



Research article

Diarylamine/diarylnitroxide cycle: quantum chemical and electrochemical estimation

Oleg A. Levitskiy, Vyacheslav V. Sentyurin, Tatiana V. Magdesieva^{*}

Lomonosov Moscow State University, Chemistry Dept., Leninskie Gory 1/3, Moscow, 119991, Russia

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ABSTRACT

Possibility for diarylamine/diarylnitroxide cycling via electrochemical N–O bond formation/bond breaking processes was considered using quantum-chemical and electrochemical methods. It was shown that electrochemically reduced diarylnitroxides undergo fast N–O bond cleavage in the presence of oxophilic Li ions. The possible reaction scheme was suggested. In contrast, in the presence of Na⁺ salts, aminoxyl anions are stable and can be considered as possible anodic redox active material in energy storage systems utilizing Na⁺ ions migration. Direct oxygenation of diarylaminy radicals with dioxygen yielding diarylnitroxide is not feasible; multiple competing routes involving the aromatic moiety are observed instead. The results obtained shed light on possibilities and limitations for functioning of nitroxide-based redox active electrode materials.

1. Introduction

Many radical-trapping processes protecting a wide variety of commercial products and organic materials (such as oils, lubricants, plastics, etc.) from oxidative degradation [1, 2, 3] have been postulated to be based on amine/nitroxide cycling [4]. Various mechanisms have been proposed to account for the ability of secondary amines to inhibit the autoxidation of hydrocarbons at elevated temperatures [2]. The main accent has been made on the H atom transfer reactions and amine regeneration which has been considered as a principal step in the catalytic inhibition of oxidation by aromatic secondary amines; formation and *in situ* reactions of the corresponding nitroxide radicals have been also postulated [3].

Electrochemically activated oxygenation/deoxygenation processes involving diarylamines, aminyl radicals and diarylnitroxides have not been probed yet. Meanwhile, electrochemical oxygenation of amines (or aminyl radicals) might be of interest as new alternative route to aryl-nitroxides. Previously, it has been reported that dialkylaminyl radical formed in electrooxidation of 2,2,6,6-tetramethylpiperidine can react with dioxygen yielding TEMPO nitroxyl radical [5, 6]. A possibility to perform similar transformation for the aryl counterparts is not that obvious. Aromatic derivatives might be advantageous since their reactivity (redox potential value or other important parameters) can be manipulated using appropriate substituents. On the other hand, a presence of the aryl moiety may provoke competing routes leading to

hydroxylation of the ring instead of the N–O bond formation.

In addition to the synthetic aspect, electrochemical deoxygenation/oxygenation of aryl-nitroxides/arylamines might be also referred to chemical processes related to energy conversion and storage systems, i.e., to Li-air batteries functioning. An application of “chemically bound” form of dioxygen which can be actualized using the compounds capable to reversible oxygenation/deoxygenation would be a possibility to solve one of the topical problems of the Li-air batteries avoiding formation of aggressive forms of dioxygen (e.g., superoxide anion which is formed in Li-air batteries and causes destruction of the solvent, supporting electrolyte, corrosion, etc.) [7, 8].

The present paper is focused on the processes of the N–O bond formation/bond breaking in diarylamines and diarylnitroxides. It is aimed at the detailed quantum-chemical and electrochemical investigation of a possibility for oxygenation/deoxygenation of diarylamines. The results obtained will shed light on possibilities and limitations for functioning of nitroxide-based redox active electrode materials. Besides, it will be useful for modeling of antioxidant properties of arylamines as well as for targeted molecular design of efficient antioxidants since these steps are involved in multistep processes of the radical trapping.

2. Results and discussion

A general scheme illustrating interconversion of diarylamines and diarylnitroxides is given in Scheme 1. Diarylaminy radicals can be

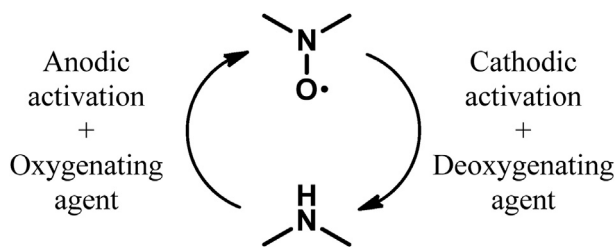
^{*} Corresponding author.

