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Photodecomposition of substituted 4-diethylaminoazobenzenes under visible light irradiation in different solvents

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Abstract

The visible light-induced decomposition of two series of 4-diethylaminoazobenzenes has been studied in solvents of different polarity, in the presence and absence of O_2, in order to clarify the reaction mechanism. Two different paths have been recognised, whose importance depends on the nature of the solvent; both involve the formation of organic free radicals. Decomposition is much faster in acetone than in the other solvents. A strong inhibiting effect of molecular oxygen has been observed in all cases.

Keywords: Photodecomposition; 4-Diethylaminoazobenzene; Visible light

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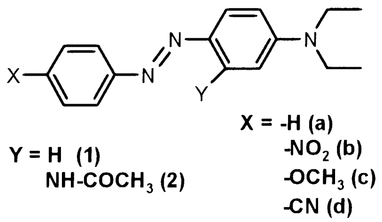
1. Introduction

Due to their outstanding stability, aromatic azo compounds represent one of the major classes of dyes employed in the textile industry mainly for synthetic fibres [1]. Donor–acceptor substituted azobenzenes recently also found application as non-linear optical chromophores and this attracted new interest on their photochemical behaviour [2].

When irradiated with visible or UV light, aromatic azo compounds exhibit both n → π* and π → π* electronic transitions. However, while the parent azobenzene cannot be used as a dye due to its low molar extinction coefficient, the introduction of an electron-releasing group, such as the diethylamino, in position 4 on one aromatic ring gives rise to a substantial hyperchromic effect. Therefore, 4-diethylaminoazobenzene and its substituted derivatives (**1a–d** and **2b–d**) are efficient, widely employed azo dyes. While the photostability of these type of molecules under UV irradiation [3] has been tested in several solvents, no study has ever been performed, to the best of our knowledge, on their stability to visible light.



After preliminary investigations on the photostability of some of these compounds either in solution, in the solid phase, or on dyed poly(ethyleneterephthalate) [4], we undertook a systematic analysis of the photochemical behaviour of compounds **1a–d** and **2b–d** under irradiation with visible light (wavelength range: 400–700 nm) in different solvents. The decomposition pathways of such dyes were investigated under conditions in which they proved to be unstable, with the main aim of providing a key to prediction of their photostability.

2. Experimental

2.1. Reagents

All the dyes used in this study, with the exception of **1d**, were obtained from ACNA and purified by flash column chromatography, with mixtures of hexane and ethyl

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acetate as the eluant, followed by crystallisation from absolute ethanol. **1d** was synthesised by diazotisation of *N*,*N*-diethylaniline with *p*-CN-benzene diazonium salt, following the literature procedure [5], and recrystallised from ethanol. Solvents and reagents were Merck analytical grade and were used as received.

2.2. Apparatus and methods

The solutions were irradiated through Pyrex glassware in a Rayonet RPR-100 reactor, equipped with eight F8T/D and eight F8T/CW 8 W lamps, all selectively emitting in the visible range (400–800 nm), and an internal merry-go-round apparatus for the homogeneous exposure of the samples to light. A Hewlett-Packard 8452A apparatus was employed for spectrophotometric measurements.

HPLC analyses were performed with an LC-42 Bruker HPLC chromatograph, equipped with a Chrompack Chromspher Si glass column (length 100 mm, internal diameter 3 mm), using a 5:1 hexane–ethyl acetate eluting mixture and a 1 ml min^{-1} flow rate.

GC analyses were performed with a Dani 6500 gas-chromatograph equipped with a Chrompack fused silica column and a flame ionisation detector, employing H_2 as carrier gas.

GC–MS analyses were performed with a Hewlett-Packard HP 6890 Series GC equipped with a HP-5 MS column (length 30 m, internal diameter 0.32 mm) and a HP 5973 mass selective detector.

^{1}H NMR analyses were performed with a Bruker 250 MHz spectrometer with TMS as internal standard.

