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Journal of Photochemistry and Photobiology A: Chemistry 188 (2007) 267–271
Journal of Photochemistry and Photobiology A:Chemistry
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# A specific resistance of aminoazo dyes to the oxidative degradation

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Received 20 October 2006; received in revised form 29 November 2006; accepted 13 December 2006
Available online 16 December 2006

**Abstract**

The primary products of one-electron oxidation of the azo dyes, 4-(*N*,*N*-diethylamino)azobenzene and 4-(*N*,*N*-dimethylamino)-4′-(*N*,*N*-diethylamino)azobenzene, have been spectroscopically characterized in cryogenic matrices. The reactivity of the radical cations has been investigated by means of pulse radiolysis in solution at room temperature and in cryogenic glasses. The primary transient products formed upon one-electron oxidation of the dyes are radical cations and alkylamino radicals. The latter products are efficiently scavenged by the dyes resulting in adduct formation. The adducts slowly decay and regenerate the parent dye. Hence the degradation of the dye initiated by one-electron oxidation becomes completely inefficient.


*Keywords:* Azobenzene dyes; Pulse radiolysis; Cryogenic matrices; Oxidative degradation; Radical cations

## 1. Introduction

Aromatic azo compounds represent the dominant class of synthetic colorants employed in various branches of industry. While the parent azobenzene, due to its low molar extinction coefficient, is not used as a dye, its derivatives carrying different electron donating groups, for example, the *N*,*N*-disubstituted aminoazobenzenes, show substantial hyperchromic effect and are widely employed. Due to the presence of stable chromophoric azo group (–N=N–) the azo dyes can be designed to resist chemical or photochemical degradation processes. A detailed knowledge on the photostability of these dyes is required for their improvement against the fading processes. On the other hand it is also necessary to understand the mechanism underlying the dye resistance to the degradation, under exposure to different utilization methods (initiated by photolysis, radiolysis or electrolysis) [1,2].

Due to an increasing environmental pollution a search for the treatment and disposal of the dyes from the industrial effluent is getting more and more importance. Oxidation and reduction processes play an important role in the degradation treatment of the azo dyes. The latter process is more effective and in consequence its mechanism is also better clarified [2–4]. Much less information is available on the mechanism of the oxidation processes, the intermediates involved in these reactions and their role in the effectiveness of the oxidative degradation of the azo dyes.

In the previous studies we have discussed mainly the photoreduction processes and the role of hydrazyl radicals identified in the degradation reactions [2]. However, it was also shown that transient species of radical character different than the hydrazyl radicals are generated upon one-electron oxidation of the aminoazo dyes. The main objective of present investigation is therefore the detailed study of the oxidation mechanism. According to the various studies the degradation process is initiated by the one-electron oxidation of the aminoazo dyes either by the reaction with $^{\bullet}$OH or electron transfer to photoexcited solvent or sensitizer molecules. The resulting radical cation undergoes either deprotonation [4] or H$^{\bullet}$ atom abstraction [5,6] to give finally iminium ion [4,6] and upon solvolysis the secondary amine [7,8].

In this paper we explore the oxidation mechanism induced by radiolysis showing some specific resistance of the dye to the oxidative degradation. Besides alkyl halides, solvents well suited for observation of oxidation processes, we have tested also a reactivity of the aminoazo dyes in ionic liquids. Ionic liquids, a commonly accepted term for low melting salts combining

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doi:10.1016/j.jphotochem.2006.12.021

bulky organic cations, such as 1-butyl-3-methylimidazolium, with organic and inorganic anions, find a wide use as novel solvents in a wide variety of commercial applications [9]. As it was shown recently this group of compounds proved to be also a right media for observation of oxidation processes initiated by radiolysis [10].

The primary transient species of the oxidation reactions are identified and characterized by time-resolved methods as pulse radiolysis, supported by kinetic arguments what in addition allows the distinction between possible reaction mechanisms. Pulse radiolysis results find support from the matrix isolation methodology applied to the radiolytical generation and stabilization of the radical species in low-temperature matrices [11,12]. The inhibitory effect of the low-temperature matrices on recombination and fragmentation processes allows direct observation of the transient species. This also allows a convenient observation of the undergoing processes upon a controlled annealing and thus softening of the rigid matrix environment. In this study we present experimental results obtained by this methodology.

## 2. Experimental

### 2.1. Materials

The procedures of the 4-(*N*,*N*-diethylamino)azobenzene (**1**) and 4-(*N*,*N*-dimethylamino)-4′-(*N*,*N*-diethylamino)azobenzene (**2**) preparation has been described elsewhere [2]. All other chemicals were purchased from Sigma–Aldrich.