E-mail address: tvm@org.chem.msu.ru (T.V. Magdesieva).

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Scheme 1. Electrochemical diarylamine/diarylnitroxide cycling.

considered as the most probable intermediates. To perform the “right part” of the cycle, deoxygenating agent is necessary, contrary to the “left part”, for which a suitable source of oxygen is required. To obtain the active species (cations, anions or radicals), electrochemical oxidation and/or reduction can be applied. Possibilities and limitations for realization of the processes given in Scheme 1 will be discussed below.

2.1. Electrochemical deoxygenation of diarylnitroxide

To probe a possibility for electrochemical deoxygenation of diarylnitroxides, electrochemical behavior of a model 4,4'-bis(*tert*-butylphenyl)nitroxide was investigated in acetonitrile solution containing various salts: Bu₄NBF₄, LiPF₆ or NaClO₄. All three salts have non-nucleophilic anions and are commonly applied in electrochemical measurements since they provide a wide potential window and are not prone to specific interactions with reactive species formed in solution. The first salt is commonly used as a supporting electrolyte in organic solvents due to high solubility of the sufficiently large cations containing four hydrophobic groups. As for the Li⁺ or Na⁺ containing salts, their properties might be expected to differ significantly. Relatively small Li⁺ cations are prone to form tight ion pairs with anionic species formed in the electrochemical process (this especially concerns hard bases, according to the Pearson classification [9]) thus influencing thermodynamics of the electrochemical reaction or facilitating various chemical follow-up steps. Lithium ions are well known to form strong bonds with negatively charged oxygen atoms [10]; their oxophilic properties have been demonstrated on multiple examples and are widely documented in literature [10, 11].

Voltammograms obtained for 4,4'-bis(*tert*-butylphenyl)nitroxide in acetonitrile solution with Bu₄NBF₄ as a supporting electrolyte exhibit two reversible redox couples, in anodic and cathodic regions with the formal potential values of $E_{Ox}^0 = 0.34$ V and $E_{Red}^0 = -1.34$ V (vs. Fc⁺/Fc, see Fig. 1a). The replacement of Bu₄NBF₄ for LiPF₆ does not alter the oxidation pattern; however, significant broadening of the reduction peak is observed (Fig. 1b). The reduction becomes completely irreversible (indicating the involvement of a chemical step of bond breaking or bond formation); the onset potential value is shifted toward positive potentials. A new anodic peak at 0.21 V vs. Fc⁺/Fc appears in the reverse scan.

Thus, comparison of the voltammograms clearly indicates that

oxophilic Li⁺ ions dramatically influence the reduction process giving rise to the follow-up chemical transformation of the initially formed aminoxyl anions. To be sure that the alteration of the CV curve observed in the presence of lithium salt is not attributed to protonation of aminoxyl anions with residual water (commonly observed for alkyl nitroxides [12]), the measurements were performed in a dry box using thoroughly dried reactants (see Experimental part).

To determine possible chemical transformations which follow the electron-transfer step yielding aminoxyl anions, quantum-chemical calculations were performed at PBE/L1 level of theory. Based on the data obtained, the following reaction scheme was suggested (Scheme 2). In the presence of the Li salt, one-electron reduction of the nitroxide is followed by thermodynamically favorable irreversible dimerization (DFT estimated $\Delta_r G_{298}^0 = -161$ kcal/mol). The dimer thus formed can be further reduced; the transfer of the second electron is irreversible and more likely followed by the N–O bond breaking yielding Li₂O and aminyl radicals. The latter can dimerize yielding tetraarylhydrazine (this step is thermodynamically favorable, see Scheme 2) or undergo an H-atom abstraction yielding diarylamine [2]. New oxidation peak which appeared in the reverse scan of the voltammogram (0.21 V vs. Fc⁺/Fc, Fig. 1b) is more likely attributed to oxidation of tetraarylhydrazine formed (E_{Ox} for Ph₂N₂Ph₂ = 0.33 V vs. Fc⁺/Fc [13]). The presence of electron-rich *t*-Bu substituents in the phenyl rings is responsible for a small cathodic shift observed in our case. An alternative mechanism for the second reduction step can be also suggested (Scheme 2). In this case, deoxygenation of the dimer yields lithium diarylamide and Li₂O₂ release. However, the second scheme seems to be less feasible since an intensive peak corresponding to amide oxidation (at the potential of ca. −0.78 V vs. Fc⁺/Fc [14, 15]) should be observed instead of the tetraarylhydrazine oxidation and it was not the case.

