

Photo-stability of Acid Dyes, Derivatives of 1-phenyl-3-methylpyrazol-5-one in Polyamide Fibers

Abstract

We have examined the photo-stability of acid dyes, derivatives of 1-phenyl-3-methylpyrazol-5-one, in polyamide fibres, including the relationship between the dye's structure and photo-stability. The part played by the substituents in diazo components was assessed, especially those in ortho positions to azo bonds. It has been found that the photo-destruction of dyes in polyamide fibres proceeds according to the mechanism of photo-oxidation. The light fastness of dyeings depends on the electron density of the azo bond (reaction centre). Some substituents in ortho positions to the azo bond increase the dye's photo-stability.

Key words: acid azo dyes, photo-degradation, light fastness, photo-oxidation, photofading.

induced molecules are characterised by different properties than those in the fundamental state due to higher energy (80 to 400 kJ/mole). Electron-induced molecules should be treated as different chemical units with different bond lengths and angles between them, as well as having different distributions of electron density.

The induction of the dye molecule is unstable, and the molecule can restore its stability in several ways:

- transferring the whole or part of its energy onto other molecules,
- emitting energy by fluorescence or phosphorescence,
- reacting with other molecules,
- splitting into two fragments or radicals,
- becoming ions by electron transmission.

As a result of light absorption, several chemical reactions take place in dyed fibres. The degradation of dyes under the influence of light has been the subject of many studies [2-14]. The photochemical stability of dyeings (dye fastness to light) depends on several factors, such as:

- the physical and chemical fibre structure,
- the physical and chemical structure of the dye and its concentration in the fibre,
- the environment in which the dyed polymer exists (humidity, temperature, pollutions, the auxiliary agents used in dyeing, etc),
- the spectral characteristics of radiation.

The tests of dye fastness to light include a change in colour of the dye-fibre system under specified conditions. Currently, acid dyes are the predominant

group of dyes used for dyeing polyamide fibres. Among acid dyes, only a few chromophore systems are characterised by high fastness to light. Light-fast dyes include azo derivatives of 1-phenyl-3-methylpyrazole-5-one, 7-amino-1-hydroxynaphthalene-3-sulphonic acid and 1,4-diaminoanthraquinone. High fastness to light is also shown by disazo acid dyes [15]. The photo-degradation of azo dyes mainly involves the azo bonds. Some significant effect on the photo-degradation is exerted by the substituents in the diazo and coupling components of azo dyes. This concerns both the character and site of the substituent in relation to the azo bond.

The aim of the present study was to assess the photo-stability of azo dyes, derivatives of 1-phenyl-3-methylpyrazole-5-one, in polyamide fibres, including the examination of the relationship between the dye structure and photo-stability, taking into special consideration the role of substituents in diazo components in ortho positions to the azo bond.

Experimental

The group of acid azo dyes, derivatives of 1-phenyl-3-methylpyrazol-5-one presented in Table 1, was selected and synthesised for the investigation; the dyes are represented by general formulae 1-3.

The purity of the synthesised dyes was determined by the HPLC method using a Water 996 photodiode array detector and a Purospher^R RP-18e column (5 μ m), 125-3 nm. The samples were dissolved in water (HPLC). The NaCl content was determined by the potentiometric method. The results are listed in Table 2.

The dyes analysed consisted of organic substances which purity was determined

Introduction

The electronic induction of a molecule takes place by radiation absorption that causes the electron's transition from an occupied orbital to a higher unoccupied orbital. Transitions such as $\pi \rightarrow \pi^*$ and $n \rightarrow \pi^*$ within the visible range are necessary for a colour to occur. The transition of an electron to a higher orbital leads to a configuration that may be characterised by two states: the singlet state (anti-parallel electron spins) and the triplet state (parallel electron spins) [1]. Electron-

Table 1. Acid azo dyes, derivatives of 1-phenyl-3-methylpyrazol-5-one; the tree general formulae, the substitute groups and substituents.