### 2.2. Pulse radiolysis

Pulse radiolysis experiments were carried out with high energy (6 MeV) 17 ns electron pulse generated from ELU-6 linear electron accelerator. The dose absorbed per pulse was determined with $N_2O$ saturated aqueous solution of KSCN (0.01 M), assuming $G((SCN)_2^{\bullet -}) = 6.2 \times 10^{-7}$ mol/J and $\varepsilon((SCN)_2^{\bullet -}) = 7600\ M^{-1}\ cm^{-1}$ ($G$ represents the radiation chemical yield and $\varepsilon$ is a molar absorption coefficient at 475 nm). The dose delivered per pulse was within the range 5–80 Gy. Details of the pulse radiolysis system are given elsewhere [13].

For the generation of radical cations solutions of the dyes in alkyl halides (2-chlorobutane was used in this work) are preferred as these solvents dissociatively capture electrons ejected from the solvent molecules (reactions (1) and (2)), while the positive charge is transferred to solute molecules of lower ionization potential (reaction (3)) [11,12,14]. The reaction scheme below summarizes the mechanism of transient species formation, under ambient and cryogenic conditions, upon pulse radiolysis of 2-chlorobutane (BuCl) solutions of the dyes.

$$BuCl \xrightarrow{\text{radiolysis}} BuCl^{\bullet +} + e^- \quad (1)$$

$$e^- + BuCl \rightarrow Bu^{\bullet} + Cl^- \quad (2)$$

$$BuCl^{\bullet +} + \mathbf{1}\ (\text{or}\ \mathbf{2}) \rightarrow BuCl + \mathbf{1}^{\bullet +}\ (\text{or}\ \mathbf{2}^{\bullet +}) \quad (3)$$

Ionic liquid, in this work 1-butyl-3-methylimidazolium hexafluorophosphate, was used for the same purpose as the ionic liquid environment is suitable for radical cations generation. Electrons ejected from the solvent are captured by the imidazolium cation, while the positive charge is transferred to solute molecules [10].

### 2.3. Organic glassy matrices

Glassy samples were prepared by quench-freezing of room temperature solutions in liquid nitrogen. The samples were 2–3 mm thick and were placed in a temperature controlled liquid nitrogen-cooled cryostat (Oxford Instruments). The desired temperature (77–150 K) of the matrix was attained by an automatically controlled heating. The samples mounted in a cryostat were irradiated with 4 μs electron pulses from ELU-6 linear accelerator. A description of the methodology of the low-temperature studies in organic matrices and frozen ionic liquids are given elsewhere [10,14].

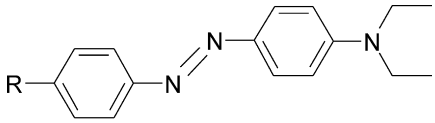
The optical absorption spectra were measured on Perkin Elmer 40P and Cary 300 (Varian) spectrophotometers.

### 2.4. Kinetic analysis

Kinetic analysis was done with Levenberg–Marquardt algorithm. The pseudo-first order rate constant values ($k_{obs}$) were evaluated from the plot of $\Delta A$ versus time. The bimolecular rate constants were determined from the slope of the linear plot of $k_{obs}$ versus solute concentration. In kinetic measurements the concentration of the dyes was kept in the range $10^{-4}$ to $10^{-2}$ M.

## 3. Results and discussion

Radiolysis of the 4-(*N*,*N*-diethylamino)azobenzene (**1**) in deoxygenated 2-chlorobutane led to the formation of product absorbing at 317 nm and above 500 nm (a broad band with the maxima at 515, 545 nm) which was observed even few hours after its generation. There was a direct dependence of the yield of the generated product and the decrease of the initial dye absorption on the radiation dose (see Fig. 1). Eventually these transient absorption bands almost completely vanished from the spectrum and the neutral dye absorption at 412 nm was completely restored. Both bands at 317 nm and above 500 nm can be assigned to a single transient species because three isosbestic points clearly seen for this transformation indicate direct transformation of the observed transient product into the neutral parent dye. This process is presented in Fig. 1. It may be accelerated to some extent by photoillumination of the sample with the visible light (through the cut off or interference filter 500 nm).