The crucial role of oxophilic Li-ions in the deoxygenation of diarylnitroxides was further supported by the electrochemical experiments performed using NaClO₄ as a supporting electrolyte. The shapes of the voltammetric curves obtained for 4,4'-(*t*-BuC₆H₄)₂NO in acetonitrile containing Bu₄NBF₄ or NaClO₄ were similar (see Fig. 1a and c), the reversibility of both oxidation and reduction peaks was reserved. The formal oxidation potential was shifted for 8 mV only, indicating no significant interaction between the oxoammonium cation and perchlorate anions. The formal reduction potential was anodically shifted for 267 mV in the presence of Na⁺ ions since formation of ion pairs facilitates stabilization of the aminoxyl anions; however, the N–O bond was not cleaved (otherwise, the reduction would be irreversible).

These experiments clearly demonstrate that diarylnitroxides can be applied as anodic redox active materials in energy conversion and storage systems utilizing Na⁺ ions migration whereas the contact of aminoxyl anions with Li⁺ ions leads to fast deoxygenation yielding diarylaminy radicals.

Thus, electrochemical experiments supported with quantum-chemical calculations showed that electrochemical deoxygenation of diarylnitroxides is feasible. The process is cathodically activated; the starting nitroxides should be reduced to corresponding aminoxyl anions.

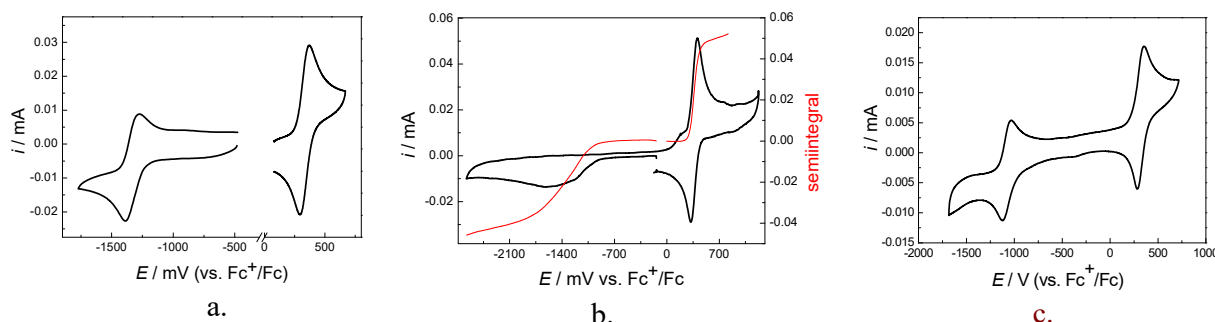
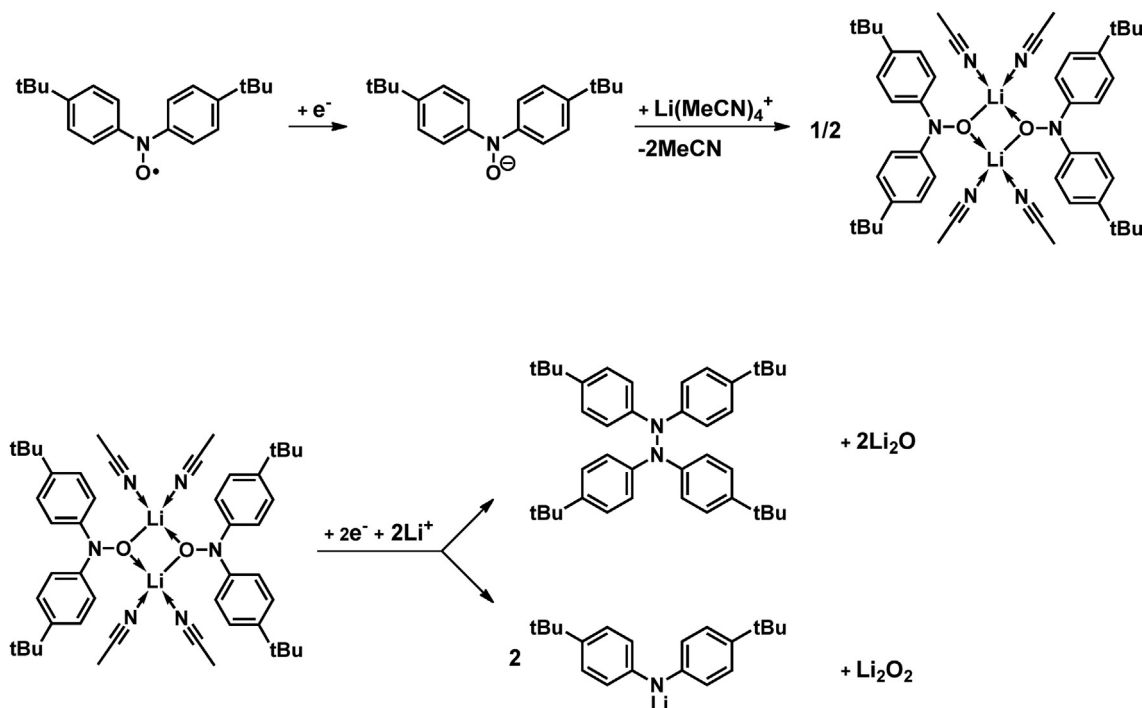


