

# UV-vis study of some non persistent nitroxyl radicals

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*N*-hydroxy-3,4,5,6-tetraphenylphthalimide has been synthesized and was employed together with other *N*-hydroxyl compounds, like *N*-hydroxyphthalimide, *N*-hydroxybenzotriazole and violuric acid to generate the corresponding nitroxyl radicals by mono-electronic oxidation with cerium salts or two-electrons oxidation with lead tetraacetate. The obtained nitroxyl radicals were analyzed by means of UV-vis spectroscopy.

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**Keywords:** *N*-hydroxyphthalimide (NHPI), phthalimide-*N*-oxyl (PINO), *N*-hydroxytetraphenyl phthalimide (NHTPPI), Tetraphenylphthalimide-*N*-oxyl (TPPINO), *N*-hydroxybenzotriazole (BTN), benzotriazole-*N*-oxyl (BTNO), Violuric acid (VA), UV-vis

## 1. Introduction

Nonpersistent *N*-oxyl radicals like phthalimide-*N*-oxyl (PINO), tetraphenylphthalimide-*N*-oxyl (TPPINO),

benzotriazole-*N*-oxyl (BTNO) and violuric acid-*N*-oxyl (VANO) (Fig. 1) have gain considerable attention in organic and catalytic chemistry.

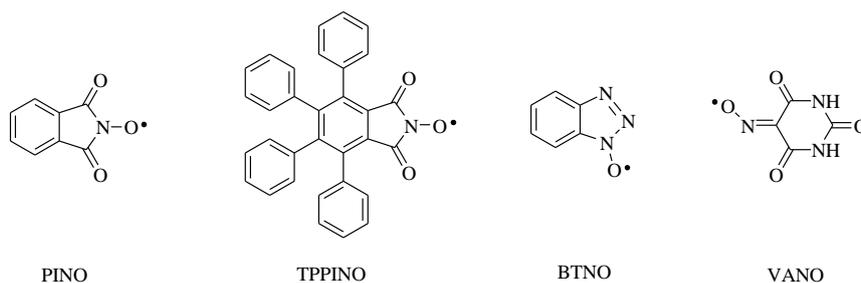
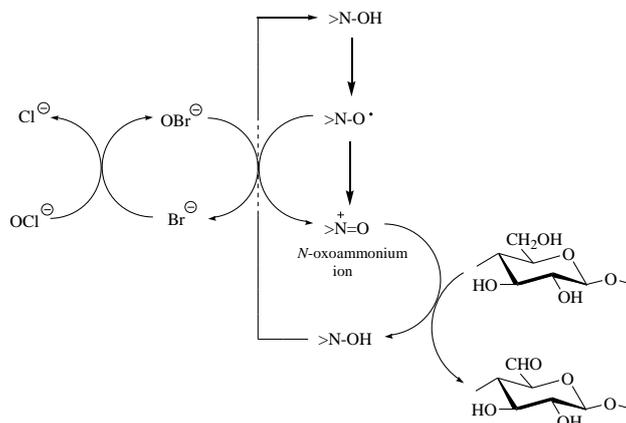


Fig. 1. Structures of non persistent radicals: PINO, TPPINO, BTNO, VANO.

This interest on studying the chemistry of non persistent *N*-oxyl radicals is due to they are valuable catalysts in aerobic oxidation of a wide range of organic compounds [1-6], and also they play an decisive role in the oxidative degradation of lignin promoted by the laccase/O<sub>2</sub> system [7-8], which is a key step in the pulp and paper industry [9]. It has been previously shown [4-6] a remarkable catalytic effect of these nitroxyl radicals for

the oxidation of alcohols, alkylarenes, amides, and even alkanes. Very recently [2, 4], a different mechanism of oxidation of viscose fibers in the presence of various non persistent nitroxyl radicals has been reported. In this case, the nitroxyl radical generated *in situ*, is converted into its corresponding *N*-oxoammonium ion, in the presence of hypobromide species, Scheme 1.



Scheme 1. Oxidation scheme of cellulose fibers using *N*-oxoammonium ions.

