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Nitro group photoreduction of 4-(2-nitrophenyl)- and 4-(3-nitrophenyl)-1,4-dihydropyridines

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ABSTRACT

The photoprocesses of nifedipine, a 4-(2-nitrophenyl)-1,4-dihydropyridine, and nimodipine and nitrendipine, two 3-nitrophenyl Hantzsch-type analogues, were studied by steady-state and time-resolved methods. The intramolecular photoreduction of nifedipine into its nitrosophenyl product takes place within a few ns. The quantum yield of conversion is $\Phi_{red} = 0.3$ and does not depend significantly on the oxygen concentration and solvent properties. Formation of the fully reduced 4-(2-aminophenyl)-1,4-dihydropyridine as minor product is indicated by fluorescence spectroscopy. The photoreduction of nimodipine and nitrendipine is inefficient, $\Phi_{red} = 0.002$ in acetonitrile, but markedly enhanced in the presence of donors such as triethylamine (TEA) and 2-propanol, e.g. for TEA Φ_{red} is up to 0.03. The triplet states of nimodipine and nitrendipine were characterized. They react intermolecularly with TEA and 2-propanol, forming radicals as intermediates and eventually several reduction products.

1. Introduction

Nifedipine is a calcium channel blocker and frequently used in the treatment of hypertension or cardiovascular diseases [1–3]. It is sensitive to UV radiation and the photochemistry is therefore the subject of various studies [1–18]. The major photoproduct is 2,6-dimethyl-4-(2-nitrosophenyl)-3,5-pyridinedicarboxylic acid dimethyl ester ($ONPhPy_1$), the corresponding 4-(2-nitroso)pyridine, Scheme 1. The photoconversion has been monitored in the UV range [1–8] and is accompanied by the formation of an absorption band centered at 770 nm due to the nitrosophenyl entity of $ONPhPy_1$ [9–11]. A similar photoreduction to a nitrosophenyl compound has been reported for furnidipine [19].

The proposed key-step of the photoconversion to $ONPhPy_1$ is an intramolecular electron transfer from the dihydropyridine moiety to the nitro group [15]. Evidence has been found for formation of a zwitterionic intermediate in the photochemistry of 4-(2-nitrophenyl)-1,4-dihydropyridines at −196 °C [15]. Alternatively, a biradical prior to water elimination can be considered [15]. The putative triplet biradical has been observed by EPR spectroscopy in the photolysis of nifedipine at −196 °C [10]. For nifedipine the quantum yield of formation of singlet oxygen (Φ_Δ), which is related to the quantum yield of intersystem crossing (Φ_{isc}), is close to zero [14].

Several studies deal with the photochemistry of 4-(3-nitrophenyl)-1,4-dihydropyridines [20–27]; a few others are related to 1,4-dihydropyridines not containing a nitro group [28,29]. The 3-nitrophenyl analogues of nifedipine are of interest since intramolecular H-atom transfer is likewise not possible [24]. Examples are nimodipine and nitrendipine, see Chart 1. Apparently, a 4-(3-nitrophenyl) group has only a small effect on the photochemical reactions of 1,4-dihydropyridines. However, evidence has been found for intermolecular H-transfer from methanol and electron transfer from triethylamine (TEA) in the photochemistry of some 4-(3-nitrophenyl)-1,4-dihydropyridines [24]. The reactivity of nifedipine toward singlet molecular oxygen is moderate and the Φ_Δ values are 0.02–0.04 [14]. The photoproducts of nimodipine and nitrendipine obtained in the presence of TEA contain either a nitroso, a hydroxylamino or an amino group resulting from reduction of the nitro group, whereas the dihydropyridine moiety is conserved intact [24]. The nitroso, hydroxylamino and amino-product forms of irradiated nicardipine, a 4-(3-nitrophenyl)-1,4-dihydropyridine, in methanol have been identified [28]. The photoinduced aromatization has been achieved for a series of unsymmetrically substituted 1,4-dihydropyridines and the resulting products were identified [26]. The photoreduction should be enhanced in the presence of an alcohol, such as 2-propanol.