Fig. 1. Voltammetric curves observed for 4,4'-(*t*-BuC₆H₄)₂NO in acetonitrile solution containing Bu₄NBF₄ (a); LiPF₆ (b); NaClO₄ (c); 100 mV/s; vs. Fc⁺/Fc.



Scheme 2. Possible chemical transformations of electrochemically generated aminoxyl anions in the presence of lithium salts.

As deoxygenating agents, lithium salts can be applied.

2.2. Electrochemical oxygenation of diarylamines: quantum-chemical calculations

A possibility for electrochemical conversion of diarylamines to corresponding nitroxides has not been studied yet. Electrosynthesis of diarylnitroxides via anodic oxidation of diarylamines in the presence of oxygenating agent, on the face of it, looks simple and rather tempting, especially, taking into account previously reported formation of TEMPO from the corresponding aminyl radical [5, 16]. Prior to experimental testing, quantum chemical DFT calculations ("Priroda" program package, PBE/L1 level of theory) of the thermodynamics for oxygenation of diarylamines and diarylaminy radicals using various oxygen sources were performed. As the oxygenating agents, molecular oxygen, hydrogen peroxide and N_2O were investigated.

The reaction path leading to diarylnitroxides formation (similar to that previously assumed for alkyl derivatives [16]) is given in Scheme 3.

However, in spite of numerous efforts, we were unable to locate a stationary structure corresponding to the peroxo-derivative of aromatic aminyl radicals, both electron rich and electron deficient at the DFT level ($\text{Ar}_2\text{NOO}^\bullet$, Ar = Ph, *t*-Bu, *o*- $\text{CF}_3\text{C}_6\text{H}_4$, *o*- OHCC_6H_4 , *o*- $\text{CH}_3\text{OC}_6\text{H}_4$ were considered). Hence, the direct oxygenation of aminyl radicals using dioxygen is not feasible.

To estimate a possibility for realization of the alternative routes for oxygenation of diarylamines as well as diarylaminy radicals or anions using O_2 and/or H_2O_2 , the free energies of the reactions between the model compounds were calculated. As the models, diphenylamine and phenoxazine were chosen. The latter has planar and rigid structure, contrary to the former one, in which rotation over the C–N bond is possible. According to the literature data, relatively stable aminyl radical

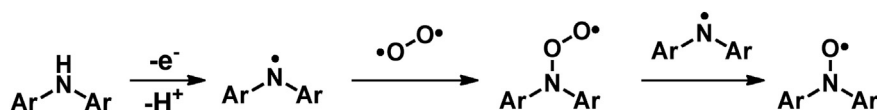
was detected in aerobic oxidation of 2,4,6,8-tetra-*tert*-butylphenoxazine [17].

The results obtained are given in Table 1.

