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A comparison between nitroxide and hydrazyl free radicals in selective alcohols oxidation

Ahmed J. Shakir,¹ Augustin M. Madalan,¹ Gabriela Ionita,² Stelian Lupu,³ Cecilia Lete,² Petre Ionita^{1,2*}

¹ University of Bucharest, Faculty of Chemistry, Department of Organic Chemistry, Biochemistry and Catalysis, Panduri 90-92, Bucharest, Romania. E-mail: pionita@icf.ro ² Institute of Physical Chemistry, Spl. Independentei 202, Bucharest, Romania ³University Politehnica Bucharest, Polizu 1, Bucharest, Romania

Abstract

Literature data are abundant in oxidations catalyzed by nitroxides free radicals, while hydrazyls free radicals are very seldom encountered. In this work we made a comparison between some nitroxides and hydrazyl free radicals towards the ability to selectively oxidize activated alcohols to the corresponding carbonyl derivatives. As nitroxides we used 2,2,6,6-tetramethylpirrolidin-*N*-oxide (TEMPO) and phtalimide-*N*-oxyl (PINO) free radicals, while as hydrazyls were used 2,2-diphenyl-1-picrylhydrazyl (DPPH) and 2,2-*p*-nitrophenyl-1-picrylhydrazyl (DN-DPPH). The differences in the physico-chemical properties between nitroxides and hydrazyls were evaluated by UV-Vis, EPR and cyclic voltammetry. For DN-DPPH the X-ray crystal structure was resolved. It has been shown that a nitroxide radical is a far better catalyst in such aerobic oxidations comparatively with a hydrazyl one. The explanation of these results consists firstly in a different mechanism involved in the oxidation procedures and secondly in the variation of the oxidation potentials of nitroxides comparatively with hydrazyls.

Keywords:

TEMPO; DPPH; PINO; Free radical; Oxidation

1. Introduction

Selective oxidation of primary and secondary alcohols to the corresponding aldehydes and ketones is one of the most problematic reactions in organic chemistry [1]. A classical procedure usually involves transition metal ions in at least stoichiometric quantities, which eventually leads to the following two important issues: *i*) separation of the desired product and *ii*) management of the large quantities of transition metal ion by-products.

As a consequence of these major difficulties, there is a continuous interest in the improvement of such procedures or in the developing of new ones [2-4]. A better approach should avoid the environmental negative matter and diminish the work-up protocol, thus making possible large-scale or even industrial applications.

Currently, there are under consideration novel catalytic methods that involve clean oxidants like air, hydrogen peroxide or sodium hypochlorite and non-metallic catalysts [5,6]. A promising and nowadays well documented procedure makes use of stable or persistent free radicals as catalyst and of air as final oxidant [7].

In the last decade nitroxides stable free radicals were successfully used as organocatalyst for a wide range of oxidations, including here those considered green (i.e. using air as oxidant, solvent free reactions, high selectivity, mild conditions, etc.) [8-10]. Among nitroxides, 2,2,6,6-tetramethylpirrolidin-*N*-oxide (TEMPO) and phtalimide-*N*-oxyl (PINO) free radicals are most known and employed in such reactions (Fig. 1), due to their effectiveness [11-13].

Other stable free radicals, which also have oxidant capacities, are hydrazyl ones, like 2,2-diphenyl-1-picrylhydrazyl free radical (well known in literature as DPPH), and its congener 2,2-*p*-nitrophenyl-1-picrylhydrazyl (DN-DPPH, Fig. 1). However, up to date, there are very few papers containing data about involving such stable hydrazyl free radicals as catalyst in oxidation reactions [14, 15].



Figure 1. Chemical structure of TEMPO, PINO, DPPH and DN-DPPH

Although there are available numerous publications of quantitative data about the efficiency of TEMPO or PINO in this type of catalytic oxidation reactions, no direct comparison between them is available; in addition, many literature data reports on different reaction conditions [13, 14]. In an attempt to compare the catalytic properties of TEMPO with PINO, in our work we used as substrates three activated alcohols (benzyl alcohol, 2-phenylethanol and diphenylcarbinol, Table 1) and several co-catalyst (different NO_x generating systems and sodium hypochlorite); moreover, we introduced in this comparative study, for the first time, the use of the stable hydrazyl free radical DN-DPPH, as it is shown below.

