogen peroxide in the same way as Fe^{+2} (equation 1.14), and that these radicals are the cause of the increase in the breakdown of the dye-cellulose bond of 2,4-fluoro-5-chloropyrimidinyl dyeings. This reaction would proceed as follows:

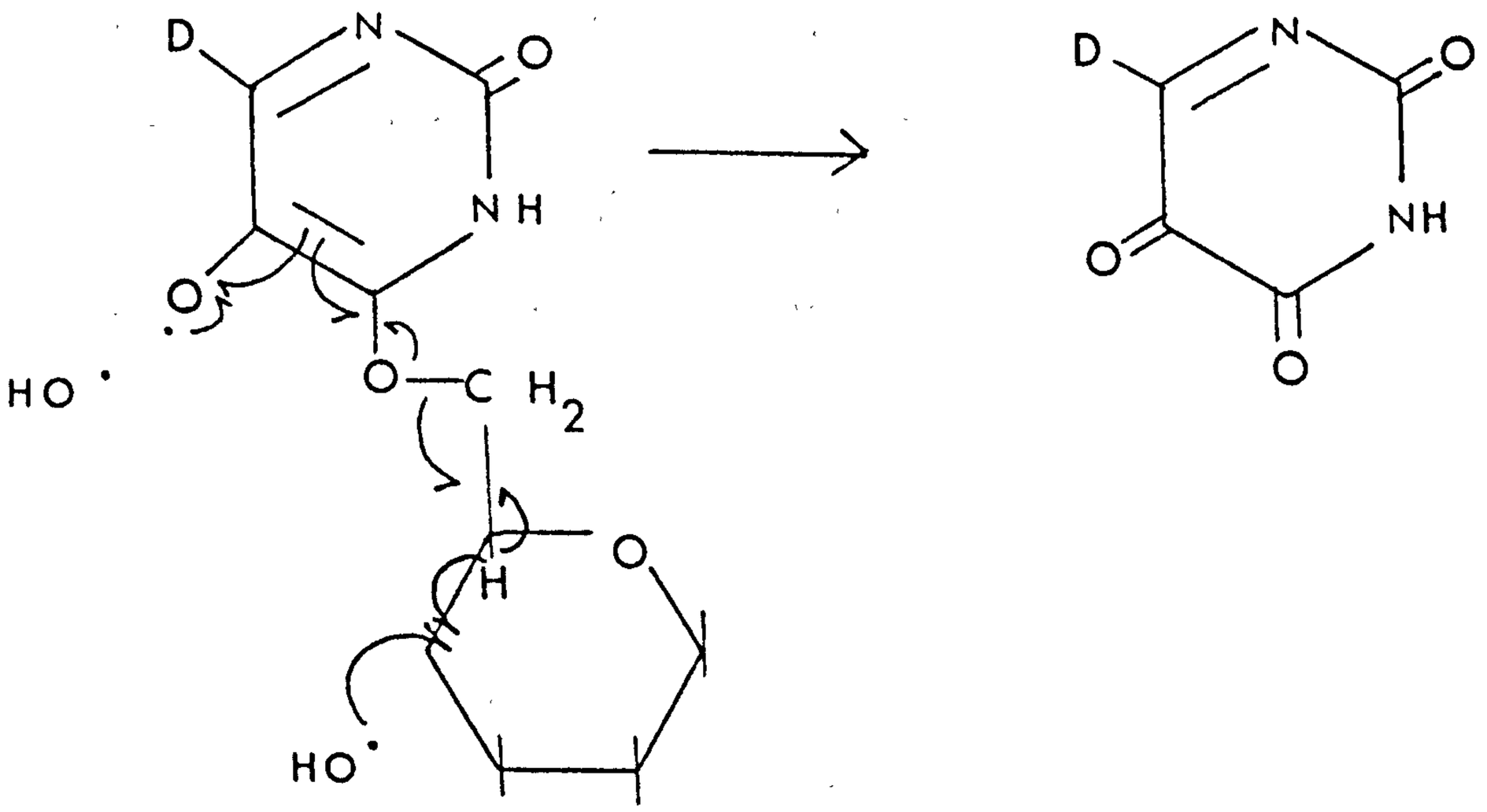
$$H_2O_2 + Cu^{II} \rightarrow HO^- + HO\cdot + Cu^{III}$$

Furthermore, antioxidants which are known to be radical scavengers, such as 2,6-di tertiary butyl phenol[104] and carbon tetrabromide reduce the breakdown of dye-fibre bond (Table 24). Another type of antioxidant which decreases the breakdown, Ni-Oxime (Table 24), has been reported to quench the triplet state of polymeric chromophores before they undergo reactions that result in polymer degradation.[105] Presumably in this case Ni-oxime quenches the triplet state of the cellulose-

peroxide product before it reacts, stopping in this way the breakdown of the dye-fibre bonds.