The results obtained for both model substrates are qualitatively similar. None of the reactions of the diarylamine with the oxygen sources considered (reactions 1–6) lead to the N–O bond formation (except reaction 2 which yields the hydroxylamine). As concerns the aminyl radicals (which can be obtained via thermodynamically favorable reaction 3 or via anodic oxidation of the starting amine followed by deprotonation of the radical cation formed), reactions 9 and 10 can yield the N–O bond formation. The hydroxylamine formed in thermodynamically favorable reactions 2 and 10 can be further converted to the corresponding nitroxide via reactions 11, 12 which are also favorable. However, the question is: how the radicals ($\text{HO}_2^\bullet$, $\text{HO}^\bullet$) required can be obtained to carry out the synthetic route? These aggressive species formed in trace amounts in harsh conditions are commonly responsible for oxidative damage of organic materials. From this point, the thermodynamic data given in Table 1 provide additional support for a feasibility of diarylamine/diarylnitroxide conversion during radical-trapping processes. However, we have to conclude that the aforementioned processes can hardly be applied for synthetic purposes.

The other problem is a possibility for competing routes leading to the hydroxylation of the aromatic moiety with the $\text{HO}^\bullet$ radicals formed. These reaction paths have low activation energy (6–9 kcal/mol) and are thermodynamically favorable (see Scheme 4). However, the impact of these competing routes can be minimized if a concerted reaction path, without intermediate formation of $\text{HO}^\bullet$ radicals, is implemented. This approach is actualized in oxidation of diarylamines to corresponding nitroxides using *meta*-chloroperbenzoic acid [18, 19, 20].

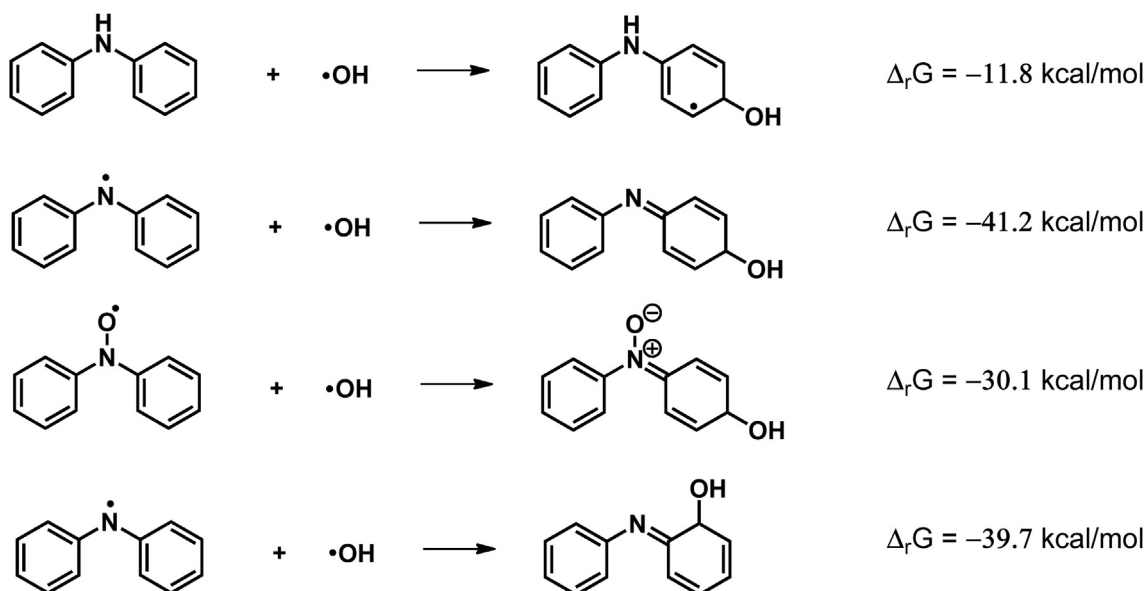
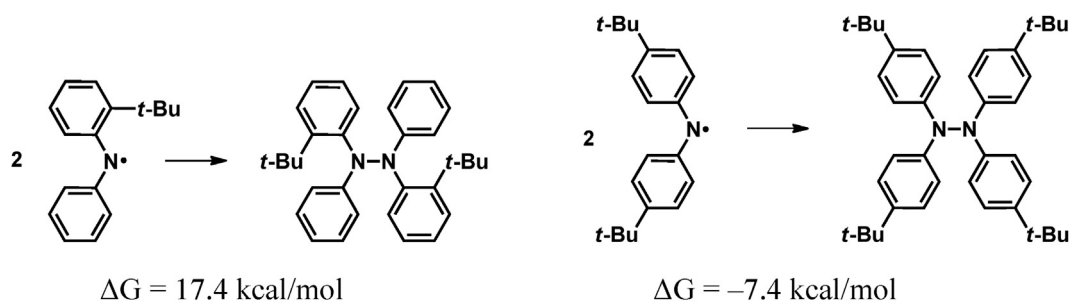
The other competing route preventing the targeted oxygenation process leading to the N–O bond formation might be dimerization of the