2. Results and Discussion

2.1 General remarks, synthesis and comparison of the free radicals characteristics

All the free radicals used in this study are known in literature. TEMPO and DN-DPPH are indefinitely stable free radicals under usual conditions (meaning that they do not decompose in time, dimerize nor react with atmospheric oxygen), while PINO is considered a persistent free radical, as is decomposing slowly in time (therefore it has to be prepared just before use; it is simply obtained *in situ* by oxidation of *N*-hydroxyphtalimide (NHPI) with different reagents, like lead dioxide, lead tetra-acetate, nitrogen dioxide, etc. [11]).

Because DN-DPPH is not a commercially available product, our first step in our work was to synthesize it starting from DPPH. This reaction is easily performed in a biphasic system by reacting DPPH (dissolved in dicloromethane, DCM) with nitrogen dioxide generated by an aqueous mixture of sodium nitrite and diluted hydrochloric acid [16]. DPPH is a good scavenger of nitrogen dioxide, leading finally to the desired product in about 90% yields (see Experimental part).

By chance, we obtained good quality crystals of DN-DPPH and therefore this compound was also characterized also by X-Ray diffraction. DN-DPPH crystallizes in the *P-1* triclinic space group and the asymmetric unit contains two DN-DPPH molecules and two DCM solvent molecules. The two crystallographically independent molecules of DN-DPPH have similar conformations (Fig. 2). The nitro groups of the *p*-nitrophenyl moieties lie almost in the planes of the phenyl rings. The dihedral angles formed by these groups with the mean planes of the corresponding phenyl rings are: 3.41° (N6O7O8), 3.85° (N7O9O10), 3.25°

(N13O17O18) and 16.68° (N14O19O20). The dihedral angles formed by the *ortho* nitro groups with the mean planes of phenyl rings in the picrylhydrazyl fragments are significant higher compared with that formed by the *para* groups: 55.45° (N2O3O4), 35.47° (N3O5O6), 48.07° (N9O13O14), 32.20° (N10O15O16), respectively 11.08° (N1O1O2) and 14.17° (N8O11O12). It is worth to mention that the N–N bond distance in DPPH is shorter than in substituted hydrazine derivatives [17-19]. The bond lengths for the two DN-DPPH molecules are gathered in Supplementary Material (SM), Table S1. Fig. 2 shows the crystal structure of DN-DPPH (DCM molecules were removed for clarity, but the packing diagram in the crystal structure along with more pictures are shown in SM, Fig. S1-S3).



Figure 2. View of the two crystallographic independent DN-DPPH molecules

Usually, the best method to characterize free radicals is by electron paramagnetic resonance (EPR). For TEMPO and PINO, the spectra showed the expected triplet, due to the interaction of the unpaired electron with the ¹⁴N nucleus; the hyperfine coupling constants are $a_N = 15.7$ G for TEMPO, while for PINO $a_N 4.8=$ G. DPPH give five lines, as the two hyperfine coupling constants are very close ($a_{N1} = 9.0$ G, $a_{N2} = 8.9$ G). A very different spectrum is recorded for DN-DPPH, showing the interaction of the unpaired electron with two different ¹⁴N nucleus ($a_{N1} = 10.9$ G, $a_{N2} = 6.9$ G). The EPR spectra are shown as Fig. S4 in SM.

Another interesting feature of these free radicals is their colour. UV-Vis spectra of TEMPO showed an absorption band at $\lambda_{max} = 440$ nm, PINO at $\lambda_{max} = 380$ nm, DPPH at $\lambda_{max} = 515$ nm, and DN-DPPH at $\lambda_{max} = 475$ nm. The UV-Vis spectra are shown as Fig. S5 in SM. It is worth to mention that there is a big change in colour of the free radical compared with the

colour of the reduced counterpart, therefore this property can be used even as a naked-eye indicator of a reaction progress.