Here the photochemical reactions of nifedipine, nimodipine and nitrendipine were studied by steady-state and time-resolved techniques. The conversion of nifedipine to the corresponding 4-(2-nitroso)pyridine $ONPhPy_1$ does not involve an observable triplet state and $ONPhPy_1$ was found to be stable. A light-induced fluorescence increase due to formation of 4-(2-aminophenyl)-1,4-dihydropyridine as product in trace amounts has not been reported as yet. The results were compared with those of the 4-(3-nitro-

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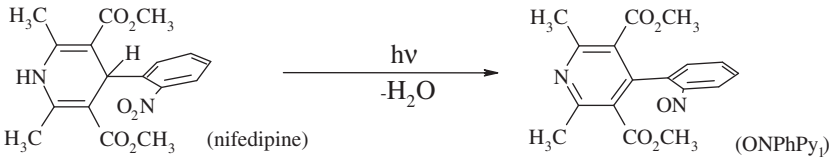


Scheme 1.

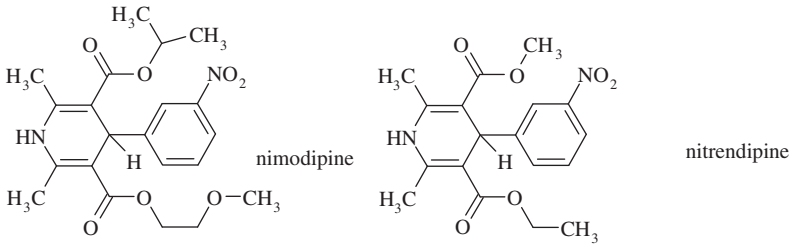


Chart 1.

phenyl)-1,4-dihydropyridines, where Φ_{isc} is above zero. These photoreactions occur intermolecularly and involve H-atom or electron transfer from an added donor to the triplet state. The triplet states of nimodipine and nitrendipine in acetonitrile were characterized. In the presence of TEA a secondary transient intermediate was observed which is ascribed to a radical.

2. Experimental

Nifedipine, nimodipine (2-methoxyethyl-1-methylethyl-2,6-dimethyl-4-(3-nitrophenyl)-1,4-dihydropyridine-3,5-dicarboxylate) and nitrendipine (ethylmethyl-2,6-dimethyl-4-(3-nitrophenyl)-1,4-dihydropyridine-3,5-dicarboxylate) were from Sigma, the other compounds (Aldrich) and the solvents (Merck) were used as received (acetonitrile: Uvasol) or purified by distillation: TEA. The molar absorption coefficient at 350 nm of nifedipine is $\varepsilon_{350} = 7 \times 10^3\ M^{-1}cm^{-1}$ [16]. The absorption spectra were monitored on a UV/vis spectrophotometer (HP, 8453). The emission and excitation spectra were measured using a spectrofluorimeter (Eclypse, Cary). For photoconversion at 313 nm, Hg lamps and either a band-pass filter or a monochromator were used. The photoconversion was carried out after bubbling argon (or oxygen) through the solutions prior to and during irradiation. To compare UV and near infrared spectral regions the samples were analyzed in 0.1 and 10 mm cells or else the solutions were 100 times diluted. Analysis was partly carried out by HPLC, however, without comparison with authentic products. A reverse phase column (ODS-3HD, PerfectSilTarget, 3 μm, 0.8 ml min^{-1}) was used with mobile phase gradient, composed of 0.5% trifluoroacetic acid and either a 1:5 mixture of acetonitrile and water or neat acetonitrile as eluent. The quantum yield of reduction (Φ_{red}) was determined using the aberchrome 540 actinometer [30]. An excimer laser (Lambda Physik, EMG 200, pulse width of 20 ns and energy <100 mJ) was used for excitation at 308 nm. The absorption signals were measured with two digitizers (Tektronix 7912AD and 390AD). Relative yields were obtained using optically matched solutions ($A_{308} = 1.5–2.0$). Photoreduction of the substrate was also achieved upon repetitive pulsing at 308 nm. Note that nifedipine is thermally degrading in water at pH 8. Therefore, photoreduction was not carried out in aqueous solution, except for one case, where the overall irradiation time was short compared to the time required for thermal degradation. The measurements refer to 24 ± 2 °C and, unless otherwise indicated, to deoxygenated solution.