Scheme 3. Supposed reaction path leading to diarylnitroxides formation.

Table 1Calculated free Gibbs energy values for oxygenation of diarylamines (Ph₂NH and phenoxazine) and corresponding aminyl radicals.

№	Reaction						$\Delta_r G$, kcal/mol, Ar ₂ NH=		
							Ph ₂ NH	phenoxazine	
1	Ar ₂ NH	+	O ₂	=	Ar ₂ N•	+	HO ₂ •	33.6	21.9
2	Ar ₂ NH	+	H ₂ O ₂	=	Ar ₂ NOH	+	H ₂ O	-20.8	-15.7
3	Ar ₂ NH	+	HO•	=	Ar ₂ N•	+	H ₂ O	-35.4	-47.1
4	Ar ₂ NH	+	HO ₂ •	=	Ar ₂ N•	+	H ₂ O ₂	0.4	-11.3
5	Ar ₂ NH	+	O ₂ ^{-•}	=	Ar ₂ N•	+	HO ₂ ⁻	27.4	15.7
6	Ar ₂ NH	+	O ₂ ^{-•}	=	Ar ₂ N ⁻	+	HO ₂ •	-27.9	-33.3
7	Ar ₂ N•	+	O ₂	=	Ar ₂ NOO•			Not possible, see the text	
8	Ar ₂ N•	+	H ₂ O ₂	=	Ar ₂ NOH	+	HO•	14.5	
9	Ar ₂ N•	+	HO ₂ •	=	Ar ₂ NO•	+	HO•	-3.0	2.1
10	Ar ₂ N•	+	HO•	=	Ar ₂ NOH			-42.3	-25.4
11	Ar ₂ NOH	+	HO•	=	Ar ₂ NO•	+	H ₂ O	-53.4	-65.1
12	Ar ₂ NOH	+	HO ₂ •	=	Ar ₂ NO•	+	H ₂ O ₂	-17.6	-29.3
13	Ar ₂ NOH	+	O ₂	=	Ar ₂ NO•	+	HO ₂ •	15.6	3.9

**Scheme 4.** Calculated free Gibbs energy values for oxygenation of diphenylamine derivatives at the aromatic moiety.**Scheme 5.** Calculated free Gibbs energy values for dimerization of the *ortho*- and *para*-substituted diphenylaminyl radicals.

aminyl radicals. This process is favorable for diphenylaminyl radicals as well as for their *para*-substituted derivatives (see Scheme 5). However, even one bulky substituent in the *ortho*-position prevents the dimerization of the aminyl radicals:

N₂O can be also considered as an oxygen source, due to the thermodynamically favorable nitrogen evolution (Scheme 6). However, quantum-chemical calculations showed that the reaction is kinetically impeded (both for the aminyl radicals and aminyl anions) due to high activation barriers.

Thus, quantum-chemical estimation showed that direct oxygenation

of the diarylamyl radicals using dioxygen or N₂O is not feasible. Indirect methods, with the OH radicals involved, might result in the formation of a certain amount of a nitroxide except for the much more favorable competing routes leading to hydroxylation of the aromatic ring.