Because these free radicals will be used in oxidation reactions, it was worth to find out their oxidation potential E_{ox} , and this was achieved by employing cyclic voltammetry (CV). The electrochemical behavior of the employed compounds was investigated in acetonitrile by Pt electrode using cyclic voltammetry (CV) at various potential scan rates ranging from 50 to 500 mV/s. Figure S6 from SM displays the CVs recorded for TEMPO, PINO, DPPH and DN-DPPH compounds, at a scan rate v of 100 mV/s. The shape of the CV recorded for TEMPO shows one redox wave (reversible oxidation-reduction process), while the DPPH and DN-DPPH compounds display two redox waves. In the case of PINO, the CV shape indicates a quasi reversible redox wave followed by an irreversible oxidation wave. The scan rate study has shown that the redox processes for all compounds are diffusion-controlled, according to the slope values of the log(i_p) vs. log(v) plots which were *ca*, 0.5.

The values obtained *vs.* Ag/AgCl were 0.54 V for TEMPO, 0.59 V for PINO, 0.08 V for DPPH and 0.39 V for DN-DPPH (similar values are presented in literature [20]).

2.2 Free radicals as oxidant catalysts

Due to our previous experience in selective oxidations of alcohols using TEMPO derivatives as catalysts [10], in this work we chosen as co-catalysts different NO_x generating systems; besides, we used also sodium hypochlorite, as this system was one of the first used in literature in such catalytic oxidation reactions [21, 22]. Thus, the co-catalyst named A was a mixture of sodium nitrite and acetic acid, as co-catalyst B was used nitrosonium tetrafluoroborate, co-catalyst C was sodium hypochlorite while co-catalyst D was gaseous nitrogen dioxide (see also Table 1).

Typically, the oxidation reactions of the chosen alcohols (Table 1) were performed at room temperature in air atmosphere, using a ration of 10% mol free radical and 20% mol cocatalyst. The yields of oxidations were quantified by ¹H-NMR and the values obtained are compiled in Table 1.

Entry	Catalyst	Co-catalyst	Alcohol	Yields (%)
1	TEMPO			63
2	PINO		UH UH	9
3	DN-DPPH			0
4	TEMPO	NaNO ₂ /		39
5	PINO	СП3СООП	ОН	10
6	DN-DPPH	(A)		0
7	TEMPO	(A)	OH	28
8	PINO			16
9	DN-DPPH			25
10	TEMPO			100
11	PINO		() OH	4
12	DN-DPPH			30
13	TEMPO	$NO^+BF_4^-$		100
14	PINO		ОН	44
15	DN-DPPH	(<i>B</i>)		16
16	TEMPO		OH	100
17	PINO			95
18	DN-DPPH			25
19	TEMPO			100
20	PINO		UH UH	16
21	DN-DPPH	N _a ClO/	×	9
22	TEMPO	NaCIO/		100
23	PINO	KDI	ОН	38
24	DN-DPPH	(\mathbf{C})		7
25	ТЕМРО	(C)	OH	100
26	PINO			28
27	DN-DPPH			53
28	TEMPO			100
29	PINO		UH	0
30	DN-DPPH			1
31	TEMPO	NO_2		16
32	PINO		ОН	10
33	DN-DPPH	(<i>D</i>)		0
34	TEMPO		OH	100
35	PINO			0
36	DN-DPPH			25

 Table 1. Yields of oxidation

As a general rule, the first thing that emerges from the Table 1 is that TEMPO is a much better catalyst compared with PINO and DN-DPPH. For all alcohols used and also for all used co-catalysts, TEMPO performed better, reaching quantitative oxidation yields for nitrosonium tetrafluoroborate and sodium hypochlorite co-catalyst (Entries 10, 13, 16, 19, 22, 25); moreover, in the case of nitrogen dioxide as co-catalyst the same yields were found for

benzyl alcohol and diphenylcarbinol (Entries 28 and 34, respectively). However, PINO seems to be particularly good for oxidation of diphenylcarbinol in the presence of nitrosonium tetrafluoroborate (yield 95%, Entry 17). Compared with the other two free radicals, DN-DPPH gave usually the lowest yields (DPPH has not been used in this procedure as it is converted to DN-DPPH by nitrogen dioxide [16]).