It has already been discussed how radicals can be formed on cellulose through the abstraction of a hydrogen by, for example, a hydroxyl radical (section 1.8). This radical is likely to be produced by the decomposition of the hydroperoxide formed in the dye during the treatment with hydrogen peroxide, since it has been shown (section 4.1) that % breakdown is directly proportional to the hydroperoxide content.

Therefore it is suggested that the reaction that causes the breakdown of the bond between 2,4-fluoro-5-chloropyrimidinyl dyes and the cellulose is as follows:

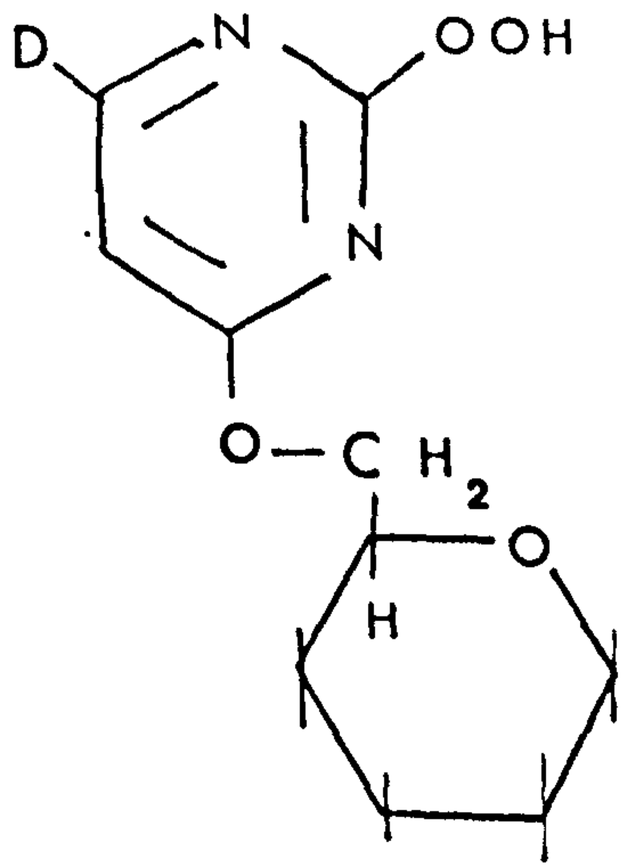


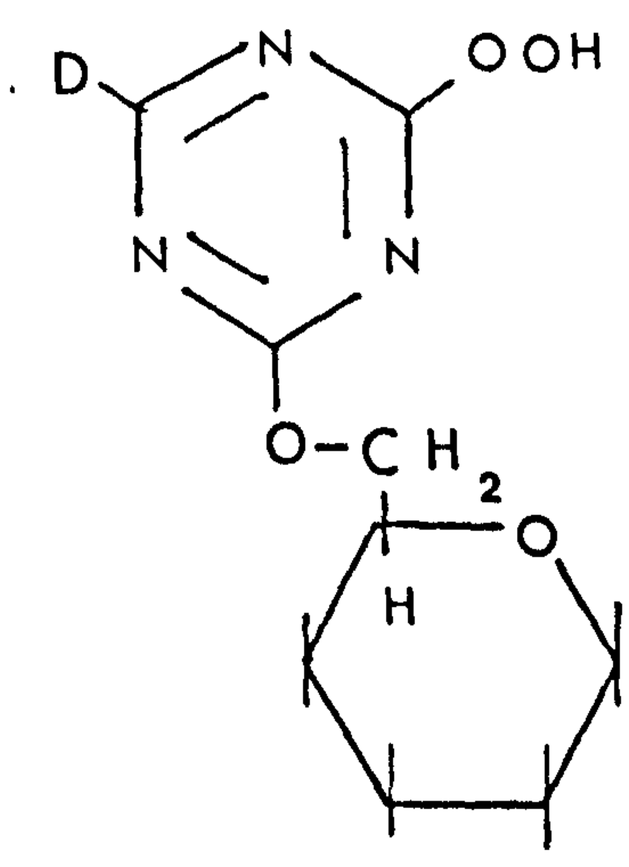
4.6 Breakdown of the hydroperoxide present in other dyes after the reaction with hydrogen peroxide and its effect on the breakdown of the dye-cellulose bond