*2.3. Preparation of the de-ethylated product **3** from **1a***

0.5 mmol of **1a** were dissolved in 20 ml of CH_3CN, 0.6 mmol of $K_2S_2O_8$ and 0.15 mmol of $AgNO_3$ dissolved in 20 ml of deionised water were then added. The mixture was heated under magnetic stirring for 6 h, then extracted with CH_2Cl_2; after evaporation of the solvent, GC analysis revealed a mixture of the starting dye and of the de-ethylated product, which was identified by MS and NMR analyses, after separation of the mixture by silica gel chromatography (eluting mixture hexane/acetate in the ratio 9:1). ^{1}H NMR δ (ppm): 1.2 (m, 3H, CH_3), 3.5 (m, 2H, CH_2), 6.7–7.9 (m, 9H, aromatic). MS, *m*/*z*: 224 $(M+1)^+$, 210 ($-CH_3$), 148, 120, 77.

*2.4. Identification of the decomposition products of **2c***

In cyclohexane, the decomposition of **2c** gave rise to product **7** only. ^{1}H NMR δ (ppm): 0.7–2.2 (m, 10H, cyclohexyl); 3.2 (s, 1H, NH); 2.8–3.3 (m, 1H, >C*H*NH); 3.5 (s, 3H, OCH_3); 6.7 (d, 4H, aromatics). MS, *m*/*z*: 205 (M^+), 162, 123. In *n*-hexane, **2c** decomposed giving two isomeric products of the same molar mass, but slightly different retention times. **8**—MS, *m*/*z*: 207 (M^+), 152. **9**—MS, *m*/*z*: 207 (M^+), 178, 164.

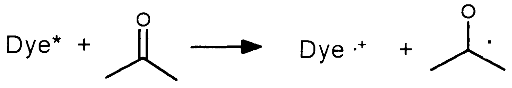
In methanol two products were detected. *p*-Methoxyaniline was identified by MS and comparison with an authentic sample. Product **10** was identified by MS analysis—*m*/*z*: 221 (M^+), 206, 188.

3. Results and discussion

Solutions of the investigated dyes were prepared in a range of solvents of different polarity, including hexane (non-polar), acetone (polar) and methanol (polar protic). Initial dye concentration (ca. 5×10^{-5} M) assured in all cases comparable initial values of maximum absorbance (around 0.7). Each solution was then irradiated with visible light either under atmospheric conditions, or after thorough freeze–pump–thaw degassing, to highlight any effect due to the presence of molecular oxygen. We tried to establish any existing relationship between the structure and polarity of the investigated 4-diethylaminoazobenzenes and the kinetics and mechanism of both decomposition and colour fading. All results discussed in the following refer to experiments carried out in different solvents after careful exclusion of oxygen. Indeed, colour fading in the presence of oxygen resulted either undetectable, or extremely slow (see below).

3.1. Acetone

In this solvent a radical mechanism is operating, originated by electron transfer (ET) from the excited state of the dye (Dye*) to an acetone molecule in its ground state [6]. This is the only mechanism through which the radical anion of acetone can be generated in this system, since visible light can only be absorbed by the dye (Table 1), and not by acetone. Besides, as the excited state of acetone is higher in energy than Dye*, energy transfer from Dye* to acetone is not viable. Therefore, in our opinion, Dye* evolves by transferring an electron to acetone, according to Eq. (1).

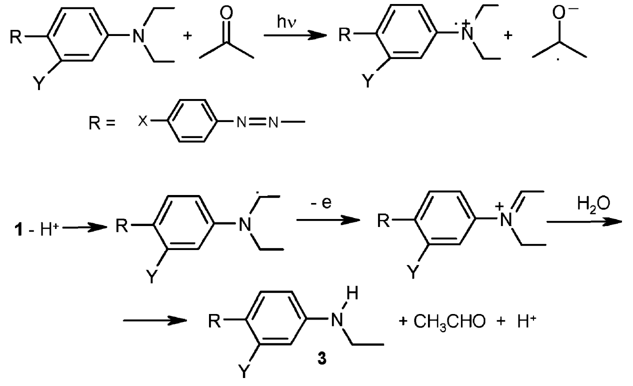


(1)

The rate of formation and the subsequent fate of the Dye$^{\bullet+}$ radical cation depend on its stability, which is influenced by the nature of X and Y substituents. Therefore, we performed

Table 1
Absorption properties of the investigated dyes in acetone

Dye	λ_{max} (nm)	ε_{max} (l mol^{-1} cm^{-1})
1a	419	32359
1b	490	37153
1c	412	33133
1d	459	40082
2b	513	51671
2c	459	36200
2d	490	45300

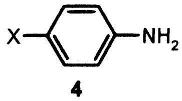


Scheme 1.

kinetic studies both on the rate of colour fading determined spectrophotometrically, and on the rate of appearance of the main fragments derived from dye decomposition, revealed by GC–MS spectrometry.