2.3 Mechanisms of oxidation

The high differences between the oxidation yields obtained by different free radicals might be attributed to different oxidation capacity and also to different reaction mechanisms. As mentioned before, the highest E_{ox} values have been recorded for TEMPO (0.54 V) and PINO (0.59 V), comparatively with DPPH (0.08 V) and DN-DPPH (0.39 V), and therefore this can explain the better performance of nitroxides comparatively with hydrazyls. Regarding the mechanisms of oxidation, there are two ways of action, one for nitroxide (*I*) type free radicals and one for hydrazyl (*II*). Fig. 3 shows these mechanistic pathways in a simplified manner.



Figure 3. The two proposed mechanisms of oxidation, involving a nitroxide (*I*) and a hydrazyl (*II*) free radical

For the type *I* mechanism, the now classical pathway involving oxoammonium salt is taking place [14, 23]. Thus, the nitroxide radical (TEMPO or PINO) is oxidized *via* one electron transfer to the more powerful oxoammonium oxidant, and this oxidizes the alcohol to the corresponding aldehyde or ketone. The hydroxylamine formed is easily re-oxidized even by air to the nitroxide radical, thus closing the catalytic cycle. Using NHPI instead of TEMPO, the same pathway is followed, as the oxidant (nitrogen dioxide or sodium hypochlorite) re-generates *in situ* the PINO nitroxide free radical.

A simpler catalytic cycle is taking place using DN-DPPH (type *II* mechanism). A hydrazyl free radical is able to directly extract hydrogens atom from the alcohol, leading finally to the desired oxidation product. While the *H*-atoms are extracted (this depends on bond dissociation energy [24, 25]), DN-DPPH is reduced to the corresponding hydrazine, and this is re-oxidized in the reaction mixture (i.e. by nitrogen dioxide) to the starting hydrazyl free radical. It is worth to mention that in both mechanisms the final oxidant is the oxygen from air, nitrogen dioxide having its own catalytic cycle, as well it is documented in literature [10-14].

3. Experimental

3.1 Chemicals, materials and methods

All chemicals, solvents and materials were purchased from Sigma-Aldrich, Acros or Chimopar and used as received.

UV-Vis spectra were recorded on a UVD-3500 spectrophotometer at room temperature using 1 cm quartz cells and acetonitrile as solvent.

EPR spectra were recorded in acetonitrile at room temperature on a Jeol JES FA 100 apparatus. NMR spectra were recorded in deuterated chloroform on a Bruker Fourier apparatus at 300 MHz.

Cyclic voltammetry (electrochemical measurements) were performed using a potentiostat/galvanostat Autolab 302N connected to a PC running the software GPES (Ecochemie, Utrecht, The Netherlands), in an electrochemical cell (Metrohm) with a three electrodes system. A Pt disk electrode (diameter of 3 mm) was used as working electrode, a glassy carbon rode was the auxiliary electrode, and a Ag/AgCl electrode was used as reference electrode. The potential of Ag/AgCl electrode was measured against the ferrocene/ferricinium redox couple (Fc/Fc⁺) potential, which was of 0.27 V. The cyclic voltammograms (CVs) were recorded in acetonitrile containing the free radical at a concentration of 2 mmol and lithium percholate (0.1 M) as supporting electrolyte, at various potential scan rates (v) ranging from 50 to 500 mV/s. Before the measurements, the surface of the working electrode was polished with alumina powder (0.1 μ m) and then sonicated for 10 min in deionized water and, finally, throughly washed with acetone. High purity Ar (5.0, Linde Romania) was bubbled through the solution before the measurements, and an Ar blanket was maintained over the solution during the electrochemical experiments. All electrochemical experiments were performed at room temperature.