**1** R = H
**2** R = $N(CH_3)_2$

The regeneration of the dye absorbance after irradiation indicates some specific resistance of the aminoazo dyes to oxidative degradation. Identification of the intermediate species, even

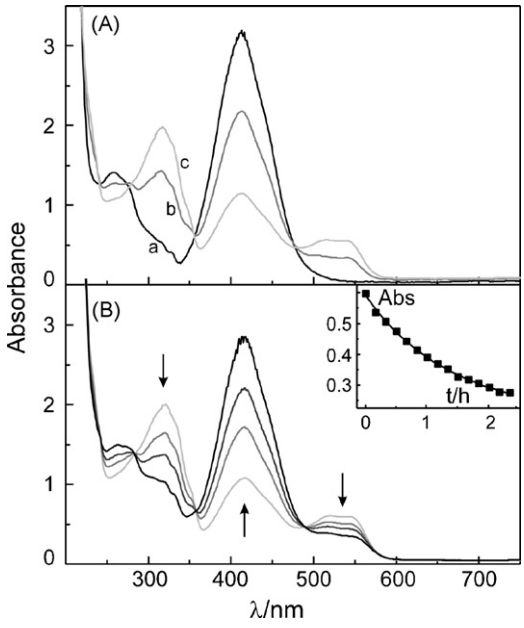



Fig. 1. Electronic absorption spectra obtained upon radiolysis of **1** (50 μM) in 2-chlorobutane at ambient conditions. (A) Spectra before (a) and after pulse radiolysis with different radiation doses of 1.5 kGy (b) and 4.5 kGy (c). (B) Spectra collected in time (time interval 150 min) after the radiolysis with a 4.5 kGy radiation dose. (Inset) First order decay of the 545 nm absorbance.

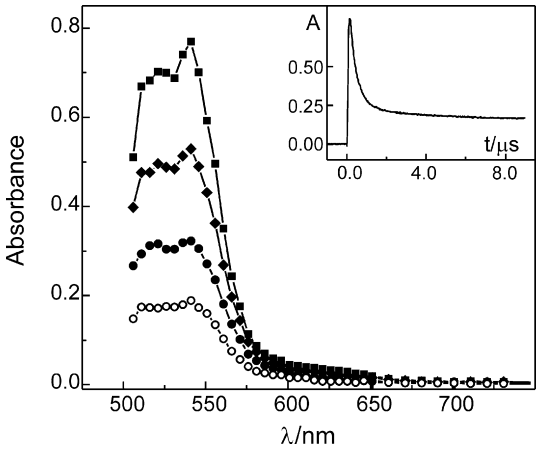



Fig. 2. Transient absorption spectra obtained by pulse radiolysis of $N_2$-saturated solution of **1** (1 mM) in 2-chlorobutane. Spectra recorded (■) 200 ns, (♦) 400 ns, (●) 800 ns and (◯) 4 μs after the pulse. The samples were 1 cm thick and received a radiation dose of 70 Gy. (Inset) Decay of the 540 nm absorbance.

by steady-state spectroscopic methods at ambient conditions, shows that, in contrast to the reduction process, formation of this quite stable transient product may be responsible for the protective effect observed.

The first order kinetics of the decay of the absorption above 500 nm was slow with the estimated rate constant $k = 1 \times 10^{-4}\ s^{-1}$. In the presence of oxygen the rate of the dye regeneration remained unchanged. It was also not very sensitive to the initial concentration of the neutral dye.

Similar picture emerged from the experiments conducted in ionic liquids. Upon radiolysis of the sample the absorption band of the dye diminished while the absorption above 500 nm was formed. Because of the high density of this medium the regeneration of the dye remained, however, extremely inefficient.

Transient absorption spectrum generated in 2-chlorobutane at ambient conditions by pulse radiolysis resembled that observed by steady-state measurements. It was, however, much stronger and decayed extremely fast compare with the species observed hours after the radiolysis (see Fig. 2). The formation of this absorption depended on the concentration of the dye and the rate constant $k_f = 2 \times 10^9\ M^{-1}\ s^{-1}$ of this process was found from the dependence of the pseudo-first order rate constant of its formation on the concentration of the dye. The absorption bands between 500 and 600 nm could not be assigned to the primary product of azo dye oxidation, i.e. to the respective radical cation of **1**, since $\mathbf{1}^{\bullet+}$ absorption is negligible in this spectral region [2]. The second order kinetics of the process and especially the dependence of its rate on the dye concentration might instead indicate formation of the adducts of radiolysis products with the azo compound. It is well documented that azo dyes show tendency to efficiently scavenge the radical species either generated from solvent molecules or from dyes themselves. Based on the similarity of the absorption of this product to the previously identified adducts of alcohol [4] or 2-methyltetrahydrofuran radicals [2] and similar rates of the formation of these species it could be assigned to the adduct of **1** with solvent radicals formed upon radiolysis of 2-chlorobutane (see Section 2). Also its fast decay within few microseconds remained in agreement with such assignment.

