

Color changes accompanying one-electron reduction and oxidation of the azo dyes

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Abstract

The primary products of one-electron oxidation and reduction of the azo dye, 4-*N,N*-diethylaminoazobenzene, have been spectroscopically characterized in cryogenic matrices. The radical anion of the dye is characterized by the absorption band at 645 nm in 2-methyltetrahydrofuran matrix and at 595 nm in alcoholic matrices. The radical cation exhibits weak absorption bands at 601, 659, 721 and 791 nm in 2-chlorobutane matrix. The reactivity of the radical ions has been investigated by means of pulse radiolysis in solution at room temperature and in cryogenic glasses. The transient products formed upon one-electron reduction and oxidation of the dye are characterized by the electronic absorption spectra and color changes of the solution.

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1. Introduction

Aromatic azo compounds represent the dominant class of synthetic colorants employed in textile, printing, agrochemical and pharmaceutical industries. Due to the presence of stable chromophoric azo group ($-N=N-$), linking different aromatic moieties carrying electron-donating and/or electron-withdrawing groups, the dyes can be designed to resist chemical or photochemical degradation processes.

A detailed knowledge on the photostability of the dyes is required for the further improvement of synthetic colorants and their resistance to the fading processes. But it is also necessary for the development of reliable procedures of their final degradation and environmental protection. In the process of utilization of hazardous dye wastes several methods have been used, including photooxidation and photoreduction processes. The complete understanding of the dye decomposition, under exposure to different utilization methods, cannot be based only on a product distribution. It is also

necessary to understand the underlying reaction mechanism [1–8].

The final products of the photoreduction processes have been identified to be the hydrazo derivatives. It was found that reduction process (initiated by photolysis, radiolysis or electrolysis) results in the effective degradation of the azo dyes in aqueous and alcoholic solutions via the radical mechanism [5–7]. The rates of reactions of azobenzene and its simple amino substituted analogues with electrons or other strongly reducing agents are diffusion controlled. The azo radical anions are the primary products of those reactions [5–7]. The reduction process is followed by a fast protonation of radical anion since the pK_a values of the protonated radical anion (hydrazyl radical) are high (13.7 and 17 for azobenzene in aqueous or 2-propanol solutions, respectively) [5]. Since the azo compounds show a tendency to form adducts with radical species, like the hydrazyl radical, this may initiate the further degradation of the dye. Similar effect can be expected in the reaction of the azo dyes with radicals generated from the solvent molecules since, for example, adducts resulting from the attachment of the isopropyl ketyl radicals to the dye can be directly converted to the hydrazyl radicals. The mechanism of this process may involve a one-step intramolecular hydrogen atom transfer or two independent steps of an electron transfer followed by the fast protonation of the radical anion formed [6,7].

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In solution the absorption bands of all different species of radical origin generated on the reduction of the azo dyes strongly overlap. Moreover, the broad structureless absorption bands observed in a solution carry a limited information of the electronic structure of the species under investigation. Therefore, the distinction between possible reaction mechanisms can only be based on kinetic arguments supported by the knowledge of the acid–base equilibria and product distribution. On the other hand, an excellent method of stabilization and characterization of the radical ions is their generation by an ionizing radiation in low temperature matrices [9,10]. The inhibitory effect of the low temperature matrices on recombination and fragmentation processes, allows direct observation of the radical species. In this paper we present experimental results, on the reduction and oxidation of the azo dyes, obtained in frozen organic matrices. This method allows a spectral characterization and identification of radical and radical ion transient products of the redox reactions.

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 4-*N,N*-diethylaminoazobenzene, show substantial hyperchromic effect and are widely used as azo dyes. In this paper, we describe our efforts which were aimed at direct characterization of the radical anion of 4-*N,N*-diethylaminoazobenzene (1), and its protonated form—the hydrazyl radical. The transient species identified in this work are characterized only by their lowest energy absorption bands, which do not overlap with the absorption bands of the dye itself. These long wavelength bands usually lie in the visible region of the spectrum and are responsible for the colors of the species [9,10]. It is very characteristic for organic radical ions that their special electronic structure is sometimes manifested by their vivid colors, which often stood at the origin of the fascination with these species. Since in the dye chemistry, and generally in the photochemistry, the color is one of the most important characteristics of the compound, it is interesting to study the radical species under conditions which allow visual inspection of the samples. It also allows characterization of the observed processes by color changes which are very often. In addition to the electronic spectra of radical ions this paper presents the changes of the color of the samples induced by one-electron oxidation or reduction of the dye.