The other dyeings were not tested as thoroughly as the 2,4-fluoro-5-chloropyrimidinyl dyeing and there is less evidence for a radical mechanism of dye-cellulose bond rupture in these cases.

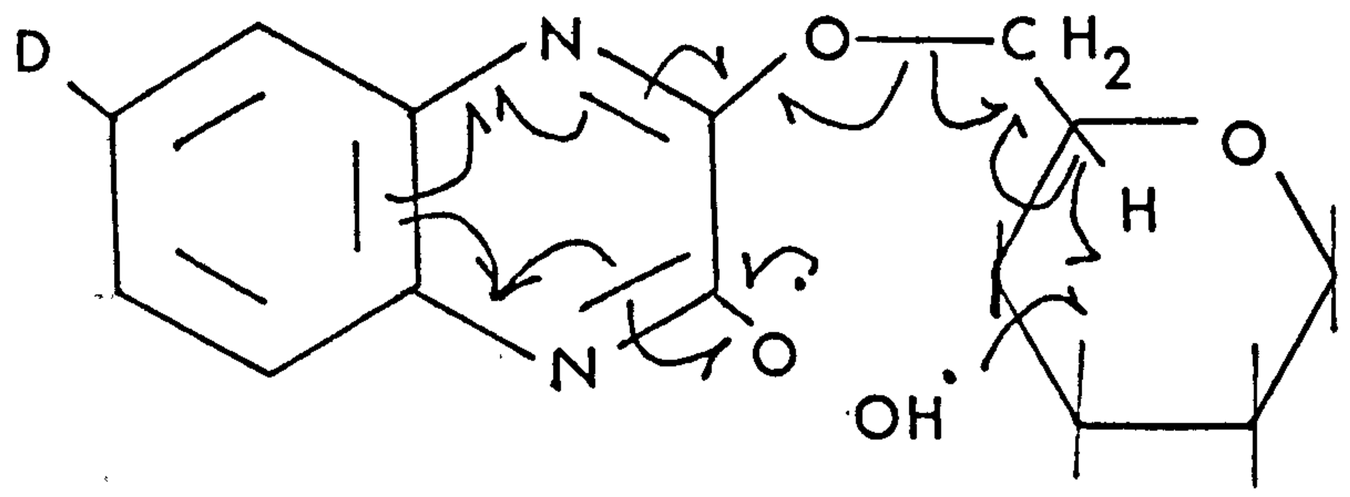
However, it is reasonable to assume that the 2,4,5-chloro and 2,4-chloro-5-cyanopyrimidinyl dyeings behave in the same way as the 2,4-fluoro-5-chloropyrimidinyl since the hydroperoxide which is exposed to heat and light has the same formula in all three cases (Resonance forms LIII and LVI in section 4.4).

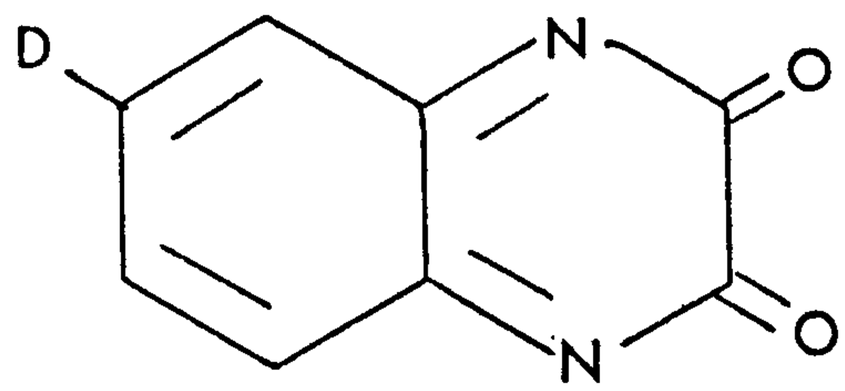
On the other hand, 2,4-chloropyrimidinyl and the dichloro-triazinyl dyeings do not show significant breakdown, and this must be due to the absence of conjugation between the hydroperoxide substituent and the cellulose substituent, i.e. once the radicals are formed they cannot combine in the same way as in the 2,4-fluoro-5-chloropyrimidinyl dyeing, to bring about the breakdown of the dye-cellulose bond. This is apparent from the formulae of their hydroperoxides below:





The fact that dichloroquinoxalinyl dyeings (dyeing V) break down at the dye-cellulose bond seems to confirm the importance of conjugation between the hydroperoxide and the cellulose substituents. The breakdown reaction of this dyeing would seem to be as follows:





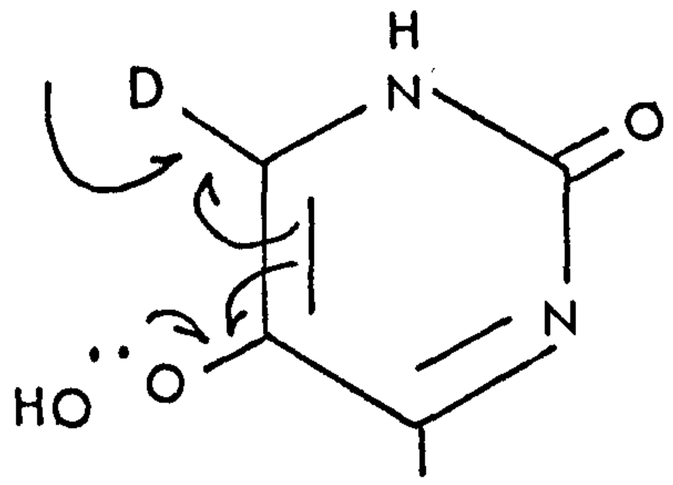
4.7 Radical attack on the chromophore of pyrimidinyl dyeings caused by the breakdown of the hydroperoxide

The samples in section 3.7 show how in some dyes the loss of brightness of the dyeing after the reaction with sodium perborate present in commercial detergent is very marked. (Sodium perborate is a source of hydrogen peroxide - see section 1.5). The orange and the yellow colours of the Levafix EA range of dyes (2,4-fluoro-5-chloro-pyrimidinyl) are the ones that show the highest deterioration in brightness.

The value of the breakdown of the Levafix Orange E3GA dyeing when it is rinsed after the reaction with hydrogen peroxide and exposed to heat and light is 2% (Table 19). However, the value of the concentration of moles of hydroperoxide in 1mg of dye is 0.821×10^{-7} (Table 13) which corresponds to approximately 5% of dye with a hydroproxide group (assuming mw. of dye 600). Thus not all of the hydroperoxide is accounted for in the breakdown of the dye-cellulose bond.

It has been discussed how all this hydroperoxide is expected to be at the 5 position and therefore cause damage to the dyeing (section 4.1).

It is reasonable to assume that some of the hydroperoxide decomposition can cause breakdown of the chromophore. Thus in the hydroperoxide formed from the other resonance form of the Type III dyeing (LVI), there would be conjugation through the ring, between the hydroperoxide and the chromophore substituents, as illustrated below:

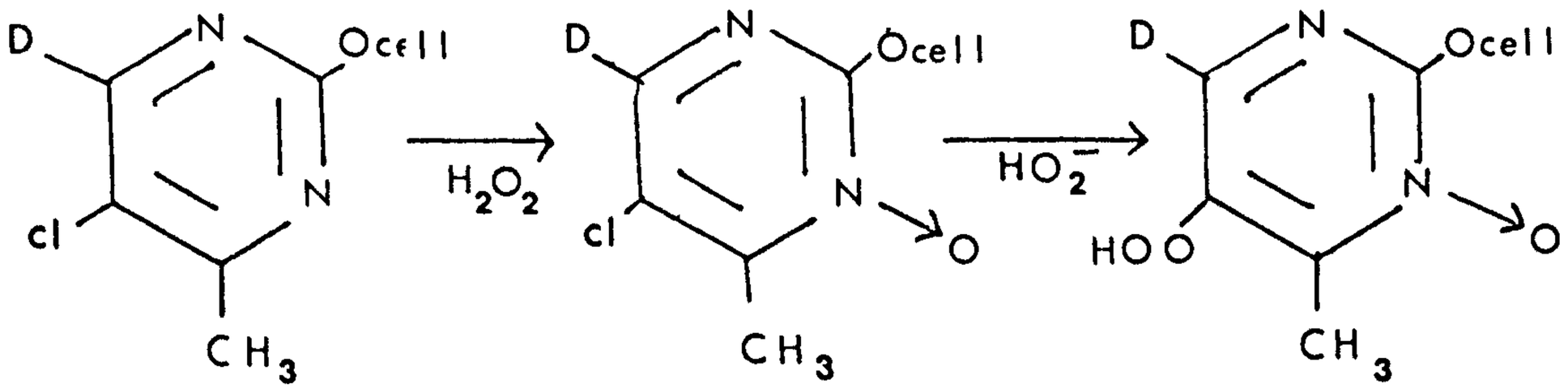


In graph 2 it can be seen how the breakdown of the dye-cellulose bond of other pyrimidinyl dyeings is proportional to the hydroperoxide content, and how all the points corresponding to dyeings of different pyrimidinyl dyes follow (approximately) a straight line. This suggests that the hydroperoxide in the other pyrimidinyl dyeings can also cause breakdown of the chromophore. Unfortunately the loss of brightness is not clearly visible from the samples, because only red colours were available for these dyes and the deterioration in the brightness in the red colour is not as noticable as in the yellow or orange, as seen with the 2,4-fluoro-5-chloropyrimidinyl dyeings.

A pretreatment of a 2,4-fluoro-5-chloropyrimidinyl dyeing with the tertiary amine 1,4 diaza 2:2:2 bicyclooctane (DABCO) prevented, almost completely, the loss in brightness caused by the sodium perborate, as can be seen when comparing samples I and II. This suggests that the chlorine at the 5 position is replaced by DABCO as shown in equation 4.5 (in section 4.4) leaving that position inert to subsequent nucleophilic attack. Thus, a hydroperoxide is not formed and consequently the radicals which cause the breakdown of the chromophore are not formed either.

4.8 Possible explanation as to why 2-methylsulphonyl-4-methyl-5-chloropyrimidinyl dyeings breakdown when treated in an alkaline solution of hydrogen peroxide

The fact that 2-methylsulphonyl-4-methyl-5-chloropyrimidinyl dyeing has the cellulose substituent at the 2 position seems to contradict the conclusion arrived at in this work that pyrimidinyl dyeings must have a keto group in the 2 position of the ring in order to be susceptible to attack at the 5 position of the ring. In section 1.7 the possibility of pyrimidines with electron donating substituents undergoing N-oxidation was discussed. This dyeing has a methyl group which is electron donating at its 4 position so it is conceivable that it might undergo N-oxidation. However, N-oxidation is favoured by acid conditions and the reaction with hydrogen peroxide is in an alkaline medium. Even so, it is possible that N-oxidation is the cause of breakdown since the breakdown noticed in this dye is very small (0.5 - 1.5%) and it would only take a very small amount of N-oxidation for it to cause the rupture of the dye-cellulose bond. N-oxidation, as already discussed, increases the reactivity of the pyrimidine ring towards nucleophilic attack. The formation of the hydroperoxide would be as follows:



APPENDIX I

(Laundering tests)

	I - Before test	II After test with PERSIL AUTOMATIC	III After test C_2 ISO C06
Dye I			
Dye II			
Dye III			
Dye IV			

APPENDIX (cont.)

	I - Before test	II After test with PERSIL AUTOMATIC (pH 10.5)
Dye V		
Dye VII		
		(pH 12)
Dye VIII		 
		(pH 12)
Dye IX		 
Dye X		

APPENDIX II

(Laundering tests on Dye I)

I - Untreated dyeing

Before test

After 1 wash

After 2 washes

II - Pretreated dyeing

Before test

After 1 wash

After 2 washes

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