However, it is evident from Fig. 2 that absorption above 500 nm did not decay completely on the time scale of pulse radiolysis experiment (see the spectrum collected 4 μs after the pulse and the kinetic trace of the 540 nm absorption signal). This long living residual absorption remained in agreement with the observation of similar absorption band in steady-state measurements (see Fig. 1). It is very likely that the same species was observed in both those experiments.

The formation of this species may not depend on the decay of the short living primary product of pulse radiolysis, although we cannot exclude the possibility that the primary product could rearrange to the more stable secondary species. The initial fast decay of the 500–600 nm band followed the pseudo-first order kinetics with rate dependent on the dye concentration. Based on this dependence the second order rate constant was estimated as $k_d = 3 \times 10^8\ M^{-1}\ s^{-1}$. However, the participation of the dye molecules in the observed decay raises the question about the nature of the product formed. It is possible that less stable adduct of the azo dye with solvent radicals could be replaced by the more stable one with the radical derived from the dye itself.

There is an alternative route to such product, concurrent to that mentioned above, throughout ionization of the dye, a process very likely present in solvents like 2-chlorobutane or ionic liquids exposed to ionizing radiation. We explored this route step by step in glassy matrix experiments to identify all transient products and to achieve their spectroscopic characterization.

Although no other transient species could be observed in solution by pulse radiolysis it was evident from our previously presented material that under matrix conditions formation of at least two different transient products preceded the forma-

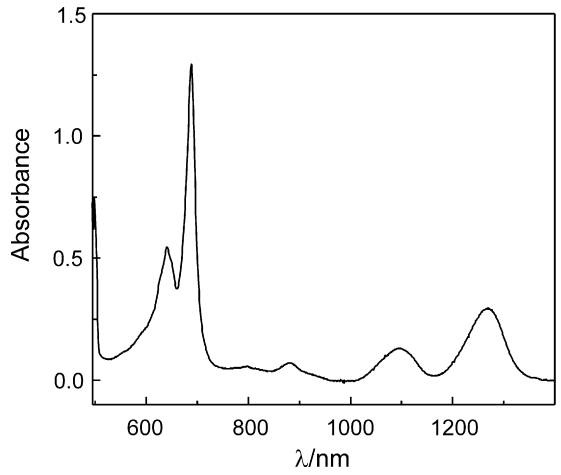
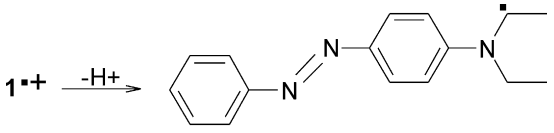



Fig. 3. Transient absorption spectrum observed upon radiolysis of **2** (0.01 M) embedded in 2-chlorobutane at 77 K; dose 600 Gy; thickness of the sample 3 mm.

tion of the final product absorption observed in the spectral region 500–600 nm. These primary species were identified as a radical cation of the dye and the product of its deprotonation, the aminoalkyl radical ($\mathbf{1} - H^{\bullet}$) [2]. Such aminoalkyl radicals are postulated as the major transient products formed upon a photodecomposition of **1** on oxidation [5].




**1-*H*•**

The formation of the radical cation of **1** was achieved in 2-chlorobutane matrix [2]. Because this species possessed only weak absorption band around 700 nm (with a distinct vibronic structure) we generated the radical cation also from the **2**. The radical cation spectrum generated from (*E*)-4,4′-bis(dimethylamino)azobenzene by two independent routs [15], ionization of the parent compound or the reaction of the para-substituted benzenediazonium salt with its one-electron reduced radical counterpart, showed that bisaminosubstituted azo dyes possess much stronger absorption bands than mono-substituted ones. In fact, as can be seen from the spectrum presented in Fig. 3 the radical cation of **2** possessed strong absorption in the visible (strong band at 690 nm and a weaker one at 640 nm) accompanied by a group of much weaker bands in the NIR (880, 1085, 1265 nm). The visible absorption remained very similar to that observed for (*E*)-4,4′-bis(dimethylamino)azobenzene [15].