| Basic formula 1 | | | |
|-----------------|---|---|--|
| | | | |
| dye designation | substituent groups | | substituents |
| D - 1 | | X = SO ₃ Na | B, C, D, Y, Z = H |
| D - 2 | | Z = SO ₃ Na | B, C, D, X, Y = H |
| D - 3 | | Y = SO ₃ Na | B, C, D, X, Z = H |
| D - 4 | | X = OCH ₃ , Z = SO ₃ Na | B, C, D, Y = H |
| D - 5 | | X = CO ₂ Na | B, C, D, Y, Z = H |
| D - 6 | | Y = CO ₂ Na | B, C, D, X, Z = H |
| D - 7 | X = CH ₃ | | A, B, C, D, Y = H |
| D - 8 | | | A, B, C, D, Y = H |
| D - 9 | Y = CH ₃ | | A, B, C, D, X = H |
| D - 10 | B = Cl, X = CH ₃ | | A, C, D, X, Y = H |
| D - 11 | C = SO ₃ Na | | A, B, D, Y, Z = H |
| D - 12 | B, D = Cl, C = SO ₃ Na | | A, Y, Z = H |
| D - 13 | | | A, B, C, D, Y, Z = H |
| D - 14 | A = NO ₂ , X = CH ₃ | | B, D, Y = H |
| Basic formula 2 | | | |
| | | | |
| dye designation | substituent groups | dye designation | substituent groups |
| D - 15 | X = SO ₃ Na, Y = H | D - 16 | Y = SO ₃ Na, X = H |
| Basic formula 3 | | | |
| | | | |
| dye designation | substituent groups | | substituents |
| D - 17 | X = SO ₃ Na | | M = NHCH ₂ CH ₂ OH |
| D - 18 | Z = SO ₃ Na | | |
| D - 19 | Y = SO ₃ Na | | |
| D - 20 | Z = SO ₃ Na | | |
| D - 21 | Y = OCH ₃ | Z = SO ₃ Na | X = H |
| D - 22 | X = CH ₃ | | Y = H |
| D - 23 | Y = CH ₃ | | X = H |
| D - 24 | X = Cl | | Y = H |
| D - 25 | X = CF ₃ | | Y = H |

by HPLC, sodium chloride, and a small amount of water ranging from 3 to 4%.

The dyes obtained were analysed by spectrophotometry to measure λ_{\max} in water and 50% ethanol. The results obtained are given in Table 2.

Application of dyes

Polyamide knitted fabric was dyed with acid dyes in a dyeing machine from Roaches Engineering Ltd. with strengths of 1/3, 1/1 and 2/1 of auxiliary standard. The dyeing conditions were as follows: liquor ratio 1:20, pH 5.0 (acetate buffer), temperature 98 °C. The dyed fibre was polyamide 6, with a thickness of 67 dtex and a crystallinity degree of 0.49.

Light fastness

Light fastness was measured according to standard ISO-105 B02, using a Xenotest 150S apparatus from Heraeus Hanau under standard conditions: RH 60%, black thermometer temperature 45 °C; the intensity of radiation on the sample surface within the range from 300 to 800nm was 1154 W/m². The light fastness values are listed in Table 2.

Kinetics of dye decomposition

The decomposition of selected dyes on fibres was examined depending on the irradiation time (the amount of energy absorbed). The examinations were carried out for specified quantities of dye in fibre amounting to 3.7, 11 and 22 milliequivalents of dye per 1 kg of polyamide fibre respectively, which corresponds approximately to strengths of 1/3, 1/1 and 2/1 of auxiliary standard. The relative concentration of dye in fibre (A), was determined by measuring the relative dyeing strength, $(K/S)_t / (K/S)_0$, according to Kubelka-Munk's equation (1), and taking into consideration the determined standard curves $K/S = f(c_f)$.

$$A = C_{f_t} / C_{f_0} \cong (K/S)_t / (K/S)_0 \quad (1)$$

The kinetics of dyes D-1 and D-2 are shown in Figures 1 and 2. The decomposition of acid dyes in polyamide fibres can be described by the general equation (2).

$$\ln[A] = -at \quad (2)$$

where:

a – photo-destruction constant,

t – time, s.

Table 2. Molecular weights, purity, spectrophotometric properties and lightfastness.

