Journal of Photochemistry and Photobiology A: Chemistry 224 (2011) 135–140

Contents lists available at SciVerse ScienceDirect

Journal of Photochemistry and Photobiology A: Chemistry

journal homepage: www.elsevier.com/locate/jphotochem

Photoreduction of nitro-1,4-naphthoquinones in solution

Helmut Görner

Max-Planck-Institut für Bioanorganische Chemie, D-45413 Mülheim an der Ruhr, Germany

ARTICLE INFO

Article history:
Received 1 June 2011
Received in revised form 9 September 2011
Accepted 17 September 2011
Available online 22 September 2011

Dedicated to Mr. Henry Gruen on the occasion of his 88th birthday.

Keywords:
Photoreduction
Nitro-1,4-naphthoquinone
Triplet
Radical

ABSTRACT

The photolysis of 2,3-dichloro-*n*-nitro-1,4-naphthoquinones (nitroN'Q, *n*: 5 and 6) was studied in benzene and acetonitrile. The triplet states of both nitroN'Qs, which can be quenched by H-atom donating solvents, e.g. 2-propanol or 1-phenylethanol, were characterized by flash photolysis. Formation and decay of nitronaphthoquinone radicals, due to H-atom transfer, were observed; the reactivities of the donors were examined and the mechanistic aspects discussed. The photoreduction of 6-nitroN'Q in the presence of the donors is efficient in contrast to 5-nitroN'Q. The major product is considered to be 6-hydroxylaminoN'Q.

1. Introduction

The photolyse of 1,4-benzoquinone (BQ), 1,4-naphthoquinone (NQ) and 9,10-anthraquinone (AQ) has been the subject of various studies [1–11]. A major process is photoreduction, e.g. in the presence of alcohols or electron donors, such as triethylamine (TEA). Efficient population of the triplet state is known for BQ, NQ and AQ, the quantum yield of intersystem crossing (Φ_{isc}) of the quinones is substantial [1–4]. For NQ and 2,3-dichloro-1,4-naphthoquinone (N'Q) in acetonitrile $\Phi_{\mathrm{isc}} = 0.74$ and 0.90, respectively [11]. The quantum yield (Φ_{Δ}) of formation of molecular singlet oxygen, $O_2(^1\Delta_g)$, which can be regarded as a minimum for Φ_{isc}, is also substantial for NQs in several solvents, e.g. for N'Q in acetonitrile $\Phi_{\Delta} = 0.6$, and only low for cases in which a side chain is present [2–4,11]. A charge transfer band centered at 679 nm appears for N'Q in dimethyl sulfoxide and ethanol in the presence of 0.1–0.6 M TEA [12]. Quinones are known to react with ascorbate (vitamin C) thermally [13] and photochemically [14].

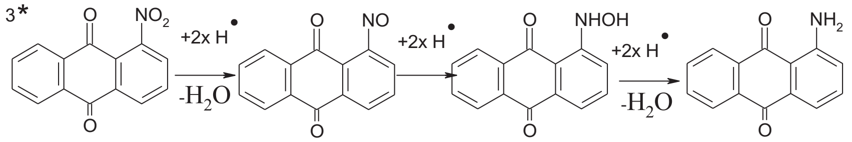
As to the photoreduction of quinonoid nitro-derivatives, 1-nitroAQ and 1-nitro-2-methylAQ have been studied [15–18], but neither nitroBQs nor nitroNQs. The major reduction photoproducts of the non-fluorescing nitroAQs are the fluorescing 1-aminoAQ and the 2-methyl derivative. The complete photoreduction in the presence of H-atom (2-propanol) or electron donors (TEA) leads to the aminoAQs due to transfer of six electron equivalents [15–18]. The quantum yield (Φ_{red}) of reduction increases with the donor concentration, approaching $\Phi_{\mathrm{red}} = 0.1$ [18]. The short-lived triplet state ($\leq$20 ns) of 1-nitro-2-methylAQ can react with 2-propanol or TEA, thereby forming the spectroscopically hidden donor radicals and AQ radicals which absorb at 400 and 540 nm; the former and latter bands are due to the nitroAQ radical and its anion, respectively. The triplet state of 1-nitroAQ was not observed at room temperature, but the radical properties and the decay to the nitrosoAQs are similar for both nitroAQs [17,18]. A simplified pathway is shown in Scheme 1.

The literature for nitro-substituted NQs is scarce [19–29] and no information is available for nitroBQs as yet. 2,3-Dichloro-5-nitro-1,4-naphthoquinone (5-nitroN'Q) undergoes 1:2 acceptor–donor complex formation with aromatic amines [28]. For 5-nitroNQ conversion to 5-aminoAQ takes place via a Diels–Alder reaction [27].

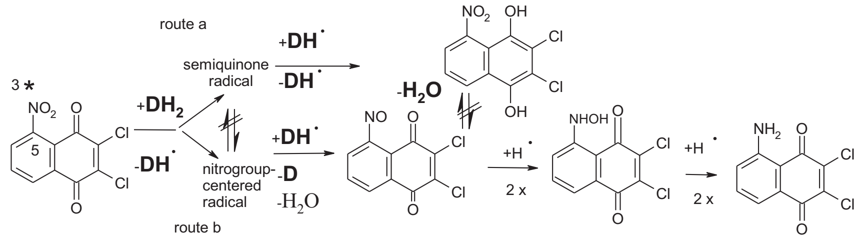
Here, 5- and 6-nitroN'Q in the presence of an H-atom donor (DH_2) were examined. The photoprocesses and reduction products of nitroNQs are unknown. Two possible pathways of reduction of 5-nitroN'Q after excitation and formation of the triplet state are shown in Scheme 2. Route (a) should yield the semiquinone radical and then the hydroquinone, while route (b) yields the nitrogroup-centered radical, the 5-nitrosoN'Q, 5-hydroxylaminoN'Q and eventually 5-aminoN'Q. Such a complete photoreduction mechanism, involving transfer of six reduction equivalents, has been proposed for 1-nitroAQ, where 1-hydroxylaminoAQ is one reduction product and 1-aminoAQ another [17,18]. However, one result of this study is that such an expectation of full and efficient photoreduction of 5-nitroN'Q is suggested not to be fulfilled.