3. Results

3.1. Photoprocesses of nifedipine

The absorption spectrum of nifedipine in acetonitrile has a major peak at 250 nm and a broad band centered at 360 nm. A photoproduct with maximum at $\lambda_p = 280$ nm and a peak at 312 nm and two isosbestic points at $\lambda_1 = 255$ and $\lambda_2 = 327$ nm appear upon pulsed excitation at 308 nm (Fig. 1, inset). The absorption changes as a function of the incident energy in Fig. 1 show that the absence or presence of oxygen has no effect. The spectral changes are the same upon continuous irradiation at 313 nm. An example for such a photoconversion of nifedipine in aqueous solution is shown in Fig. 2. Similar results were found in a series of solvents, some characteristic data are compiled in Table 1.

The major photoproduct of nifedipine is the corresponding 4-(2-nitrosophenyl)pyridine, $ONPhPy_1$, Scheme 1 [1–15]. The quantum yield Φ_{red} of conversion is insensitive to the presence or absence of oxygen. This is in agreement with the recent literature [15]. For nifedipine in acetonitrile it was found that variation of $\lambda_{irr} = 254$ or 366 nm has no effect on Φ_{red}. Moreover, Φ_{red} depends only little on solvent properties, the values obtained using illumination at 308/313 nm are listed in Table 2. Φ_{red} is between 0.2 and 0.3.

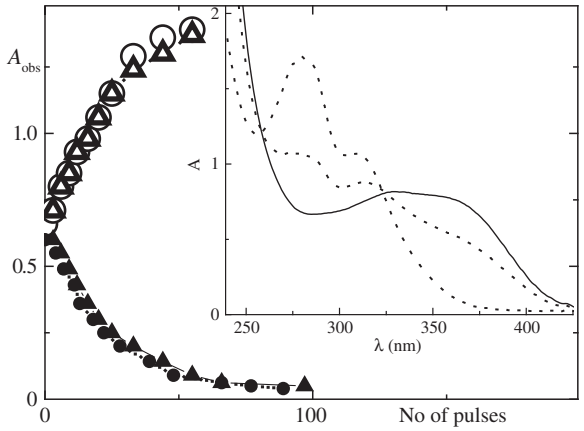


Fig. 1. Plots of A_{280} (open) and A_{380} (full) for nifedipine (0.1 mM) in argon-(circles) and oxygen-saturated (triangles) acetonitrile as a function of 308 nm excitation; inset: absorption spectra at 0, 20 and 100 pulses.

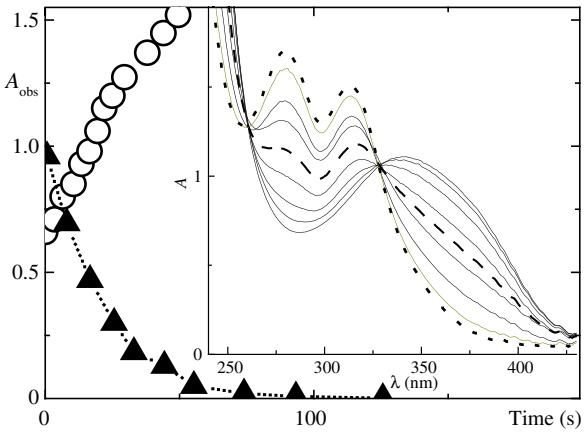


Fig. 2. Plots of A_{260} (o) and A_{360} (▲) for nifedipine in argon-saturated acetonitrile–water (1:9, pH 8) as a function of time of irradiation at 313 nm; inset: absorption spectra, 10 s interval.