NHPI has been found to catalyse the mild oxidation of two types of regenerate cellulose fibres with molecular oxygen as ultimate oxidizing agent. It is worth to note that the degree of polymerization and molar mass of the oxidized fibres determined viscometrically, has been found to be almost unaffected after oxidation in these conditions [10].

Since the literature information about these four nitroxyl radicals are presented only in disparate manner, we have found of interest to study the *in situ* generation of the above mentioned radicals by using a near at hand technique, such as UV-vis absorption spectroscopy.

## 2. Experimental

### Materials

*N*-Hydroxyphthalimide (NHPI), 1-hydroxybenzotriazole (BTN) and violuric acid (VA) were used as received.

Cerium (IV) ammonium nitrate (CAN) was oven-dried before use. Lead tetraacetate (Aldrich) was used without purification. Reagent grade glacial acetic acid and spectrophotometric grade acetonitrile (CH<sub>3</sub>CN), distilled over CaH<sub>2</sub> were used as solvents. Ferrocene (FcH) is commercially available and was purified by sublimation.

The synthesis of *N*-hydroxy-3,4,5,6-tetraphenylphthalimide (NHTPPI) was performed using an improved procedure of a method already described in the literature, [11] tetraphenylphthalic anhydride (0.44 g, 0.98 mmol) and hydroxylamine hydrochloride (0.076 g, 1.09 mmol) were mixed in pyridine (5 mL). After stirring at room temperature for 2 hours, the reaction mixture was heated at 100 °C for 4 h. Pyridine was next evaporated at vacuum, and a 2 M solution of hydrochloric acid was added to the crude reaction mixture until pH becomes acidic (2-3). The yellow precipitate was filtered, washed with water and dried under vacuum. Twice recrystallization from ethanol gave pure NHTPPI (0.33 g) in 71% yield.

Melting point 295 – 297 °C; <sup>1</sup>H NMR (CDCl<sub>3</sub>) δ = 7.21-7.18 (m, 6H), 7.11-7.08 (m, 4H), 6.90-6.88 (m, 6H), 6.74-6.71 (m, 4H), 1.7 (bs, 1H); <sup>13</sup>C NMR (CDCl<sub>3</sub>) δ = 163.4, 147.9, 139.5, 137.8, 135.1, 130.6, 129.8, 127.3, 127.2, 126.9, 126.3, 125.1; IR (KBr): 3255, 3061, 1777, 1731, 1444, 1092 cm<sup>-1</sup>.

MS (DCI, NH<sub>3</sub> + isobutene) *m/z* = 525, 508, 485, 469, 452.

### Instrument

The electronic absorption spectra were recorded using a SPECORD 200 Analytik Jena spectrometer.

## 3. Results and discussion

Fig. 2 shows the UV-vis absorption spectra of the starting materials. The hydroxyl precursors exhibit strong absorptions in the range of 250 – 320 nm, thus λ<sub>max</sub> has a value of 250 nm for VA, 294 nm for NHPI, 258 nm for BTN and 320 nm for NHTPPI, respectively.

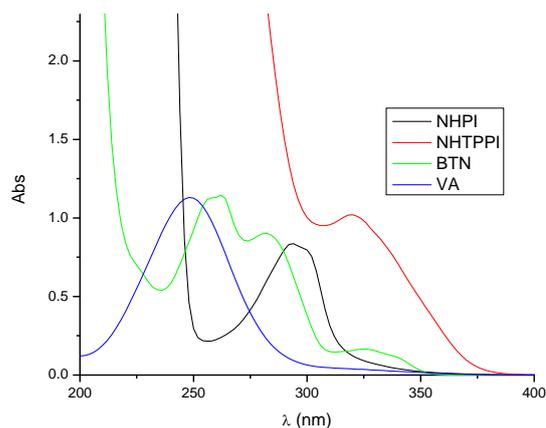
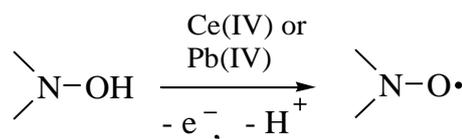


Fig. 2. UV-vis spectrum of NHPI, NHTPPI, BTN and VA (0.5 mM) in MeCN in the absence of any cocatalyst.