2. Experimental

2.1. Materials

The procedure of 4-*N,N*-diethylaminoazobenzene preparation has been described elsewhere [2]. 2-Propanol (2-PrOH), 2-chlorobutane (*sec*-BuCl) and 2-methyltetrahydrofuran (MTHF) were purchased from Aldrich (Steinheim, Germany), ethanol (EtOH) was from POCh (Gliwice, Poland).

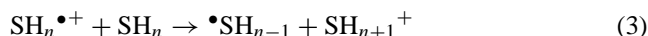
2.2. Pulse radiolysis

Pulse radiolysis experiments were carried out with high energy (6 MeV) 17 ns electron pulses generated from ELU-6 linear electron accelerator. The dose absorbed per pulse was determined with N₂O saturated aqueous solution of KSCN (0.01 M), assuming $G((\text{SCN})_2^{\bullet-}) = 6.0$ and $\epsilon((\text{SCN})_2^{\bullet-}) = 7600 \text{ M}^{-1} \text{ cm}^{-1}$ (G represents yield of radicals per 100 eV of energy absorbed and ϵ is a molar extinction coefficient at 475 nm). The dose delivered per pulse was within the range 5–80 Gy. The concentration of solute was kept in the range of $(0.5\text{--}10) \times 10^{-3} \text{ M}$. Details of the pulse radiolysis system are given elsewhere [11].

The radiolysis of frozen alcohols and 2-methyltetrahydrofuran leads to the formation of solvated electrons (e_s^-) and the radical cations of solvent molecules (reaction 1).

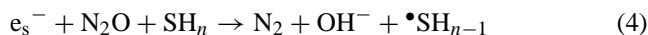


The solvated electrons react with the solute molecules (A) to give corresponding radical anions (reaction 2), while the ionized solvent molecules easily deprotonate onto neighboring neutral molecules (reaction 3).



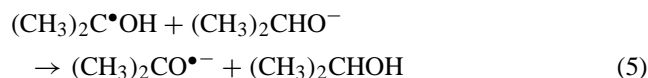
On annealing of the matrix the products of this latter process can act as a proton source and hydrogen atom donors via addition–elimination reaction. Because of the rigidity of matrix at 77 K the bimolecular reactions are, however, significantly suppressed, but can be observed on softening of the matrix upon its annealing.

Similar processes can be observed in liquid solvents. In alcohol solutions ketyl radicals, $\bullet\text{SH}_{n-1}$, which are strongly reducing species (for 2-propanol, $E^\circ((\text{CH}_3)_2\text{CO}, \text{H}^+/(\text{CH}_3)_2\bullet\text{COH}) = -1.39 \text{ V}$ in aqueous solution) [12] can also react with many compounds via one-electron transfer. In fact, in alcohol solutions saturated with N₂O, which acts as a scavenger of solvated electrons (reaction 4), the ketyl radicals remain the only reducing species.



The reduction method via reaction with ketyl radicals was used in the determination of pK_a of hydrazyl radicals, assuming that the yield of generated alcohol radicals does not change within the acidity/basicity range used.

In the case of radiolysis of N₂O saturated 2-propanol solutions carried out in the presence of 0.2 M 2-PrO⁻Na⁺, isopropyl ketyl radicals undergo deprotonation ($pK_a \sim 16$ in 2-PrOH) [5] with the formation of a stronger one-electron reducing species—the acetone radical anion (reaction 5).



For the generation of radical cations solutions of the dye in alkyl halides (2-chlorobutane was used in this work) are preferred as these solvents dissociatively capture electrons ejected from the solvent molecules, while the positive charge is transferred to solute molecules of lower ionization potential [9].