| Dye | Molecular weight, g/mol | NaCl content, % | Purity HPLC, % | Spectrophotometric properties | | | | Lightfastness | | |
|------|-------------------------|-----------------|----------------|-------------------------------|--|----------------------|--|---------------|-----|-----|
| | | | | water | | 50% ethanol | | 2/1 | 1/1 | 1/3 |
| | | | | λ_{max} , nm | ϵ_{max} , dm ³ /mol cm | λ_{max} , nm | ϵ_{max} , dm ³ /mol cm | | | |
| D-1 | 535 | 10,7 | 96,2 | 391,8 | 17800 | 393,7 | 19000 | 6-7 | 6 | 5-6 |
| D-2 | 535 | 6,9 | 94,4 | 391,8 | 18200 | 394,3 | 19600 | 6 | 5-6 | 4-5 |
| D-3 | 535 | 17,5 | 93,3 | 394,9 | 16000 | 398,1 | 19800 | 6 | 5-6 | 5 |
| D-4 | 565 | 19,7 | 93,0 | 418,6 | 14000 | 419,5 | 16000 | 5 | 4-5 | 4 |
| D-5 | 499 | 3,6 | 94,7 | 401,3 | 16200 | 403,7 | 18000 | 3-4 | 3-4 | 3 |
| D-6 | 499 | 3,9 | 95,3 | 401,9 | 15600 | 408,5 | 19200 | 6 | 5-6 | 5 |
| D-7 | 549 | 11,0 | 92,6 | 396,8 | 17600 | 399,4 | 18500 | 7 | 7 | 6 |
| D-8 | 579 | 13,1 | 93,2 | 396,8 | 17200 | 399,4 | 18000 | 7 | 7 | 6 |
| D-9 | 549 | 26,9 | 93,2 | 394,9 | 17600 | 398,2 | 18100 | 6-7 | 6-7 | 5-6 |
| D-10 | 584 | 10,3 | 94,2 | 403,9 | 17000 | 403,2 | 17400 | 6 | 6 | 4-5 |
| D-11 | 563 | 2,5 | 96,1 | 386,2 | 15000 | 390,5 | 17700 | 7 | 6-7 | 5-6 |
| D-12 | 632 | 3,9 | 95,8 | 388,4 | 15100 | 392,9 | 16700 | 6-7 | 6 | 5 |
| D-13 | 535 | 12,3 | 94,2 | 388,2 | 17400 | 388,2 | 18300 | 6 | 6 | 5 |
| D-14 | 580 | 10,3 | 92,1 | 402,3 | 19000 | 406,2 | 19000 | 5-6 | 5 | 4-5 |
| D-15 | 585 | 3,6 | 94,4 | 427,1 | 12000 | 433,0 | 16400 | 4 | 3-4 | 3 |
| D-16 | 585 | 5,3 | 94,1 | 436,9 | 12000 | 437,8 | 18000 | 3-4 | 3 | 2-3 |
| D-17 | 926 | 26,1 | 80,3 | 395,9 | 32600 | 388,2 | 40900 | 6-7 | 6 | 5-6 |
| D-18 | 926 | 30,2 | 82,2 | 384,9 | 38400 | 389,8 | 46600 | 6 | 5-6 | 5 |
| D-19 | 926 | 28,6 | 79,9 | 395,5 | 37700 | 396,7 | 48000 | 6-7 | 5-6 | 5 |
| D-20 | 970 | 31,2 | 75,8 | 386,9 | 39400 | 389,9 | 45400 | 6 | 5-6 | 4-5 |
| D-21 | 988 | 32,6 | 82,3 | 400,2 | 41000 | 401,5 | 43000 | 5-6 | 4-5 | 4 |
| D-22 | 954 | 29,2 | 79,3 | 391,2 | 34800 | 396,8 | 44900 | 6 | 5-6 | 5 |
| D-23 | 954 | 27,1 | 81,2 | 397,2 | 22600 | 396,2 | 40100 | 6 | 5 | 4-5 |
| D-24 | 995 | 24,3 | 83,2 | 387,4 | 33800 | 390,8 | 41000 | 6-7 | 5-6 | 5 |
| D-25 | 1062 | 24,2 | 84,1 | 383,0 | 24700 | 387,8 | 46700 | 7 | 6-7 | 5-6 |

Results and discussion

Tests of light fastness were carried out with a group of acid monoazo dyes, derivatives of 1-phenyl-3-nethylpyrazol-5-one containing a sulphonamide group in a molecule. Another group includes disazo compounds doubled by means of 2,4,6-trichloro-1,3,5-triazine. Dyes of this type contain several by-products formed during their synthesis. Such impurities do not disqualify these compounds as useful dyes. Both groups of dyes are used for dyeing polyamide fibres.

The tests we performed of the photo-destruction of acid dyes in polyamide fibres show different light fastness values depending on the dye chemical structure and concentration in fibre. A considerable influence on light fastness is exerted by the diazo component. The dyes derived from amino-naphthalene-sulphonic acids are characterised by low light fastness, and the effect of the sulphonic group position on the photo-stability of dyeings is clearly visible (D-15 3-4; D-16 3). In addition, the substituents in the aniline ring of diazo component considerably affect

light fastness. Electro-donor substituents placed in para- and meta-positions in relation to the azo bond decrease the light fastness, while electron-acceptor substituents increase this fastness.