The first step of the process appears to be the de-ethylation of the *N*,*N*-diethylamino substituent, according to the formerly proposed [4,6,7] mechanism reported in Scheme 1. The formation of **3** from the parent 4-diethylaminoazobenzene is not directly responsible for colour fading, since this product is itself coloured, with just a slight displacement of the maximum absorbance wavelength (e.g., in the case of **1a**, the original dye shows an absorption peak at 419 nm, while its de-ethylated derivative exhibits an absorbance maximum at 409 nm).

The amount of the de-ethylated product **3** was measured for dyes **1a**–**c** after 30 min irradiation, starting from ca. 10^{-3} M dye concentration in order to obtain enough **3** for isolation, while stopping the process before complete fading. The amount of **3** found was higher for **1c** (21% of the starting amount of dye), lower for **1a** (6%) and lowest for **1b** (2%), which is consistent with the oxidation potential of the different substrates: the greater is the electron availability, the higher is the rate of formation of the $\text{Dye}^{\bullet+}$ radical cation. Product **3** was isolated in all cases and characterised by NMR, GC, GC–MS and by comparison with authentic samples prepared as described in Section 2.



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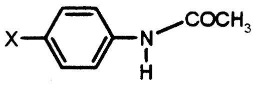

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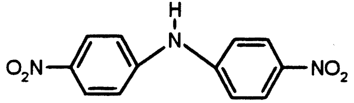

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When irradiation was further continued, the concentration of **3** decreased, new products of lower mass (**4**, **5** and in the case of **1b**, **6**) appeared and the colour faded. Different product distributions were obtained depending on the nature of the X and Y substituents. In acetone, no products deriving from the Ar–N(Et)$_2$ moiety were ever detected. In the case of **1a** the fragmentation products were not formed in sufficient amount to allow their isolation, so that the whole reaction mixture, without any separation of its components, was characterised through GC–MS analysis, and the spectral data compared with those of authentic samples.

Table 2
Residual absorbance expressed as A_t/A^0 ratios after 5 min irradiation in acetone[a]

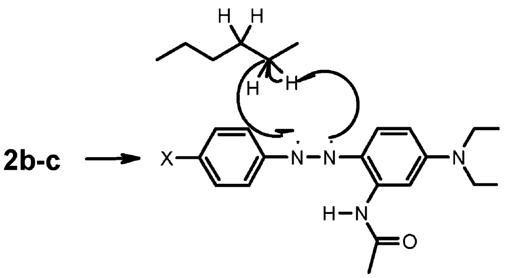
Dye	A^0	A_t	A_t/A^0
1a	1.872	0.414	0.22
1b	1.750	0.632	0.36
1c	1.823	1.077	0.59
1d	1.571	0.887	0.56
2b	1.980	0.985	0.43
2c	2.446	1.412	0.58

[a] Initial concentrations in the range 3×10^{-5} to 5×10^{-5} M.

While the rate of de-ethylation increases with increasing electron availability of the starting dye, hence depends on the ease of ET, the rate of fading seems to depend also on the radical stability. In this solvent the de-ethylated intermediate **3** may undergo a further ET step, giving rise to a second cation radical, whose fragmentation rate inversely depends on its stability, which is higher when X is an electron-donating group. According to the spectrophotometric monitoring of acetone solutions of dyes **1a**–**d**, the rate of colour disappearance followed the order: **1a** > **1b** > **1d** ≥ **1c**. In series **2** the trend is the same, with **2b** > **2c** (Table 2).