2.3. Cryogenic measurements

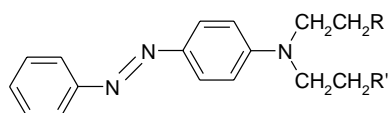
The glassy samples of the MTHF, alcohol solutions and 2-chlorobutane were prepared by immersing the room temperature solutions in liquid nitrogen. The samples were 0.5–3 mm thick and were placed in a temperature controlled, liquid nitrogen-cooled cryostat (Oxford Instruments). The desired temperature (77–150 K) was achieved by automatically controlled heating. The optical absorption spectra were measured on Cary 5 (Varian) spectrophotometer. The samples mounted in a cryostat were irradiated with 4 μ s electron pulses from ELU-6 linear accelerator. The transient absorption spectra are presented as difference spectra (the spectrum before irradiation is subtracted) for the direct comparison with the spectra from the pulse radiolysis experiments.

2.4. Quantum chemical calculations

The geometries of all species were optimized by the B3LYP density functional method [13] as implemented in the Gaussian 98 suite of programs [14]. The above calculations were done at the B3LYP/6–31G(d) level in the case of the species of neutral charge and at B3LYP/6–31+G(d) in the case of radical anions. Relative energies were calculated at the B3LYP/6–31G(d) level for optimized structures of the two tautomeric forms of the hydrazyl radical.

3. Results and discussion

A group of investigated amino substituted azobenzene dyes is presented in Scheme 1. 4-*N,N*-diethylaminoazobenzene (**1**) represents a typical disperse azobenzene dye widely employed in textile industry. Very often simple modification of the alkylamino substituent, by an introduction of –CN or –OH groups, leads to a substantial hyperchromic effect and to a change of the dye properties, such as, for example, their photostability or sublimation fastness [2]. Our investigation



- 1** - R, R' = H
2 - R, R' = OH
3 - R = CN, R' = H

Scheme 1.

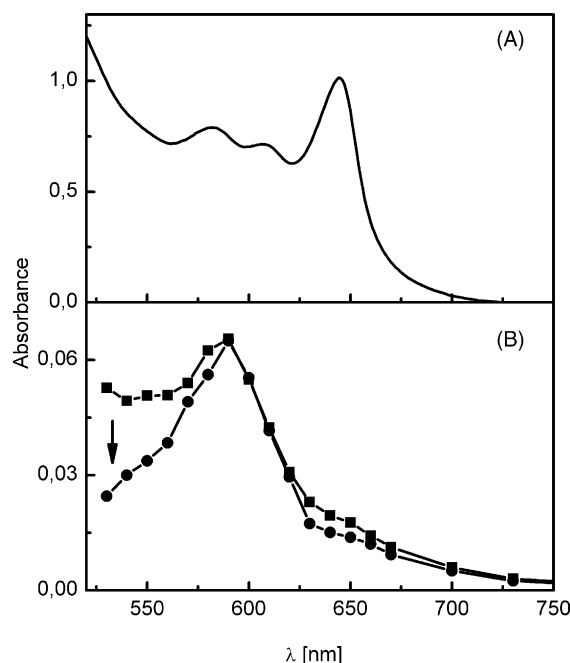


Fig. 1. Transient absorption spectra observed upon radiolysis of: (A) **1** (0.005 M) in MTHF at 77 K; dose 2.5 kGy; thickness of the sample, 2.5 mm. (B) **1** (0.005 M) in MTHF at room temperature; dose 55 Gy; solution was deoxygenated by bubbling with N₂; thickness of the sample, 1 cm. Spectra recorded (■) 0.8 μ s and (●) 5.0 μ s after a 17 ns electron pulse.

reveals, however, that this does not change significantly the redox properties of the dyes presented in Scheme 1. Therefore, in this paper we discuss in details only the reactivity of **1**. The differences among the group are mainly limited to the small shifts of the absorption bands of identified species.