Table 1
Absorption maximum of nitrophenyl-1,4-dihydrophenylpyridines upon irradiation and isosbestic points[a].

Compound	Solvent	λ_1 (nm)	λ_p (nm)	λ_2 (nm)
Nifedipine	Benzene		<290	330
	Acetonitrile	255	280, 310sh	327
	2-Propanol	260	280, 310sh	325
	H_2O[b]	260	280, 310	328
Nimodipine	2-Propanol	265	290	320
Nitrendipine	2-Propanol	265	285	320

[a] Using λ_{irr} = 313 nm.
[b] No thermal effect within a short time interval of <5 min.

Table 2
Quantum yield of conversion of nifedipine to $ONPhPy_1$[a].

Solvent	Φ_{red}	Φ_{red}[b]
Benzene	0.25	0.22
Acetonitrile	0.30	0.26
Methanol	0.33	0.3
2-Propanol	0.30	0.3
H_2O[c] pH 7	0.32	0.3
H_2O[c] pH 11	0.32	

[a] In argon-saturated solution using irradiation at 313 nm.
[b] Using pulses at 308 nm.
[c] Plus 1% methanol, pH 7.

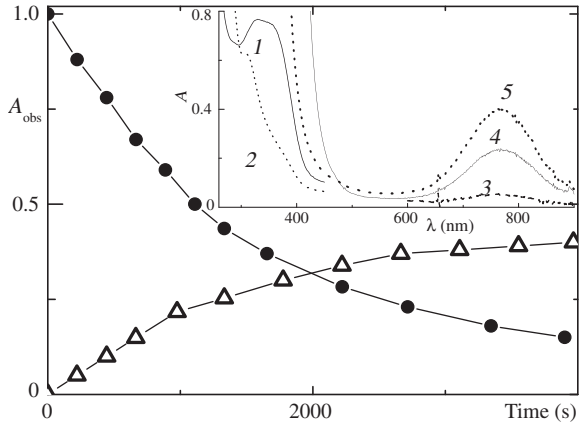


Fig. 3. Plots of A_{380} (●, 0.1 mm) and A_{760} (Δ, 1 cm) of the conversion of nifedipine (12 mM) to $ONPhPy_1$ in air-saturated acetonitrile as a function of time of irradiation at 313 nm; inset: absorption spectra at 400, 2000 and 4000 s, 3–5, respectively.

Irradiation of nifedipine in high concentration, e.g. 8–30 mM, in argon-saturated acetonitrile was carried out to follow the appearance of an absorption band centered at 770 nm (Fig. 3, inset). The molar absorption coefficient of $ONPhPy_1$ was found to be ε_{770} = 60 M^{-1} cm^{-1}, in agreement with values in the literature [9–11]. An example of the absorption changes as a function of time is shown in Fig. 3. Product analyses, carried out by HPLC, reveal one major product: $ONPhPy_1$, which is not further affected upon prolonged illumination. Interestingly, $ONPhPy_1$ in acetonitrile was found to be stable for several days. No transient was detected upon photolysis of nifedipine in argon-saturated acetonitrile. The absorbance at 300–380 nm decreases during the pulse. This bleaching remains permanent (Fig. 4) and indicates conversion without involvement of a triplet state.

3.2. Fluorescence of photoreduced nifedipine

The fluorescence spectrum of nifedipine in acetonitrile has no marked peak and is very weak. After irradiation at 308 or 313 nm a new photoinduced fluorescence emission with peak centered at 440 nm appears which becomes stronger upon further illumination. A plot of the intensity I_f as a function of the time of irradiation at 313 nm is shown in Fig. 5. It is noteworthy that the fluorescence excitation maximum at 370 nm is red-shifted by 60 nm with respect to that of the absorption at λ_p = 312 nm. The suggested reason is strong fluorescence of a trace product rather than of $ONPhPy_1$ itself. A comparison with absorption changes excludes secondary photolysis as origin of the fluorescence. Furthermore, the emission and excitation spectra (inset (a) of Fig. 5) are attributed to 4-(2-aminophenyl)-1,4-dihydropyridine, the fully reduced product. However, the 4-(2-hydroxylaminophenyl)-1,4-dihydropyridine (the precursor) is expected to have similar spectra.