Another decomposition route can be envisaged, similar to that observed in the other solvents (as described below), which may act in parallel to ET. This is started by the breaking of the π bond in the azo group, occurring as first step in the *trans*–*cis* photoisomerisation process, which notoriously represents the main energy dissipation pathway for azobenzenes under visible light irradiation [7]. The perpendicular excited state Dye* may abstract hydrogen from the solvent (see below), or if this is impossible due to the polarity of the solvent, as in the case of acetone, it could react with the radical anion of acetone in a redox process, yielding acetone and the hydrazo derivative [8]. This latter then evolves by fragmentation of the labile N–N single bond, which may again result in the formation of **4** and **5**. The two routes to decomposition may be operating simultaneously in acetone.

Product **5** probably arises from the attack onto the nitrogen atom closer to the X-substituted ring, either of acetaldehyde, produced during de-ethylation (Scheme 1), or more likely on account of its great excess, of acetone itself. The attack of the positively charged carbonyl carbon would be actually favoured by the presence of the electron-donating methoxy substituent, but would also be possible in the absence of any substituent, even if to a lower extent. On the other hand, the strongly electron-attracting nitro substituent would prevent this attack; actually, in this case a different product (**6**) was observed for series **1**. As for the mechanism of formation of **6**, several hypotheses could be put forward, including the attack of the carbonyl group onto the azo nitrogen closer to



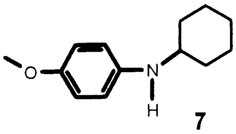
Scheme 2.

the more electron-rich ring, with the subsequent cleavage of the azo bond. The arising fragment could then attack the nitro-substituted aromatic ring of another dye molecule, expelling a diazo compound.

3.2. Hydrocarbons

ET does not take place in non-polar solvents, such as cyclohexane or *n*-hexane. In this case Dye* evolves, as mentioned above, through hydrogen abstraction from the solvent, coupling of the dye and the solvent radicals (Scheme 2) and cleavage of the N–N bond. This process is favoured by polar effects, since nitrogen-centred radicals are electrophilic.

Such route, leading to colour fading, was confirmed by the isolation of some products (**7**–**9**), deriving from addition of the hydrocarbon solvent (cyclohexane or *n*-hexane) to the dye fragment.



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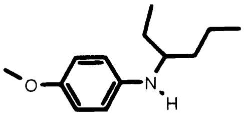

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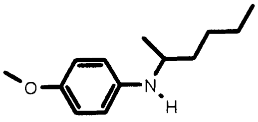

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The fading rates appeared to follow the same trend as in acetone, with **1c** decomposing more slowly than **1d** (after 7 h of irradiation, the residual absorbance A_t/A^0 is 0.787 for **1c** and 0.429 in the case of **1d**). This behaviour is not unexpected; indeed, the more electrophilic is the N–N bridge in the excited state, the faster will be the hydrogen abstraction that occurs from the electron-rich hexane.

3.3. Methanol

The photodecomposition behaviour of the investigated dyes in this solvent was similar to that observed in hydrocarbons, with the only difference that the product obtained by radical coupling underwent hydrolysis (see Scheme 2) giving the substituted aniline and formaldehyde.

Table 3
Fading of **1a** in solutions of various solvents

Solvent	t	A_t/A^0 [a]
Hexane	24 h	0.507
Methanol	2 h 30 min	0.392
Acetone	25 min	0.137

[a] A^0 is in all cases ∼1.6.

In all cases (**1a**–**c** and **2a**–**c**) and in all solvents *p*-substituted anilines (**4**) were isolated and characterised. Product **10** (Scheme 3), instead, was isolated only in methanol, which is a much better hydrogen donor than hexane. A stabilising effect of substituents of opposite polarity onto the radical (captodative effect) [9] might also be envisaged. In any case, the decomposition in methanol, though slower than in acetone, was definitely faster than in hexane (Table 3).