E-mail address: goerner@mpi-muelheim.mpg.de

1010-6030/$ – see front matter © 2011 Elsevier B.V. All rights reserved.
doi:10.1016/j.jphotochem.2011.09.016



Scheme 1.



Scheme 2.

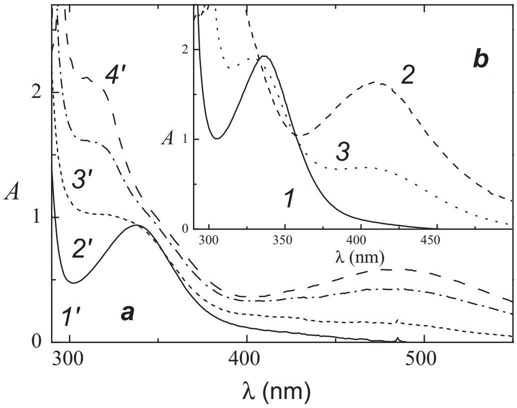


Fig. 1. Absorption spectra of 6-nitroN'Q in (a) argon-saturated acetonitrile in the presence of 0.01 M TEA at 0, 1, 3 and 7 min (*1'–4'*, respectively) and (b) air-saturated, 50% water in the presence of 0.01 M ascorbate at 0, 3 and 30 min, *1–3*, respectively.

2. Experimental

5- and 6-NitroN'Q were purchased (TCI) and used as received. The other compounds and the solvents were used as commercially available (Aldrich, Merck) and checked for impurities. Acetonitrile was Uvasol quality, TEA was purified by distillation and 1- and 2-phenylethanol were from Fluka, 1-phenylethanol contains ca. 10 mM acetophenone. Water was from a millipore (milli Q) system. The molar absorption coefficient of 6-nitroN'Q in acetonitrile was determined to be $\varepsilon_{340} = 4 \times 10^3$ M^{-1} cm^{-1}. For photoconversion a 1000 W Xe–Hg lamp and a monochromator were applied. Alternatively, irradiation was performed with a 250 W high pressure Hg lamp and a band-pass filter for 366 nm. The UV–vis absorption spectra were recorded on a diode array spectrophotometer (HP, 8453). For various donor concentrations the quantum yield of conversion was obtained, keeping the initial absorbance at $\lambda_{irr} = 366$ nm constant. The quantum yields Φ_{red} were determined using $\Phi_{red} = 0.9$ of 2,3-dimethylAQ in an argon-saturated mixture of acetonitrile and 2-propanol (9:1) as actinometer [9]. The experimental error in the quantum yield determination is typically ±15% and ±30% for values smaller than 0.01. For 5- and 6-nitroN'Q a ground state reaction with TEA takes place, this prevents observation of a possible triplet quenching when the TEA concentration is larger than ca. 10 mM. Flash photolyses operated at $\lambda_{exc} = 355$ nm (Nd-YAG laser, GMU Lasertechnik), the absorption signals were measured by a Luzchem system. All measurements refer to 24 °C.

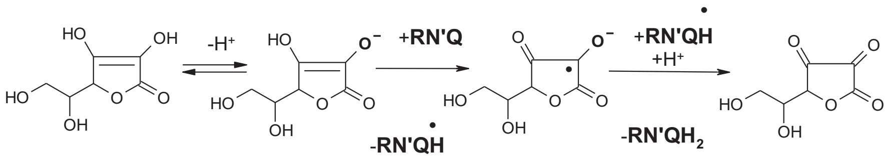
3. Results and discussion

3.1. Ground state interaction

The absorption spectra of 5- or 6-nitroN'Q in benzene or acetonitrile solution have a band centered at $\lambda_a = 340$ nm. A ground state reaction occurs for 6-nitroN'Q in air-saturated 1:1 (vol) mixtures of acetonitrile and water in the presence of ascorbate/ascorbic acid. The latter has a pK_a of 3. The spectral changes of 6-nitroN'Q with 10 mM ascorbate are shown in Fig. 1b. The process is attributed to thermal reduction, see Scheme 3. One product of RN'Q (R: NO_2) is attributed to the nitroso form (nitrosoN'Q). Spectroscopically, it can probably not be distinguished from a dihydroquinone (nitroQH_2-H_2O) as yet. Further reaction of nitrosoN'Q (R: NO) leads to hydroxylaminoN'Q (R: NHOH).

A similar reaction does not take place for 5-nitroN'Q, indicating different reduction potentials for the two nitroN'Qs. The thermal reaction of 6-nitroN'Q with ascorbate is unique and has not reported for nitroAQs. Interestingly, the time-dependence of thermal reduction of 6-nitroN'Q shows a reversibility, see curve *3* vs. *2* in Fig. 1b. This partial oxidation (hydroxylaminoN'Q + $2O_2$ → nitrosoN'Q → nitroN'Q, see below) does not occur in the absence of oxygen.

Another ground state interaction was observed with TEA. The spectral changes of 6-nitroN'Q in argon-saturated mixtures of acetonitrile and water in the presence of 10 mM TEA are shown in Fig. 1a. For N'Q in dimethyl sulfoxide and ethanol the presence of 0.3 M TEA is required for the charge transfer band [12].



Scheme 3.