The generation of the aminoxyl radicals from their OH correspondents have been achieved by using either a mono-electronic oxidation with CAN or two-electrons oxidant such as Pb(OAc)<sub>4</sub>, in MeCN, Scheme 2.



Scheme 2. Generation of nitroxyl radicals from their OH correspondents.

Generation of the PINO radical from its OH precursor, NHPI is not easily detectable by UV-Vis technique. Thus in the case of using lead tetraacetate as cocatalyst, no characteristic absorption bands for PINO generation has been found, (Fig. 3, a). Replacing lead tetraacetate by cerium salts, i.e. CAN, an absorption band close to 382 nm instantly appears, which correspond to the PINO formation, (Fig. 3, b). The PINO radical presence can be better distinguished in the presence of β-cyclodextrin, (Fig. 3, c).

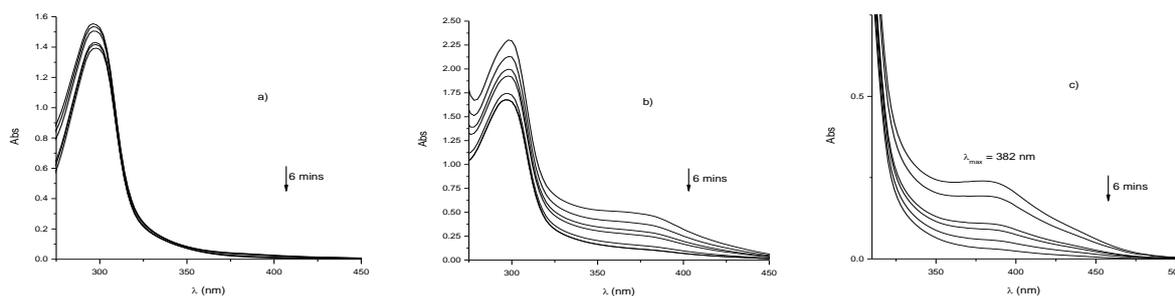
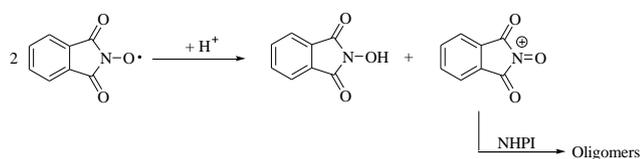


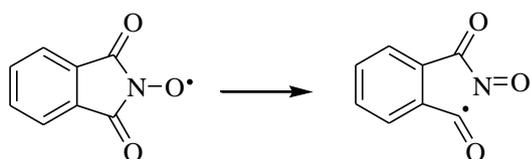
Fig. 3. UV-vis spectra of a  $\text{CH}_3\text{CN}$  solution containing NHPI (0.5 mM) in the presence of (a) lead tetraacetate (0.5 mM), (b) CAN (0.5 mM), (c) lead tetraacetate (0.5 mM) and  $\beta$ -cyclodextrine (1 mM).

The self-decomposition reaction of nitroxyl radicals obeys second-order kinetics [12]. Scheme 3 illustrates this reaction in the case of PINO radical.



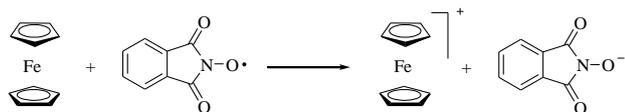
Scheme 3. The self-decomposition reaction of PINO following second-order kinetics.

However, it was reported that PINO self-decomposition could obey first-order kinetics with the fragmentation of the carbonyl carbon-nitrogen bond, Scheme 4 [13].



Scheme 4. The self-decomposition reaction of PINO following first-order kinetics.

The reactions, however, were too fast to be followed spectrophotometrically, we have considered it worthwhile by investigating the reactivity of PINO and other highly reactive nitroxyl radicals in the oxidation with ferrocene to the corresponding ferrocenium cations, a genuine electron-transfer reaction [14], Scheme 5.



Scheme 5. Reaction of PINO with ferrocene.

In this case, the characteristic absorption band of the nitroxyl radical, i.e.  $\lambda_{\text{max}}$  382 nm for the PINO disappeared and is immediately replaced by that of the

ferrocenium cation, characterized by absorption maxima in the 600 – 675 nm region of the spectrum (Fig. 4) [15].