As it was pointed out previously radical cations are very often more acidic than their neutral precursors and some of them are even superacids [12]. Therefore they readily undergo deprotonation. Under matrix conditions this process starts, however, only upon matrix softening. Indeed, annealing of the matrix led to the spectral changes and a group of new bands was formed at the expense of the radical cation absorption. In both cases three new bands were observed (610, 557, 520 nm for **1**, and 640, 550, 517 nm for **2**) (see Fig. 4). Not all of them could be assigned to the appropriate alkylamino radicals ($\mathbf{1} - H^{\bullet}$ or $\mathbf{2} - H^{\bullet}$) which would be the products of radical cations deprotonation although they all grew initially in a parallel manner on the decay of $\mathbf{1}^{\bullet+}$ or $\mathbf{2}^{\bullet+}$, respectively. It can be conveniently seen in the spectra obtained for **2** since its radical cation, $\mathbf{2}^{\bullet+}$, strongly absorbs at 690 nm (compare spectra a and b in Fig. 4B). Then, the bands at 610 and 640 nm (for **1** and **2**, respectively) after the initial growth began to decay while the bands at 520 and 550 nm (very similar in both cases of the azo dyes used) continued to grow. Therefore we assigned the band at 610 nm to the $1 - H^{\bullet}$ (Fig. 4A) and the band at 640 nm to the $2 - H^{\bullet}$ (Fig. 4B).

It is evident from the spectra presented in Fig. 4 that for both dyes the changes above 500 nm are accompanied by the decrease in the absorption of the parent azo dye. It was noticed that the dye fading continued till the radical cation and/or radical absorptions were present in the spectrum. Moreover, it was observed that upon further matrix annealing, when matrix almost begin to melt, bands above 500 nm began vanish while the natural color of the dye was emerging again. Therefore it is reasonable to assign it to the same species as that observed by steady-state spectrophotometric methods in liquid 2-chlorobutane and ionic liquid. In this latter solvent similar transient species were identified under glassy matrix conditions.

Since the absorption of the final transient product lies at the spectral region characteristic for the absorption of the adducts of the dyes with radical species and because formation of these species was observed under the experimental conditions when the alkylamino radicals were formed and till they decayed completely, it is reasonable to assign this product to the adduct between alkylamino radicals and the parent azo dyes, or to the products of further rearrangement of such complex. It is very likely that stabilization of the radical in the form of its adduct

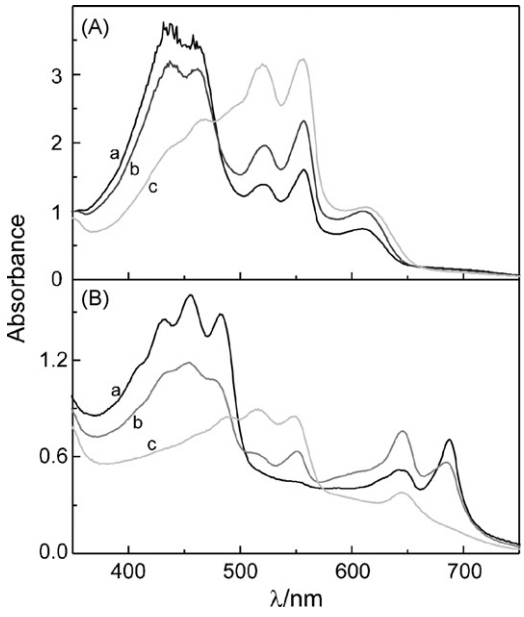



Fig. 4. Changes in the electronic absorption spectra obtained on pulse radiolysis of (A) **1** (1 mM) and (B) **2** (0.5 mM) embedded in 2-chlorobutane matrix triggered by limited annealing of the matrix at (a) 105 K for 10 min, (b) 105 K for 30 min and (c) 115 K for 10 min. The samples were 2 mm thick and received a radiation dose of 2.4 kGy.

with neutral parent dye may prevent its further decomposition, for example through the subsequent oxidation of the radical, as in the process observed upon photoinduced degradation of the dye in the acetone [5].

## 4. Conclusions

The transient radical cations generated upon one-electron oxidation of the 4-(*N*,*N*-diethylamino)azobenzene and 4-(*N*,*N*-dimethylamino)-4′-(*N*,*N*-diethylamino)azobenzene has been stabilized and spectroscopically characterized under cryogenic matrix conditions. The reactivity of the oxidized dyes was further monitored on thermal annealing of the matrix. Under those experimental conditions the radical cations underwent fast deprotonation to form aminoalkyl radicals. These two products of the one-electron oxidation processes were identified as primary transient species on the route to quite stable adducts of radicals with neutral parent dyes.

The results obtained in matrix experiments remained complementary to the results observed in solution at ambient temperatures. The pulse radiolysis experiments confirmed the scavenging properties of the dyes towards neutral radical species. Azo dyes form adducts with solvent or aminoalkyl radicals. Formation of these latter adducts accounts for observed stability of the azo dyes against oxidative degradation since such complexes decay and slowly regenerate the initial neutral dye.

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