X-ray diffraction measurements were performed on a STOE IPDS II diffractometer, operating with Mo-K α ($\lambda = 0.71073$ Å) X-ray tube with graphite monochromator. The structure was solved by direct methods and refined by full-matrix least squares techniques based on F^2 . The non-H atoms were refined with anisotropic displacement parameters. Calculations were performed using SHELX-2014 crystallographic software package. A summary of the crystallographic data and the structure refinement for crystal of DN-DPPH are given in Table 2. CCDC reference number: 1526824.

Compound	DN-DPPH
Chemical formula	C ₁₉ H ₁₂ Cl ₂ N ₇ O ₁₀
M (g mol ⁻¹)	569.26
Temperature, (K)	2002)
Wavelength, (Å)	0.71073
Crystal system	Triclinic
Space group	P-1
a(Å)	12.2010(13)
b(Å)	14.4162(15)
c(Å)	14.6132(15)
<i>α</i> (°)	113.119(8)
β (°)	93.134(8)
<i>γ</i> (°)	96.763(8)
V(Å ³)	2333.1(4)
z	4
$D_{\rm c}~({\rm g~cm}^{-3})$	1.621
μ (mm ⁻¹)	0.350
F(000)	1156
Goodness-of-fit on F^2	0.971
Final <i>R1</i> , $wR_2[I>2\sigma(I)]$	0.0557, 0.1409
$R1$, wR_2 (all data)	0.0944, 0.1600
Largest diff. peak and hole $(e^{A^{-3}})$	0.865, -0.740

Table 2. Crystallographic data, details of data collection and structure refinement parameters

 for the stable free radical DN-DPPH

3.2 Synthesis of DN-DPPH

Attention: toxic nitrogen dioxide evolves during reaction and a fume hood with good ventilation is required. To 1 g DPPH (this can be also easily synthesized, see [16]) dissolved into 50 mL DCM was added 50 mL of diluted hydrochloric acid (1 M) and under vigorous stirring was added from time to time about 100 mg sodium nitrite (about 20 times during 8 h), and the mixture left overnight. Next day another portion of sodium nitrite was added and the stirring continued for 1 h (for the water solution, the pH was checked from time to time to be acidic- if not, this should be corrected by adding small amount of acid). The organic layer was separated (it is possible that DN-DPPH to precipitate partially), dried over anhydrous sodium sulphate and the solvent removed. The residue was dissolved in DCM (about 100 mL) to which 10 g of lead dioxide together with 5 g of anhydrous sodium sulphate was added; the mixture was vigorously stirred for 1 h, filtered off and the solvent removed. DN-DPPH is thus obtained as dark solid crystals. Yield ~90%.

3.3 General procedure for the oxidation of alcohols

To 0.5 mmole of one of the chosen alcohols, dissolved in 5 mL of DCM, was added 10% mol of the free radical as catalyst (TEMPO, DN-DPPH or NHPI- as precursor of PINO) and one of the co-catalysts *A-D*, and the mixture was stirred at room temperature for 24h under air. As co-catalyst *A* was used a mixture of 20% mol sodium nitrite in 5 mL of water and 0.2 mL of acetic acid; co-catalyst *B* consisted in 20% mol of nitrosonium tetrafluoroborate; co-catalyst *C* was a mixture of 0.5 mL sodium hypochlorite (5%) and 10 mg of potassium bromide [19] dissolved in 5 mL of water; co-catalyst *D* was gaseous nitrogen dioxide (5 mL) bubbled slowly into DCM solution. After completion of the reaction, the solution was filtered of using a small cotton pad and the solvent was removed using a rotavap. The residue was dissolved in 1 mL of deuterated chloroform and the NMR spectrum recorded. The yields of the reactions were calculated using the integral values obtained from ¹H-NMR spectra.

4. Conclusions

By comparing the stable nitroxide TEMPO free radical with the persistent nitroxide PINO and stable hydrazyl DN-DPPH it can be concluded that TEMPO performed much better in selective alcohol oxidation processes, in specific conditions being able to quantitatively oxidize activated alcohols to the corresponding aldehydes or ketones. Two distinct mechanisms of oxidations are involved for the nitroxide and hydrazyl radicals. In addition, the different ability of oxidation can be correlated with their oxidation potential, as measured by cyclic voltammetry.