In fact, thermal reduction of $ONPhPy_1$ in argon-saturated acetonitrile (plus H^+/Zn) leads to a red-shifted absorption band centered at 380 nm and a similar fluorescence excitation spectrum and an emission band at 440 nm (inset (b) of Fig. 5). This is in agreement with a literature report [31]. Note that such a thermal reduction takes place only after vigorous deoxygenation. The 440 nm band obtained in the dark is similar (but not the same) as the photoinduced spectrum.

3.3. Photoreduction of 3-nitrophenyldihydropyridines

The 360 nm band of the absorption spectrum of nimodipine in argon-saturated propanol decreases upon irradiation at 313 nm (Fig. 6) and the spectral changes (inset of Fig. 6) are analogous to those of nifedipine. For nimodipine or nitrendipine in argon-saturated propanol Φ_{red} = 0.02, while it is only 0.001 in acetonitrile (Table 3). The changes are similar in argon-saturated acetonitrile in

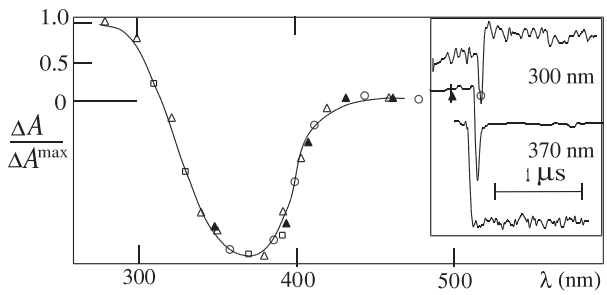


Fig. 4. Transient absorption spectra of nifedipine in argon-saturated acetonitrile at 20 ns (○), 1 μs (Δ), 10 μs (□) and 1 ms (▲) after the 308 nm pulse; insets: kinetics at 300 (upper) and 370 nm (lower).

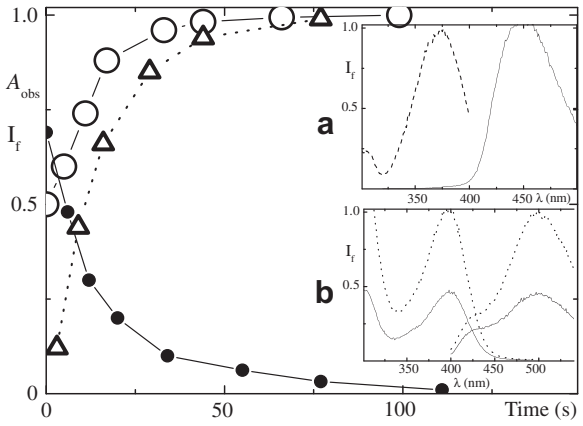


Fig. 5. Plots of A_{260} (o) and A_{380} (●) and the relative fluorescence intensity at 440 nm (Δ, λ_{exc} = 350 nm) of nifedipine in acetonitrile as a function of time of irradiation at 313 nm; insets: emission and excitation spectra (a) after 1 min irradiation and (b) thermally; argon-saturated, in the presence of 1 M $HClO_4$ 3 (full) and 10 min (broken) after addition of Zn powder.