Since it is important to compare the spectra of radical anions generated in aprotic and protic solvents to determine an effect of stabilization of the radical anion by hydrogen bonding we have used 2-methyltetrahydrofuran, 2-propanol and ethanol as the frozen solvents.

Electronic absorption spectrum of the radical anion generated from the 4-*N,N*-diethylaminoazobenzene in MTHF matrix at 77 K is presented in Fig. 1A. This spectrum consists of a strong absorption band at 645 nm and two smaller peaks at shorter wavelengths, at 580 and 610 nm. The process of the reduction of the dye in MTHF is accompanied by the change of the color of the sample from yellow to green. All three absorption bands observed after radiolysis of the matrix can be assigned to the **1**^{•-} radical anion since they grow in parallel manner on the photobleaching of the residual absorption of solvated electrons (absorption band at 1200 nm) [15]. These bands also decay in the same manner on limited warming of the matrix. Softening of the irradiated frozen solutions, upon controlled increase of the matrix temperature above its glassy transition temperature, removes an inhibitory effect of the matrix on bimolecular reactions, among them on recombination processes.

Decay of the absorption bands of $1^{\bullet-}$ on annealing of the matrix is not accompanied by any significant shift of their maxima. However, as the temperature goes significantly over the glassy transition temperature (88 K for MTHF) [15] and matrix becomes more fluent, the decrease of the absorption of $1^{\bullet-}$ is accompanied by the loss of its vibronic structure. Finally, an absorption spectrum of the $1^{\bullet-}$ radical anion in MTHF at room temperature is characterized by a structureless band, which extends from 540–680 nm, such as under matrix conditions, but with a maximum at 590 nm (see Fig. 1B). An absence of any shift of the radical anion bands upon softening of the matrix indicates that radical anion geometry is not significantly different from the geometry of its neutral precursor. It is often observed that the changes in the spectra of radical ions observed on softening of the matrix accompany the relaxation of these species (initially “frozen” in the geometry of their neutral precursors) to the thermodynamically more stable geometry [9,10,16]. Indeed, according to DFT calculations the capture of an additional electron slightly elongates the central azo bond (by about 0.06 Å) but the molecule remains planar [17].

Although MTHF is an aprotic solvent, positive ions, $C_5H_{11}O^+$, generated on irradiation of this matrix in some cases can act as proton donors. The best known example is a formation of ketyl radicals generated from benzophenone and acetophenone [9,18]. The protonation of radical anions of these compounds is observed on limited warming of the MTHF matrix. This process is, however, absent for radical anions of the azo dyes despite the fact that the formation of the hydrazyl radical in protic solvents at ambient temperature is extremely fast. Therefore, the absorption band at 590 nm observed in liquid MTHF can be assigned to the radical anion. However, the initial spectrum observed in MTHF upon radiolysis is also composed of an absorption of a second product, partially overlapping with the absorption of radical anion, but with maximum blue shifted compared with the $1^{\bullet-}$ band. While **1** reacts with solvated electrons with the diffusion controlled rate constant ($k = 3 \times 10^9 M^{-1} s^{-1}$) and the radical anion formed has a lifetime of 60 μs under these conditions, this second product decays already on much faster time scale (its lifetime has been estimated as 0.8 μs).

Based on the similarity of the absorption of this product to the previously identified adducts of alcohol radicals [6,7], we assigned it to the adduct of **1** with $\bullet C_5H_9O$ radicals formed upon radiolysis of MTHF. Analogically to the adducts of the azo compounds with $\bullet CH_2OH$ radicals no further products in the spectra could be detected on the adducts decay [6].