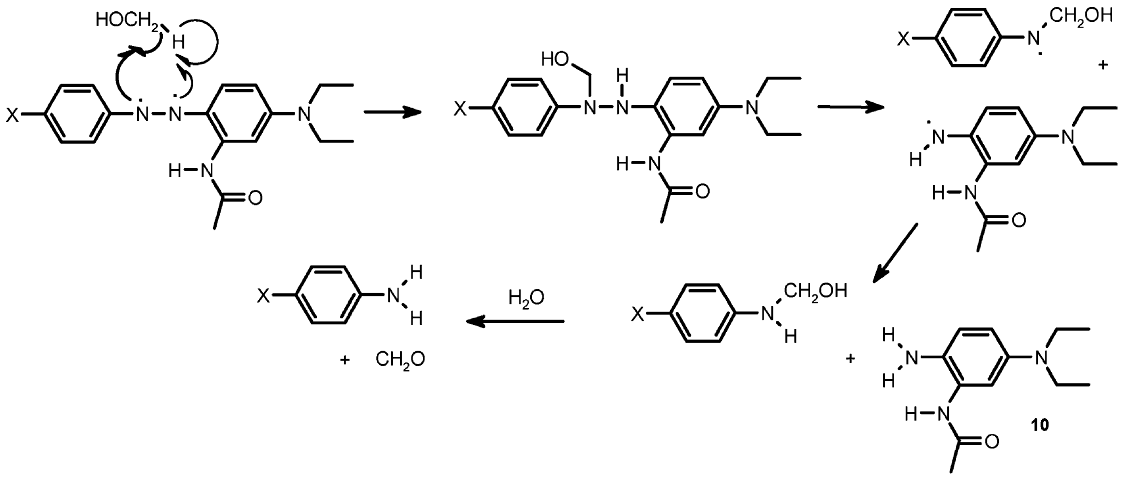
This is reasonable on the basis of the greater hydrogen donating ability of methanol compared to hydrocarbons. Such interpretation is further supported by the observation that no fading at all was ever observed in acetonitrile, a solvent which cannot undergo ET and whose polarity prevents any hydrogen abstraction by electrophilic radicals.

3.4. Effect of the –NH–COCH$_3$ substituent

The rate of colour fading was somewhat lower in acetone for series **2**, respect to series **1**, the rate difference being barely detectable in some cases (see Table 2). The effect of the –NH–COCH$_3$ substituent was more pronounced in the other solvents, where series **2** decomposed at a higher rate than series **1**: after 2 h of irradiation in *n*-hexane, **2c** dropped to 44% of the initial absorbance, while **1c** remained almost unchanged. A similar trend was observed also for **1d** and **2d**. This effect could be accounted for by considering that the presence of the *ortho*-substituent may hinder the *trans*–*cis* isomerisation of the excited azo dye thus favouring its reaction with the solvent. Another possible explanation may involve the formation of a hydrogen bond between the azo group and the neighbouring acetamide moiety.

3.5. Effect of oxygen

The inhibiting effect of oxygen could be explained by considering that molecular oxygen is known to act as a quencher of the excited state of the dye [10]; the interaction results in the formation of singlet oxygen, $^1O_2$, and in the return of the dye to its ground state. This explanation was experimentally confirmed by trapping $^1O_2$ with methyl oleate [4]. Actually, the effect of oxygen was extremely marked, so that even just traces of it completely block colour fading. Oxygen removal from the solutions by a nitrogen stream resulted in slow and poorly reproducible photodecomposition runs, while repeated cycles of freeze–pump–thaw prior to irradiation, assuring complete oxygen removal, allowed



Scheme 3.

the photoinduced decomposition reaction to proceed quite rapidly.

4. Conclusions

The photochemical behaviour of the investigated 4-diethylaminoazobenzene dyes depends on the nature of the solvent. In acetone, an ET process takes place, leading firstly to de-ethylation of the dye molecule and then to its fragmentation; the efficiency of this process is such that fading is much faster than in all other tested solvents. The effects of substituents X are consistent with the suggested mechanism, which may anyhow work in parallel with another, slower, decomposition path involving the photoreduction of the azo group. In hexane and methanol this latter path, originated from the well-known photoinduced cleavage of the N–N azo bond, is the only operating decomposition route, leading to the attack of the intermediate radical species to a solvent molecule. This mechanism is supported by the decomposition products isolated and identified in this study. Molecular oxygen strongly inhibits both routes to photofading by quenching the excited state of the dye. No photodecomposition takes place in polar acetonitrile.

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