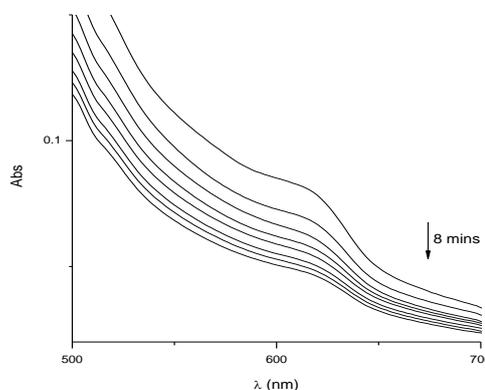


Fig. 4. UV-vis spectra of a  $\text{CH}_3\text{CN}$  solution containing NHPI (1.52 mM) and  $\text{Pb}(\text{OAc})_4$  (0.64 mM) in the presence of ferrocene (0.5 mM) and 1% (v/v) acetic acid.

In the case of NHTPPI, the presence of the corresponding nitroxyl radical, TPPINO, when a CAN solution was added is hardly visible spectrophotometrically, Fig. 5.

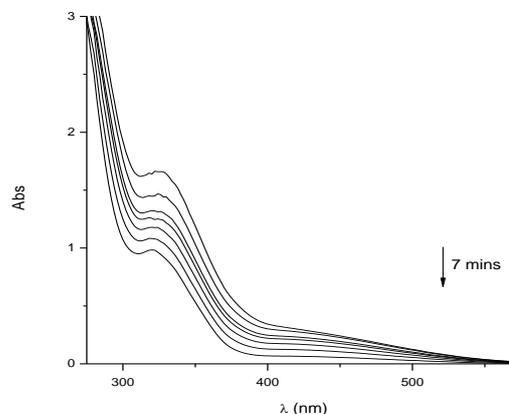


Fig. 5. UV-vis spectra of a  $\text{CH}_3\text{CN}$  solution containing NHTPPI (0.48 mM) and CAN (0.51 mM).

In this case, we have also used the reaction of NHTPPI with ferrocene, which allow to determine indirectly the presence of TPPINO, by the formation of ferrocenium cation which absorb in the range of 600 – 650 nm, Fig. 6.

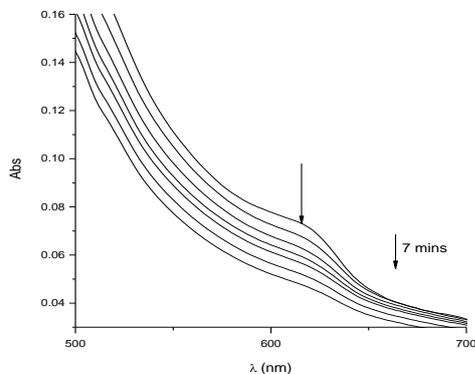


Fig. 6. UV-vis spectra of a  $CH_3CN$  solution containing NHTPPI (0.48 mM) and CAN (0.51 mM) in the presence of ferrocene (0.5 mM).

Hydroxylamines, such as BTN or VA, have recently shown their proficiency towards phenols oxidation in lignin in the presence of enzyme laccase [16, 17]. The nitroxyl radical intermediate from these >N-OH mediators, generated in situ, through laccase mediation, performs as active species and promoted the radical cleavage of benzylic C-H bonds. The first generation of the aminoxyl BTNO by monoelectronic oxidation with CAN in acetonitrile has been recently reported [18]. The absorption spectrum of a 0.52 mM BTN solution in acetonitrile in the presence of 0.53 mM CAN is presented in Fig. 7.