When alcohols are used as matrices (2-propanol, ethanol) the color of the sample changes upon radiolysis into green similarly to the MTHF matrix. The absorption spectrum of $1^{\bullet-}$ is, however, significantly blue shifted (50 nm compared to the strongest band of $1^{\bullet-}$ in MTHF at cryogenic conditions) indicating a strong hydrogen bonding between the radical anion of **1** and alcohol molecules. The spectrum

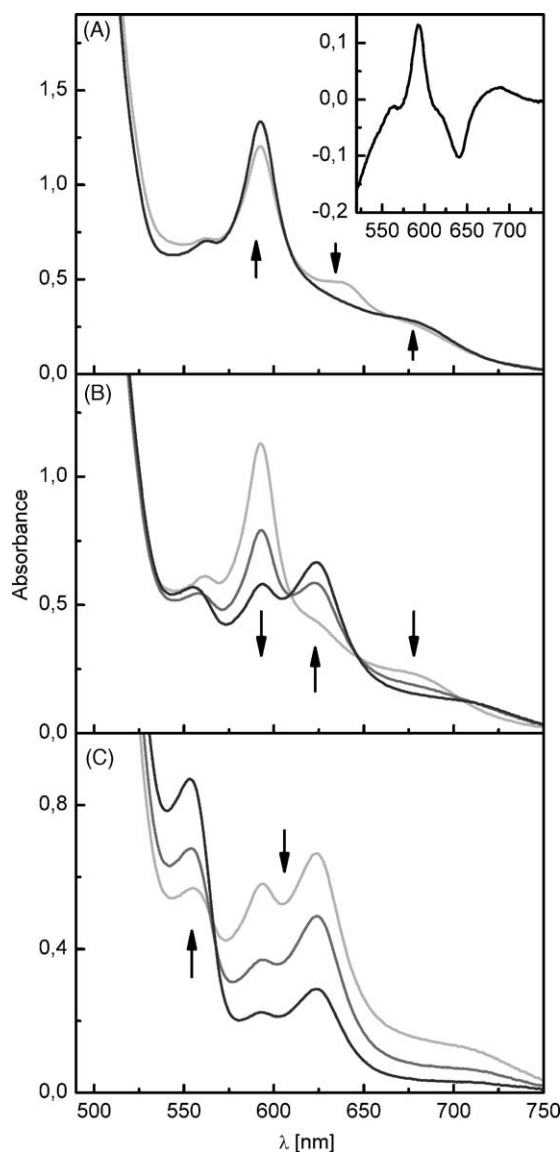


Fig. 2. Electronic absorption spectra obtained on reduction of **1** (0.02 M) embedded in 2-propanol matrix. Arrows indicate changes in the spectra upon limited warming of the matrix: (A) spectra were collected after radiolysis at 77 K and upon annealing of the matrix at 95 K for 15 min. Inset presents difference spectrum; (B) annealing at 105 K for 10 min, at 115 K for 20 min, and at 120 K for 10 min; (C) annealing at 120 K for 10, 30 and 50 min. The sample was 2 mm thick and received a radiation dose of 2.8 kGy.

of $1^{\bullet-}$ in 2-propanol at 77 K is shown in Fig. 2A. The strongest band in this spectrum possesses a maximum at 595 nm, with a shoulder at shorter wavelengths (565 nm), but on the lower energy side it is extended up to 700 nm. Note that a small residual absorption at 645 nm (seen in the initial spectrum), which decays already upon very modest increase of matrix temperature or on photobleaching, can be assigned to the residual absorption of the solvated electrons [19]. The decay of the solvated electron absorption is accompanied by the growth of the strongest band, but it also leads to the increase of the lower energy shoulder (see inset

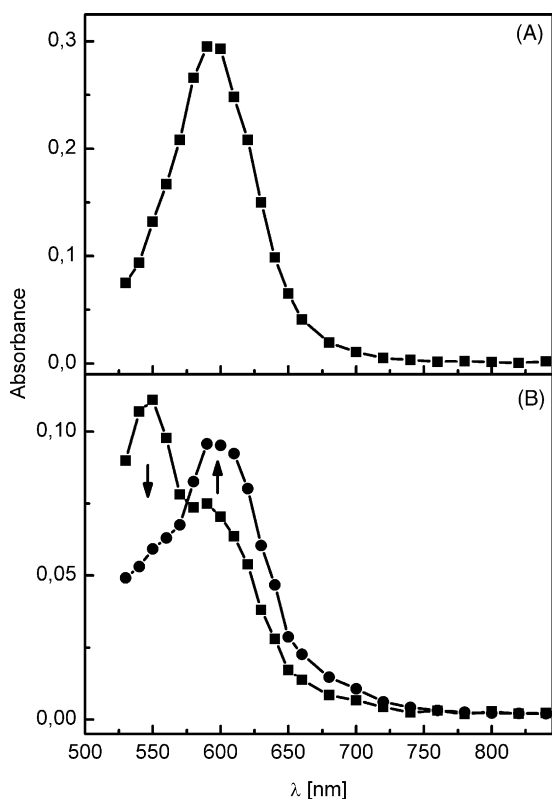
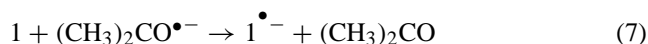
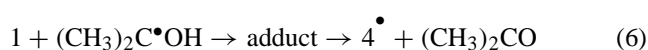