The results of quantum-chemical investigation were supported by electrochemical testing. The behavior of the electrochemically oxidized diarylamine in the presence of dioxygen was investigated using cyclic voltammetry. 4,4'-bis(*tert*-butylphenyl)amine was taken as a model (similar to the deoxygenation process discussed above). The comparison

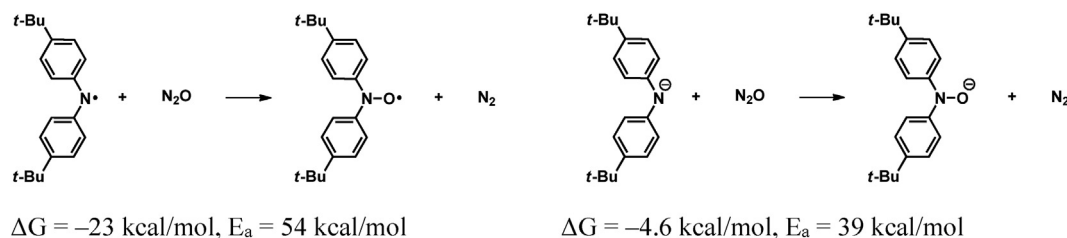
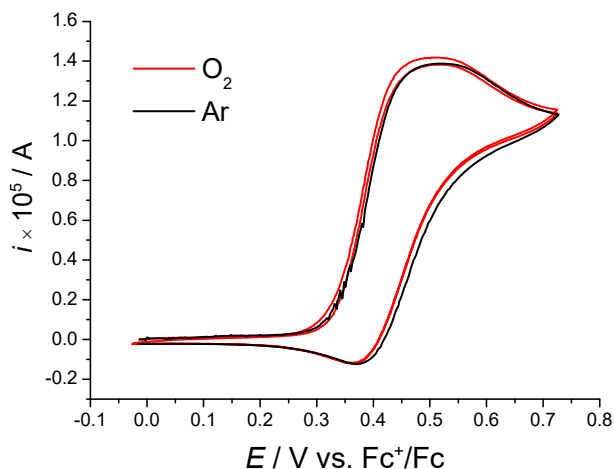
Scheme 6. N_2O as an oxygen source: quantum-chemical estimation.

Fig. 2. Electrochemical oxidation of 4,4'- $(t\text{-BuC}_6\text{H}_4)_2\text{NH}$ under Ar (black line) and in the presence of O_2 (red line) (acetonitrile, Bu_4NBF_4 , Pt, 10 mV/s, vs. Fc^+/Fc).

of the voltammetric curves measured under argon and in the presence of the dioxygen showed their identity (Fig. 2). This result is in line with the computational data given above indicating that O_2 does not participate in the follow-up chemical transformations of the initially formed radical cation of the diarylamine. The irreversibility of the oxidation curve in both cases evidences in favor of relatively fast chemical follow-up steps. A detailed analysis of the possible reaction routes initiated by electrochemical oxidation of diarylamines has been performed in the recent publication [15]. The mechanism and kinetics of the reactions were elucidated using digital simulation of the voltammetric curves. It was shown that acidity of the radical cation of diphenylamine in acetonitrile solution is relatively low (the K value is $4.10 \times 10^{-5} \text{ mol/l}$) resulting in a low equilibrium concentration of aminyl radicals. Thus, deprotonation of the radical cation of the starting amine is rate-determining step, the subsequent reactions between aminyl radicals and radical cations of the diarylamine (the electrophilic C–N coupling, aromatization and intramolecular electrophilic cyclizations, see [15]) are fast. Consequently, a low concentration of the aminyl radicals, together with much more thermodynamically favorable competing routes, precludes the reaction of the radicals with dioxygen.

Thus, both quantum-chemical and electrochemical estimation showed that the direct oxygenation of diarylaminy radicals with dioxygen is not feasible (contrary to their alkyl counterparts) and can not lead to diarylnitroxide formation.

3. Experimental

4,4'-bis(tert-butylphenyl)nitroxide was synthesized as described in [21]. Its identity was verified using ESR and UV-vis spectra. ESR: $g = 2.00586$, $a_N = 9.74 \text{ G}$, $a_H = 1.81 \text{ G}$ (4H), 0.91 G (4H); UV-vis, λ_{max} , nm: 530 (sh), 484, 462 (sh), 447, 427 (sh), 402, 320, 310, 287 (sh), 249, 201.

ESR spectra were recorded from toluene solutions containing

approximately 5×10^{15} radical molecules, which were deaerated by using standard freeze-pump-thaw techniques.

UV/Vis spectra were recorded for solutions of the nitroxides in dry acetonitrile ($5 \times 10^{-5} - 1 \times 10^{-4} \text{ M}$).