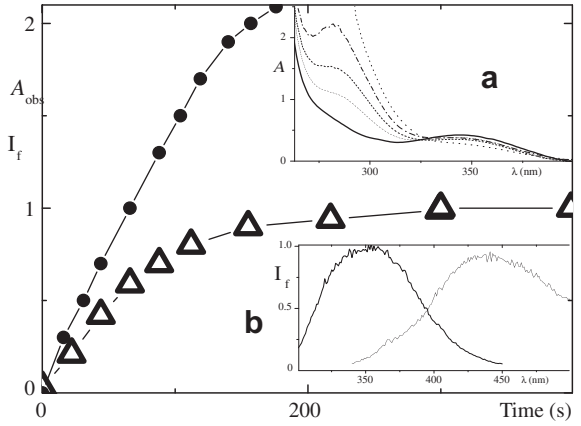


Fig. 7. Plots of A_{290} (●) and the fluorescence intensity at 460 nm (Δ, λ_{exc} = 350 nm) for nitrendipine in argon-saturated acetonitrile in the presence of 0.1 M TEA as a function of the time of irradiation at 313 nm; inset: (a) absorption spectra at 0, 30, 80, 120 and 180 s and (b) fluorescence emission and excitation spectra after 3 min irradiation.

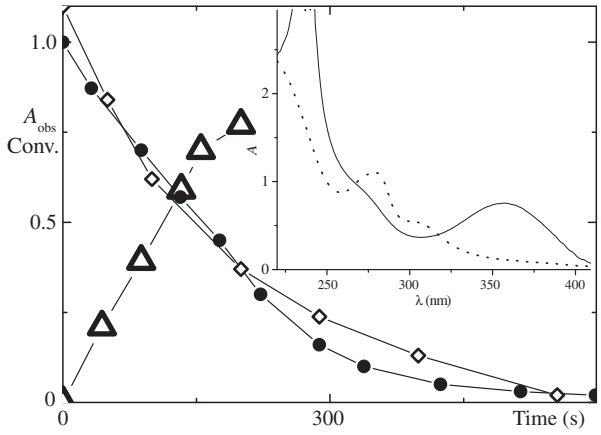


Fig. 6. Plots of A_{260} (o) and A_{360} (▲) and the fraction of decomposition for nimodipine (●) in argon-saturated 2-propanol as a function of the time of irradiation at 313 nm; inset: absorption spectra at 0 and 500 s.

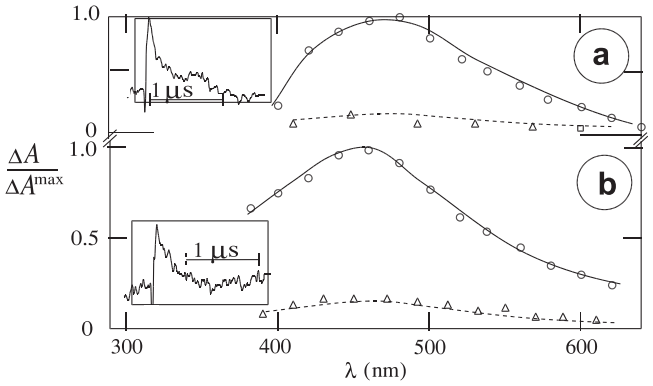


Fig. 8. Transient absorption spectra of (a) nimodipine and (b) nitrendipine in argon-saturated acetonitrile at 20 ns (○) and 1 μs (Δ) after the 308 nm pulse; insets: kinetics at 460 nm.

Table 3
Quantum yield of reduction of 4-(3-nitrophenyl)-1,4-dihydrophenylpyridines[a].

Compound	Solvent	Additive	Φ_{red}
Nimodipine	Acetonitrile	None	0.002
	Acetonitrile	TEA[b]	0.01
	Methanol	Methanol	0.02
	2-Propanol	2-Propanol	0.03
Nitrendipine	Acetonitrile	None	0.002
	Acetonitrile	TEA[c]	0.03
	2-Propanol	2-Propanol	0.02

[a] In argon-saturated solution using λ_{irr} = 313 nm.
[b] 0.1 M.
[c] 0.7 M.

the presence of TEA, an example is shown in Fig. 7 for nitrendipine. Insets (a) of the absorption spectra prior to and upon irradiation at 313 nm and (b) of the fluorescence emission and excitation spectra of the photoproducts are consistent with reduction via intermolecular electron transfer.