Fig. 3. Transient absorption spectra obtained by pulse radiolysis of N_2O -saturated solution of **1** (0.005 M) in 2-propanol: (A) basic solution, $[\text{iso-PrO}^- \text{Na}^+] = 0.1$ M, spectrum recorded 1 μs after the pulse; (B) neutral solution, spectra recorded (■) 2 μs and (●) 9 μs after the pulse. The samples were 1 cm thick and received a radiation dose of 50 Gy.

to Fig. 2A). This additionally confirms an assignment of the observed absorption bands to $\mathbf{1}^{\bullet-}$. Observation of the much wider band of $\mathbf{1}^{\bullet-}$ in liquid 2-propanol (spectrum presented in Fig. 3A), but with the maximum at 590 nm) seems to be the additional support of the above presented assignment.

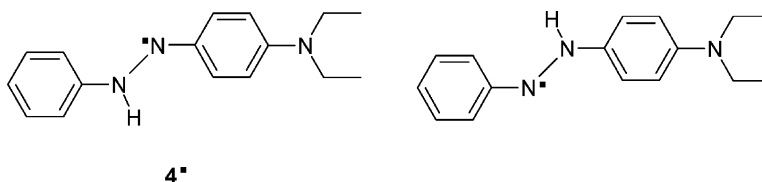
On the other hand, one might expect the addition of proton to the radical anion in the protic matrix to yield neutral radical. All the more, in solution the protonated radical anion and radical anion itself absorb in the same spectral region as radical anion (compare spectra in Fig. 3A and B) and the distinction between the absorptions of both species in liquid phase is only possible based on their different extinction coefficients. The pH dependence of the absorption at 590 nm allowed to determine the $\text{p}K_{\text{a}}$ value of 17.5 for the neutral radical of the investigated dye. The determined $\text{p}K_{\text{a}}$ value is close to the value found for azobenzene hydrazyl radical [5,20] suggesting that protonation takes place on the azo group yielding hydrazyl radical ($\mathbf{4}^{\bullet}$).

The process of reduction of **1** proceeds via different pathways in neutral and basic 2-propanol solutions. In neutral solution the reaction with alcohol radicals proceeds via a formation of the adduct (absorption maximum at 550 nm, see Fig. 3B). Then, the formation of $\mathbf{4}^{\bullet}$ can take place with the mechanism of intramolecular hydrogen atom transfer, as previously suggested by Flemingi and Monti [6] or as a stepwise electron–proton transfer. The rate constant of the reaction of the dye with ketyl alcohol radicals $(\text{CH}_3)_2\text{C}^{\bullet}\text{OH}$ (reaction 6) has been estimated as $k \cong 2 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$, while the adduct formed in this reaction has a lifetime of 6 μs . On the other hand, the formation of the radical anion under strong basic conditions proceeds via electron transfer from acetone radical anion to the dye (reaction 7) with the rate constant $k = 1 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$.