Spectrophotometric measurements performed for dye solutions in water and in 50% ethanol show one absorption band within the range of 390-440 nm. This band can be ascribed to the azo-hydrazone structure of dye stabilised by the intermolecular hydrogen bond [16, 17].

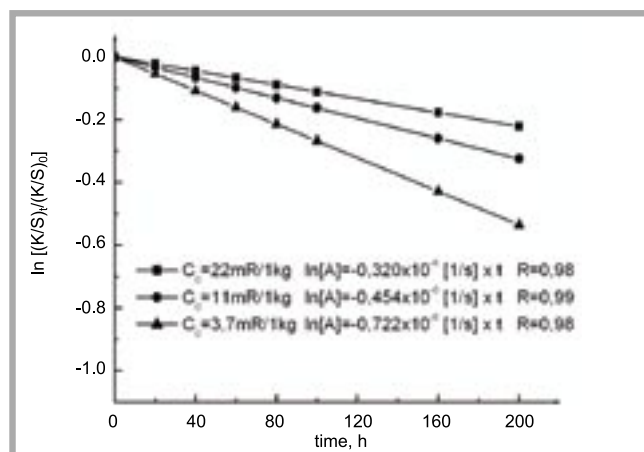


Figure 1. Decomposition kinetics of dye D-1.

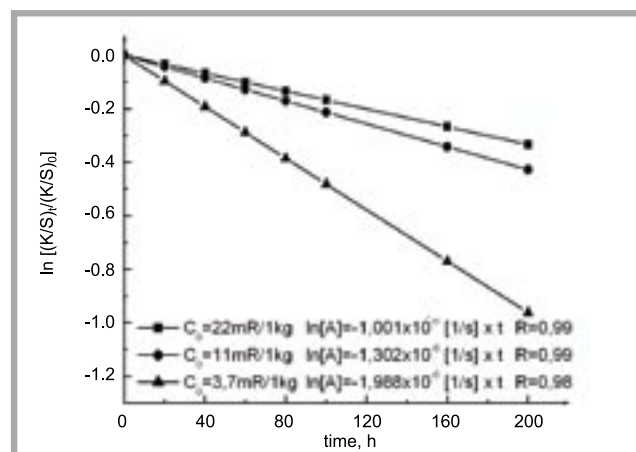


Figure 2. Decomposition kinetics of dye D-2.

This arrangement is very stable. Within the pH range from 2 to 10, absorption curves in 50% acetone do not undergo any change. Moreover, the structure of the dyed polyamide fibre decides the azo-hydrazone structure of the dye as well as its aggregation in fibre. In the group of dyes under investigation, a relationship between the effect of substituents δ_0 [19] and the energy of absorbed photons (equation 3) and photo-destruction constants is observed.

$$E = h c / \lambda N_A \quad (3)$$

where:

h – Planck's constant 6.625×10^{-34} , Js
 c – velocity of light 2.998×10^{17} , nm/s
 λ – wavelength, nm
 N_A – Avogadro number, 1/mole.

The energy of 1 mole of absorbed photons was calculated for λ_{\max} in 50% ethanol. The photo-destruction coefficients (a) were determined for concentrations 1.85 mR/1 kg of fibre. The results obtained are listed in Table 3 and shown in Figure 4.

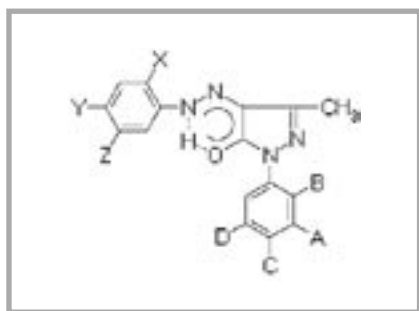


Figure 3. Dye arrangement of the azo-hydrazone structure stabilised by the intermolecular hydrogen bond.

A straight slope such as that seen in Figure 4 indicates that the photo-degradation of the dyes examined has proceeded according to the mechanism of photo-oxidation. This fact is confirmed by the absence of amines in the products of photo-degradation.