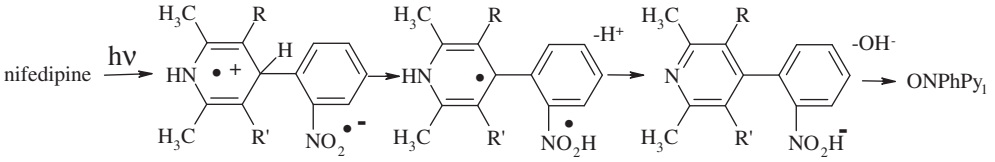
The transient absorbance of nimodipine and nitrendipine in acetonitrile upon 308 nm excitation is weak, examples are shown in Fig. 8. The end-of-pulse transient is attributed to the triplet state. The lifetime of the nimodipine or nitrendipine triplet state in argon-saturated acetonitrile is ca. 0.3 μs. The triplet state is quenched by oxygen and 2-propanol. In the presence of 2-propanol a longer lived radical is formed. Decay of the triplet state is also accelerated on addition of TEA, thereby yielding a radical anion which decays within 0.005–0.5 ms (not shown).

4. Discussion

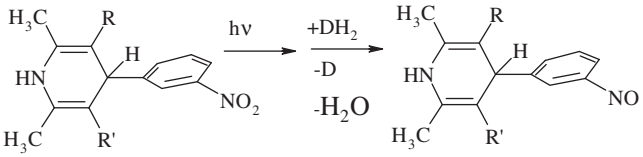
4.1. Mechanism of photoreduction of nifedipine

The absorbance of nifedipine at 300–380 nm decreases during the pulse and this bleaching remains permanent (Figs. 1–4), indicating conversion without involvement of a triplet state. This is in agreement with a negligible Φ_Δ value [14]. The fast conversion of nifedipine into $ONPhPy_1$ without involvement of a triplet state is compatible with intramolecular H-atom transfer and a biradical intermediate [15], Scheme 2, Φ_{red} = 0.3. The reaction could take place in the excited singlet state, but the triplet pathway in most nitroarenes [32–34] makes this singlet pathway unlikely. The conversion is relatively insensitive to variation of the solvent polarity (Table 2).

A minor photoproduct of nifedipine could be the corresponding nitrophenylpyridine. This photodehydrogenation has been proposed to be enhanced by UV-light [2], but this idea was later rejected [3]. Apparently, the photoreduction stops at the stage of



Scheme 2.



Scheme 3.

the nitroso compound. This is due to the absence of H-atom donors. Nevertheless, further reduction of $ONPhPy_1$ in 4-(2-hydroxylaminophenyl)-1,4-dihydropyridine or 4-(2-aminophenyl)-1,4-dihydropyridine, which requires the respective two or four additional electron equivalents, is indicated by fluorescence spectroscopy, see Fig. 5. Oxidation of various 3,4-dihydropyimidin-2-(1*H*)-ones and 1,4-dihydropyridines have been reported [35,36].