The $\text{p}K_{\text{a}}$ value of 17.5 of the hydrazyl radical compared to the $\text{p}K_{\text{ROH}} = 20$ of 2-propanol [5] indicates that under matrix conditions the absorption with maximum at 590 nm can be assigned to $\mathbf{1}^{\bullet-}$, although with a strong hydrogen bonding to the surrounding solvent molecules. In contrast, as can be calculated from above $\text{p}K_{\text{a}}$ values the acid–base equilibrium in liquid 2-propanol will be shifted towards $\mathbf{4}^{\bullet}$. Moreover, alcohol solvents become more acidic upon irradiation, since the ionized alcohol molecules readily deprotonate (a proton is stabilized by neutral neighboring molecules, for example, as $(\text{CH}_3)_2\text{CHOH}_2^+$ in 2-propanol).

Since in a rigid environment of the matrix bimolecular reactions are almost completely inhibited, softening of the matrix is required to “selectively” uncage intermolecular processes. Usually the fastest processes observed upon matrix relaxation are protonation/deprotonation reactions. Therefore, it is not surprising that on a modest increase of the matrix temperature the radical anion absorption decays in favor of a new absorption band at 625 nm. The isosbestic points clearly seen in the spectra presented in Fig. 2B indicates direct conversion of $\mathbf{1}^{\bullet-}$ to a product. As the yield of the product does not depend on the concentration of the dye and there is a direct conversion of $\mathbf{1}^{\bullet-}$ to the 625 nm product we identify, it as the hydrazyl radical ($\mathbf{4}^{\bullet}$) formed on the protonation of $\mathbf{1}^{\bullet-}$. Absorption of the hydrazyl radical is red shifted compared with the strongest absorption band of $\mathbf{1}^{\bullet-}$, what results in the color change of the sample to dark green. According to DFT calculations attachment of a proton leads to a small elongation of the central bond (by about 0.01 Å) accompanied by a loss of planarity.



The blue shift of the strongest band of radical anion in protic versus aprotic solvents and moreover the blue shift of this band compared to the absorption band of hydrazyl radical may suggest that strong stabilization of the radical anion in alcohols is achieved through more than one hydrogen bond. According to calculations an alkylamino substitution alters to small extent the azo bond and thus the distribution of an additional electron between two nitrogen atoms of the azo bond is not completely symmetrical in radical anion. Uneven distribution of the negative charge may result in uneven strength of the hydrogen bonds and is also reflected by a difference in the heat of formation of two tautomeric forms of hydrazyl radical. The hydrazyl radical with protonated nitrogen atom attached to unsubstituted phenyl ring (4^\bullet) is a more stable form (by $1.1 \text{ kcal mol}^{-1}$).

The final spectral changes are observed on prolonged annealing of the alcoholic matrices at elevated temperatures. The color of the sample changes to orange and the final product absorbs at 555 nm (see spectra in Fig. 2C). For the higher concentration of the azo dye embedded in the matrix the stronger absorption of this product is observed. It indicates a reaction of the hydrazyl radical with the parent azo dye. Since the absorption of this product corresponds to the absorption of adducts of solvent radicals with the azo dyes we assigned it to the association product of hydrazyl radical to the dye assuming similar bonding as in the solvent radical adducts.

However, one can imagine that the presence of alkylamino substituents changes the reactivity of the radicals with neutral dyes. Instead of adduct formation, the hydrazyl radical could react with the dye through a hydrogen atom abstraction from the aminoalkyl group with the formation of hydrazobenzene and the aminoalkyl radical. Such aminoalkyl radicals are postulated as the major transient products formed upon a photodecomposition of **1** on oxidation [4]. To check whether the observed absorption band at 555 nm can be assigned to aminoalkyl radical the reactivity of the radical cation of **1** has been investigated.

The formation of the radical cation of **1** can be achieved in 2-chlorobutane matrix. It possesses weak absorption band around 700 nm, with a distinct vibronic structure (bands at 601, 659, 721 and 791 nm, see Fig. 4), which is responsible for a weak orange color of the sample. We assign this band to the radical cation of the dye ($1^{\bullet+}$). Because the observed absorption band is different from the absorption band of azobenzene radical cation [9,21] it can be concluded that electron is removed from the n-orbital of the amino nitrogen atom.