The process of photo-degradation is a first-order reaction (e.g. 1 and 2). The decrement of dye concentration is a function of the irradiation time (high correlation coefficients). On the other hand, the light fastness increases with the increase in dye concentration in fibre, which is connected with a possible dye aggregation. In aggregates, the dissipation of absorbed energy is easier, and consequently the photo-degradation process is slower. The type of dye aggregates formed in the

Table 3. Relationship between the electronic effect of substituents (δ), energy of absorbed photons (E) and constants of dye decomposition rate (a).

| No. of dye | Substituent Y | δ_0 | λ_{\max} , nm | E, kJ/mol | $a \cdot 10^6$, 1/s |
|------------|------------------|------------|-----------------------|-----------|----------------------|
| D – 18 | H | 0 | 389,8 | 306,97 | 1,00 |
| D – 23 | CH ₃ | -0,17 | 396,2 | 301,91 | 1,30 |
| D – 21 | OCH ₃ | -0,27 | 401,5 | 297,92 | 1,99 |

fibre depends on the chemical structure of both the dye and the fibre. Within the examined group, all the dyes increase their resistance to photo-degradation with their concentration in fibre.

A significant influence on the photo-stability of the dyeings is exerted by the substituents placed in the diazo component in the ortho position to the azo bond. Groups such as sulphonic, sulphonamide, trifluoromethyl and methyl in ortho positions increase the light fastness in relation to the corresponding para-isomers. Steric and polar effects appear between substituents and the azo-hydrazone structure of dye. The polar effects result in the intermolecular dissipation of absorbed energy over the more developed system, and consequently the light fastness of dyeings is increased. The interaction between substituents in ortho positions and the azo-hydrazone structure of dye is confirmed by the broadening and simultaneous lowering of the absorption band, and by the higher pH at which the azo-hydrazone system is ionised. In the case of dye D-2, the ionisation in 50% ethanol takes place at a pH over 10, while that of dye D-1 at a pH over 11 [18].

The substituents placed in ortho positions of the phenyl ring of pyrazolone decrease the light fastness. The derivatives of 1-(2'-chlorophenyl)- or 1-(2',5'-dichloro-4'-sulphophenyl)-3-methylpyrazol-5-one possess lower light fastness than those of the derivatives of 1-phenyl-3-

methylpyrazol-5-one. The light fastness values of D-10 are lower than those of D-8, and those of D-12 are lower than those of D-11. The decrease in light fastness is probably due to the torsional deflection of the phenol ring plane in relation to the pyrazole ring, which prevents the formation of aggregates in the chromophore system.

An accelerated decomposition of dye D-5 was observed, caused by the presence of the carboxyl group in the ortho position to the azo bond. Thus, the carboxyl group in the ortho position to the azo bond plays the role of a catalyst to photo-destruction.

In dye D-14, the change in colour under the influence of light (Xenotest) is connected, among other things, with the reduction of the nitro group in the phenol ring of pyrazole to an amine group. This fact was confirmed by HPLC analysis. The reduction of the nitro group proceeds more quickly than the destruction of the azo bond.

Conclusion

The photo-destruction of acid dyes, derivatives of 1-phenyl-3-methylpyrazol-5-one in polyamide fibres, takes place on their azo bonds according to the mechanism of photo-oxidation. The light fastness of the dyeings depends on the electron density in the centre of reaction. Electron-donor substituents increase the

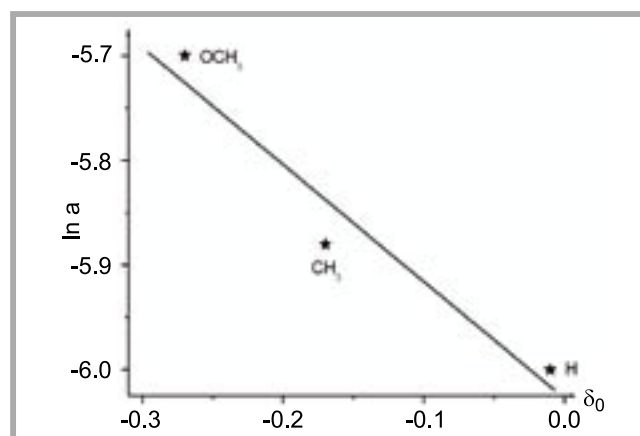


Figure 4. Relationship between the electronic effect of substituents (δ_0) and the constants of dye decomposition rate (a).

decomposition rate. In condensed systems, the photo-degradation proceeds more slowly. The light fastness increases with the increase in the dye concentration in fibre, due to the easier dissipation of the absorbed energy over the adjacent molecules (intermolecular dissipation). The dissipation of absorbed energy can take place inside the dye molecule with substituents in the ortho position. Some substituents in the ortho position increase the photo-stability of the dyeings. A significant part in the photo-degradation processes is also played by the structure of the fibre, by creating an appropriate dye-fibre system.



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