Acetonitrile (Aldrich spectroscopic quality, <0.02% water content) was distilled over P_2O_5 in dry argon.

Supporting electrolytes:

$n\text{-Bu}_4\text{NBF}_4$ (Aldrich, purity >99%) was recrystallized from water and dried by gentle heating under reduced pressure (0.05 Torr) prior to use.

LiPF_6 (Aldrich, 98%) was stored in a glove box and used without purification.

NaClO_4 (Aldrich, 98%) was dried at 100°C for 6 h under reduced pressure ($5 \cdot 10^{-2}$ Torr).

Voltammetric experiments were performed with AutoLab PGSTAT100 N potentiostat, in a three-electrode cell of 10 ml with a Pt disk working electrode (an active surface area of 0.077 cm^2), a platinum wire counter electrode and Ag/AgCl , KCl (sat.) reference electrode. The reference electrode was connected to the electrolyte solution via a salt bridge containing acetonitrile solution. The half-wave potential of the ferrocene couple (Fc^+/Fc) versus this reference electrode was about 0.48 V in 0.05 M Bu_4NBF_4 in acetonitrile. The experiments with LiPF_6 were performed in a glove box and referenced against anhydrous $0.01 \text{ M Ag}^+/\text{Ag}$ reference electrode ($E_{1/2}(\text{Fc}^+/\text{Fc}) = +83 \text{ mV}$). All solutions were thoroughly deaerated by passing an argon flow through the solution prior to the CV experiments and above the solution during the measurements.

3.1. Computational details

Unrestricted DFT calculations were performed in the PRIRODA quantum chemistry program [22, 23]. The gradient-corrected exchange-correlation Perdew, Burke, and Ernzerhof (PBE) functional [24], and double-zeta quality basis set L1 were used for structure optimizations and thermal correction calculations [25]. The 10^{-6} threshold on the molecular gradient at the geometry optimization procedure was employed.

4. Conclusion

Quantum-chemical and electrochemical investigations performed in the present paper showed that the electrochemically induced reversible diarylamine/diarylnitroxide cycling is not feasible. The limiting step is oxygenation of diarylaminy radicals which is unfavorable thermodynamically. Aminyl radicals can be generated via electrochemical oxidation of diarylamines followed by deprotonation of the radical cations. Delocalization of the spin density over the phenyl rings inherent to aromatic derivatives decreases the reactivity of the N radical center, as compared to alkyl counterparts, giving rise to multiple competing routes involving the aromatic moiety. Oxygenation of the aromatic moiety occurring in the presence of O_2 or hydrogen peroxide precludes the targeted oxygenation process. Some other favorable competing transformations of the intermediate species (C–N and C–C couplings, intermolecular cyclizations, etc.) which are known to occur under argon are also possible.

Contrary to direct oxygenation of amines, deoxygenation of diarylnitroxides can be performed electrochemically. It was shown that

diarylaminoxyl anions formed under electrochemical reduction of diarylnitroxides undergo fast deoxygenation in the presence of Li salts. The possible reaction scheme was suggested. Highly oxophilic Li ions are strongly coordinated to aminoxyl anions yielding the N–O bond cleavage.

Contrary to Li-ions, addition of Na⁺ salts in the acetonitrile solution containing the diarylnitroxide (4,4'-^t-BuPh₂NO●) influences reversibility of neither oxidation nor reduction of the nitroxide, only anodic shift of the formal reduction potential is observed. Thus, 4,4'-(^t-BuC₆H₄)₂NO can be considered as a potential candidate to be applied as anodic redox active component in pair with sodium-ion intercalating material. It should be emphasized that organic molecules suitable for application as anodic redox active materials are still rare; contrary to cathodic organic materials which scope is rather wide.

Declarations

Author contribution statement

Tatiana Magdesieva: Conceived and designed the experiments; Analyzed and interpreted the data; Wrote the paper.

Oleg Levitskiy: Performed the experiments; Analyzed and interpreted the data; Contributed reagents, materials, analysis tools or data.

Vyacheslav Sentyurin: Performed the experiments; Analyzed and interpreted the data.

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Competing interest statement

The authors declare no conflict of interest.

Additional information

No additional information is available for this paper.

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