Radical cations are more acidic than their neutral precursors and some of them are even superacids [10], therefore they readily undergo deprotonation. There are numerous examples of the proton transfer from the alkyl substituents of radical cations of dialkylanilines to the suitable proton acceptors including parent molecule of dialkylanilines [22]. Moreover, it has been postulated that during photodecomposition of dialkylamino azo dyes the radical cation formed

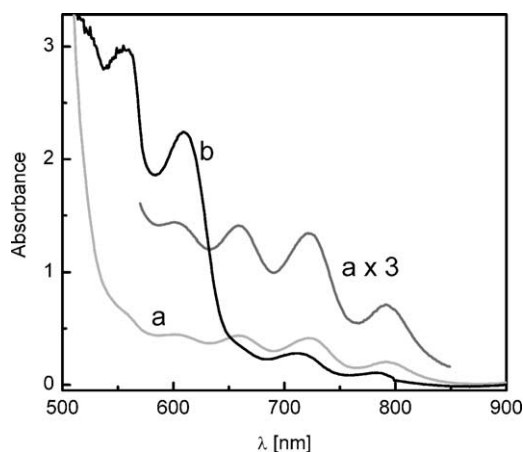
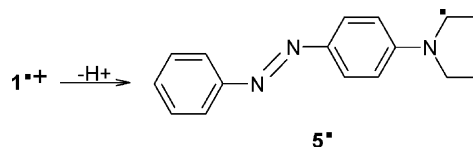


Fig. 4. Absorption spectrum of irradiated **1** (saturated solution, $<0.02 \text{ M}$) in a glassy *sec*-BuCl matrix at 77 K (a). Spectrum (b) was obtained upon warming of the sample to 90 K and cooling back to 77 K. The sample was 2 mm thick and received a radiation dose of 1.4 kGy.

deprotonates to give corresponding aminoalkyl radical [4]. Under matrix conditions the radical cation deprotonation can only start upon matrix softening. Indeed, in the present case the color of the sample changes to dark brown on annealing of the matrix. The spectrum of the aminoalkyl radical (5^\bullet) which is a product of deprotonation is composed of two strong bands at 555 and 610 nm. Both bands growth in a parallel manner on the decay of $1^{\bullet+}$.



The spectrum of the aminoalkyl radical does not match any of the spectra previously analyzed. Therefore, we can exclude the aminoalkyl radicals as transients in reactions which follow the process of the reduction of **1**. Photodecomposition of the azo dyes with alkylamino substituents proceeds through different routes on reduction and oxidation. On reduction the key part of molecule is azo bond while on oxidation it is an alkylamino group that determines the fate of the dye.

4. Conclusions

The transient radical anion generated upon reduction of the 4-*N,N*-diethylaminoazobenzene has been stabilized and spectroscopically characterized under cryogenic matrix conditions. Both the protic and aprotic solvents were used to show strong stabilization of $1^{\bullet-}$ by a hydrogen bonding to solvent alcohol molecules. The reactivity of the reduced dye was further monitored on thermal annealing of the matrix. The radical anion undergoes fast protonation to form a hydrazyl radical. In addition, the pulse radiolysis experiments

revealed scavenging properties of the dyes towards radical species. Azo dyes form adducts with solvent or hydrazyl radicals. The results obtained in matrix experiments remain complementary to the results observed in solution at ambient temperatures.

The products of an one-electron oxidation of **1** were also identified. The removal of an electron produces the $1^{\bullet+}$ radical cation, which further deprotonates to give the 5^{\bullet} aminoalkyl radical.

An investigation of the reduction and oxidation processes under the matrix conditions allows visual inspection of the color changes accompanying addition or removal of an electron to/from the dye. The yellow color of the dye solution changes to green upon one-electron reduction of the dye both in MTHF and in alcoholic matrices. Following protonation of $1^{\bullet-}$ results in the color change to dark green. Finally, the formation of the adducts of the azo dye with radical species results in the color change to dark orange. Also one-electron oxidation of the dye embedded in cryogenic glass leads to the change of the color of the sample. The orange glassy samples indicate the presence of the radical cation but the color changes to dark brown as a result of the radical cation deprotonation.

Acknowledgements

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