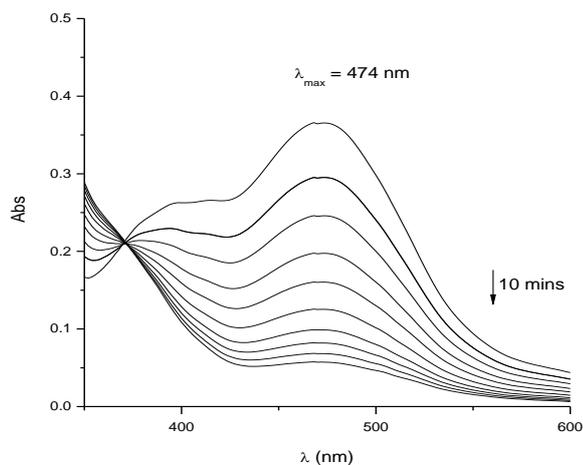


Fig. 7. UV-vis spectra of a  $CH_3CN$  solution containing BTN (0.52 mM) and CAN (0.53 mM).

Following the addition of the monoelectronic oxidant CAN in acetonitrile at 25 °C, a new strong and broad

absorption band in the 350 - 600 nm range develops having  $\lambda_{max}$  at 474 nm which corresponds to the newly BTNO radical formation. The BTNO radical formation can be also distinguished when ferrocene has been used to react with the parent >N-OH, BTN, see Fig. 8.

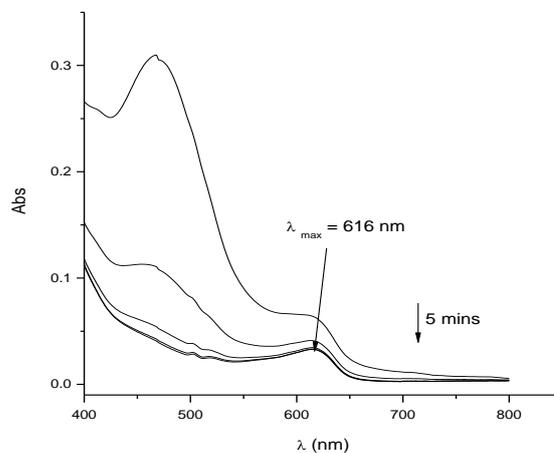


Fig. 8. UV-vis spectra of a  $CH_3CN$  solution containing BTN (0.52 mM) and CAN (0.53 mM) in the presence of ferrocene (0.5 mM).

Fig. 8 shows the ferrocene absorption together with spectra of an acetonitrile solution containing 0.52 mM BTN, 0.53 mM CAN and ferrocene 0.5 mM. It can be seen that at the first stage (after 1 minute, the BTNO absorption at 474 nm is present together with the corresponding absorption of the ferrocenium cation at 616 nm. After 2 minutes, the BTNO absorption totally disappeared being replaced by the absorption of ferrocenium cation.

The absorption spectrum of a 0.5 mM VA solution in acetonitrile in the presence of 0.5 mM CAN is presented in Fig. 9.

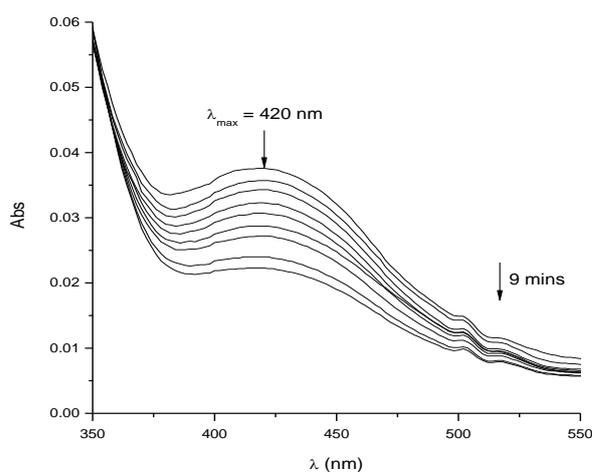


Fig. 9. UV-vis spectra of a  $CH_3CN$  solution containing VA (0.5 mM) and CAN (0.5 mM).

After the addition of CAN in acetonitrile at 25 °C, in a 0.5 mM solution of VA, a new and broad absorption band

in the 375-500 nm range develops having  $\lambda_{\text{max}}$  at 420 nm which corresponds to the newly VANO radical formation.

#### 4. Conclusions

Supplemental characterization of PINO, TPPINO, BTNO and VANO by laser flash photolysis, EPR and cyclic voltametry are in progress and would be reported at a later due.

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