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Supplementary Material (SM)

A comparison between nitroxide and hydrazyl radicals as catalyst in alcohols oxidation

A. J. Shakir, A. M. Madalan, G. Ionita, S. Lupu, C. Lete, P. Ionita

Table S1. Selected bond distances (Å) for the	ne DN-DPPH molecule
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N1-O2 = 1.220(4)	C1-C2 = 1.368(5)	C19-C20 = 1.371(5)
N1-O1 = 1.228(4)	C1-C6 = 1.381(5)	C19-C24 = 1.376(5)
N2-O4 = 1.212(4)	C1-N1 = 1.461(4)	C19-N8 = 1.465(4)
N2-O3 = 1.213(4)	C2-C3 = 1.372(4)	C20-C21 = 1.370(4)
N3-O6 = 1.223(4)	C3-C4 = 1.413(4)	C21-C22 = 1.408(4)
N3-O5 = 1.225(4)	C3-N2 = 1.458(4)	C21-N9 = 1.463(4)
N4-N5 = 1.340(3)	C4-N4 = 1.379(4)	C22-N11 = 1.381(4)
N6-O8 = 1.219(4)	C4-C5 = 1.411(4)	C22-C23 = 1.410(4)
N6-O7 = 1.222(4)	C5-C6 = 1.378(4)	C23-C24 = 1.379(5)
N7-O10 = 1.214(4)	C5-N3 = 1.467(4)	C23-N10 = 1.470(4)
N7-O9 = 1.215(4)	C7-C8 = 1.392(4)	C25-C30 = 1.382(4)
N8-O12 = 1.218(4)	C7-C12 = 1.393(4)	C25-C26 = 1.393(4)
N8-O11 = 1.224(4)	C7-N5 = 1.422(4)	C25-N12 = 1.433(4)
N9-O13 = 1.216(3)	C8-C9 = 1.375(5)	C26-C27 = 1.371(5)
N9-O14 = 1.220(4)	C9-C10 = 1.384(4)	C27-C28 = 1.380(4)
N10-O16 = 1.219(4)	C10-C11 = 1.383(4)	C28-C29 = 1.381(4)
N10-O15 = 1.227(4)	C10-N6 = 1.465(4)	C28-N13 = 1.469(4)
N11-N12 = 1.349(3)	C11-C12 = 1.379(4)	C29-C30 = 1.382(4)
N13-O18 = 1.214(4)	C13-C14 = 1.379(4)	C31-C32 = 1.397(4)
N13-O17 = 1.217(4)	C13-C18 = 1.396(4)	C31-C36 = 1.404(4)
N14-O20 = 1.218(5)	C13-N5 = 1.422(4)	C31-N12 = 1.412(4)
N14-O19 = 1.223(5)	C14-C15 = 1.379(4)	C32-C33 = 1.371(5)
	C15-C16 = 1.383(5)	C33-C34 = 1.389(5)
	C16-C17 = 1.375(5)	C34-C35 = 1.369(5)
	C16-N7 = 1.475(4)	C34-N14 = 1.467(4)
	C17-C18 = 1.382(4)	C35-C36 = 1.378(5)

SCRIP





Figure S2. Packing diagram in crystal structure of DN-DPPH, view along the crystallographic *b* axis





Figure S3. Packing diagram in crystal structure of DN-DPPH, view of the supramolecular dimers formed by π - π interactions

Figure S4. EPR spectra of TEMPO (a), PINO (b), DPPH (c) and DN-DPPH (d), recorded at room temperature in acetonitril (scale range 100 G).



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Figure S6. Cyclic voltammetry of TEMPO (a), PINO (b), DPPH (c), and DN-DPPH (d).

Graphical Abstract



The two proposed mechanisms of alcohol oxidation, involving a nitroxide (I) and a hydrazyl

(II) free radical

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Highlights

- Accepter • Properties of nitroxide free radicals compared with hydrazyl free radicals.
 - ٠ Nitroxide radicals better catalysts in selective aerobic oxidations.