4.2. Photoreduction of 4-(3-nitrophenyl)-1,4-dihydropyridines

The quantum yield of formation of singlet molecular oxygen using $\lambda_{irr} = 355$ nm is $\Phi_\Delta = 0.04$, 0.02 and 0.001 for nitrendipine in benzene, acetonitrile and ethanol, respectively [14]. This indicates a low Φ_{isc} for 4-(3-nitrophenyl)-1,4-dihydropyridines and is in agreement with a weak triplet state formation of nimodipine (Fig. 8(a)) and nitrendipine (Fig. 8(b)) and a low Φ_{red} in acetonitrile. In fact, $\Phi_{red} = 0.004$ for nimodipine in acetonitrile, while $\Phi_{red} = 0.01$ in methanol [24]. A 10-fold enhancement in ethanol ($\Phi_{red} = 0.02$, $\lambda_{irr} = 366$ nm) vs. acetonitrile ($\Phi_{red} = 0.002$) has been reported [25]. An enhancement of Φ_{red} was also found with TEA [24]. Reactions of the triplet state of nimodipine and nitrendipine with alcohols and TEA are indicated by weak longer lived transients at 400–500 nm (not shown). The photoprocess is ascribed to electron transfer from TEA to the triplet state [2] and H-transfer from the alcohol as reactive steps. HPLC analyses for nimodipine and nitrendipine revealed more than three product peaks and one of the primary photoproducts is nitrosoPhH_2Py (Scheme 3), derived via radical termination, step 3.

$$^{1*}O_2NPhH_2Py \rightarrow {}^{3*}O_2NPhH_2Py \rightarrow O_2NPhH_2Py \quad (1)$$

$$^{3*}O_2NPhH_2Py + NEt_3 + H^+ \rightarrow {}^{\cdot}HO_2NPhH_2Py + {}^{+\cdot}NEt_3 \quad (2)$$

$$2 \times {}^{\cdot}HO_2NPhH_2Py \rightarrow ONPhH_2Py + O_2NPhH_2Py + H_2O \quad (3)$$

No equilibrium between the $^{\cdot}HO_2NPhH_2Py$ and $^{-\cdot}O_2NPhH_2Py$ radicals appears to be established in benzene or wet acetonitrile. The TEA-derived radicals decay within 0.1 ms. The rather long ranging intermediacy of the radicals excludes electron back transfer as a major reaction which, however, occurs in the presence of DABCO. A 3-hydroxylamino or 3-amino product is indicated by fluorescence analysis of a 4-(3-nitrophenyl)-1,4-dihydropyridine/TEA system (inset (b) of Fig. 7). For a series of unsymmetrically substituted 1,4-dihydropyridines reduction products have been characterized [27]. Thermal degradation has also been reported for nitrendipine, the rate is largest at pH 12 [21].

4.3. Comparison with photoreduction of other nitroarenes

The full intramolecular reduction of nifedipine into the 4-(2-aminophenyl)-1,4-dihydropyridine, which requires six electron equivalents, is feasible as minor side reaction (see above). A related intermolecular full reduction into the corresponding 4-(3-aminophenyl)-1,4-dihydropyridines was not observed. For various nitrocompounds the full reduction does not take place. For nitrobenzene, a combination (self-termination) of the radicals leads to dimerization products [32–34,37–44]. Apparently, this radical dimerization is much more efficient than a pathway to the amino-product. This is different for 1-nitro-9,10-anthraquinone and the 2-methyl derivative [45,46]. The first step is population of the triplet state, then H-transfer from the alcohol generates nitroAQ-derived radicals which combine bimolecularly into nitroAQ and nitrosoAQ. The same radical can be produced by electron transfer from an amine. Further electron transfer steps occur, whereby 1-aminohydroxylAQ is formed. The quantum yield of complete reduction is up to 0.2. Various sensitizer-donor couples with ketones and alcohols or amines can be used to achieve efficient conversion. For 1-nitroAQs the carbonyl groups function as H-atom acceptor sites [47].

5. Conclusion

The conditions for the efficient photoconversion of nifedipine into its corresponding 4-(2-nitrosophenyl)pyridine were examined, the nature of the solvent has only a minor influence. The photoreduction of nifedipine is a rare case, where the formation of a stable nitroso compound is documented. The fully reduced 4-(2-aminophenyl)-1,4-dihydropyridine as minor primary photoproduct was observed by fluorescence spectroscopy. The triplet states of nimodipine and nitrendipine in acetonitrile has been observed by flash photolysis. The intermolecular photoreduction steps of the two 3-nitrophenyl-1,4-dihydrophenylpyridines in the presence of TEA and 2-propanol were analyzed.

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