Research article

Diarylamine/diarylnitroxide cycle: quantum chemical and electrochemical estimation

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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 diarylaminyl radicals with dioxygen yielding diarylnitroxides 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 aroylnitroxides. Previously, it has been reported that dialkylaminyl radical formed in electrooxygenation of 2,2,6,6-tetramethylpiperidine can react with dioxygen yielding TEMPO nitroxy 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 hydroxylolation 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. Diarylaminyl radicals can be 

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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 $E^\circ_{ox} = 0.34$ V and $E^\circ_{red} = -1.34$ V (vs. Fe+/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. Fe+/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 $\Delta G_{dimer}^\circ = -161$ 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. Fe+/Fc, Fig. 1b) is more likely attributed to oxidation of tetraarylhydrazine formed ($E^\circ_{ox}$ for Ph2N2PBu = 0.33 V vs. Fe+/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 diarylamine 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. Fe+/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-BuC6H4NO 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 diarylaminyl 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.

\[ E^\circ_{ox} = 0.34 \text{ V vs. Fe}^+/\text{Fc}, \]

\[ E^\circ_{red} = -1.34 \text{ V vs. Fe}^+/\text{Fc}, \]

\[ \Delta G_{dimer}^\circ = -161 \text{ kcal/mol} \]

\[ E^\circ_{ox} = 0.33 \text{ V vs. Fe}^+/\text{Fc} \]

Fig. 1. Voltammetric curves observed for 4,4'-t-BuC6H4NO in acetonitrile solution containing Bu4NBF4 (a); LiPF6 (b); NaClO4 (c); 100 mV/s vs. Fe+/Fc.
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 aminal 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 diarylaminyl radicals using various oxygen sources were performed. As the oxygenating agents, molecular oxygen, hydrogen peroxide and N2O 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 peroxy-derivative of aromatic aminyl radicals, both electron rich and electron deficient at the DFT level (Ar2NOO•, Ar = Ph, t-Bu, o-CF3C6H4, o-OHCC6H4, o-CH3OC6H4 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 diarylaminyl radicals or anions using O2 and/or H2O2, 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 diarylamidine 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 (HO2•, HO•) 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/diaryl nitroxide 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 HO• 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 HO• 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
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:

\[ \text{N}_2\text{O} \text{ can be also considered as an oxygen source, due to the thermodynamically favorable nitrogen evolution (Scheme 6). However, quantum-chemical calculations showed that the reaction is kinetically impeded (both for the aminyl radicals and aminyl anions) due to high activation barriers.} \]

Thus, quantum-chemical estimation showed that direct oxygenation of the diarylamyl radicals using dioxygen or \(\text{N}_2\text{O}\) 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-butylyphenyl)amine was taken as a model (similar to the deoxygenation process discussed above). The comparison

### Table 1

| N | Reaction | \(\Delta G, \text{kcal/mol, Ar}_2\text{NH}^-\) |
|---|----------|-----------------|
| 1 | \(\text{Ar}_2\text{NH}^- + \text{O}_2 \rightarrow \text{Ar}_2\text{N}^+ + \text{HO}_2^-\) | 33.6 21.9 |
| 2 | \(\text{Ar}_2\text{NH}^- + \text{H}_2\text{O}_2 \rightarrow \text{Ar}_2\text{N}^+ + \text{HO}_2^-\) | –20.8 –15.7 |
| 3 | \(\text{Ar}_2\text{NH}^- + \text{H}_2\text{O} \rightarrow \text{Ar}_2\text{N}^+ + \text{HO}_2^-\) | –35.4 –47.1 |
| 4 | \(\text{Ar}_2\text{NH}^- + \text{HO}_2^- \rightarrow \text{Ar}_2\text{N}^+ + \text{H}_2\text{O}_2\) | 0.4 –11.3 |
| 5 | \(\text{Ar}_2\text{NH}^- + \text{O}_2 \rightarrow \text{Ar}_2\text{N}^+ + \text{HO}_2^-\) | 27.4 15.7 |
| 6 | \(\text{Ar}_2\text{NH}^- + \text{O}_2^- \rightarrow \text{Ar}_2\text{N}^+ + \text{HO}_2^-\) | –27.9 –33.3 |
| 7 | \(\text{Ar}_2\text{N}^+ + \text{O}_2 \rightarrow \text{Ar}_2\text{NOO}^-\) | Not possible, see the text |
| 8 | \(\text{Ar}_2\text{N}^+ + \text{H}_2\text{O}_2 \rightarrow \text{Ar}_2\text{NOH} + \text{HO}_2^-\) | 14.5 |
| 9 | \(\text{Ar}_2\text{N}^+ + \text{HO}_2^- \rightarrow \text{Ar}_2\text{NO}^- + \text{HO}_2^-\) | –3.0 2.1 |
| 10 | \(\text{Ar}_2\text{NO}^- + \text{H}_2\text{O} \rightarrow \text{Ar}_2\text{NO}^- + \text{HO}_2^-\) | –42.3 –25.4 |
| 11 | \(\text{Ar}_2\text{NO}^- + \text{HO}_2^- \rightarrow \text{Ar}_2\text{NO}^- + \text{H}_2\text{O}_2\) | –63.8 –65.1 |
| 12 | \(\text{Ar}_2\text{NO}^- + \text{O}_2 \rightarrow \text{Ar}_2\text{NO}^- + \text{HO}_2^-\) | –17.6 –29.3 |
| 13 | \(\text{Ar}_2\text{NO}^- + \text{O}_2 \rightarrow \text{Ar}_2\text{NO}^- + \text{H}_2\text{O}_2\) | 15.6 3.9 |

### Scheme 4. Calculated free Gibbs energy values for oxygenation of diphenylamine derivatives at the aromatic moiety.

\[ \Delta G = -11.8 \text{ kcal/mol} \]

\[ \Delta G = -41.2 \text{ kcal/mol} \]

\[ \Delta G = -30.1 \text{ kcal/mol} \]

\[ \Delta G = -39.7 \text{ kcal/mol} \]

### Scheme 5. Calculated free Gibbs energy values for dimerization of the ortho- and para-substituted diphenylaminyl radicals.

\[ \Delta G = 17.4 \text{ kcal/mol} \]

\[ \Delta G = -7.4 \text{ kcal/mol} \]
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 diarylaminal 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, aQ = 9.74 G, aH = 1.81 G (4H), 0.91 (4H); UV-vis, λmax 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 × 10^{-5} – 1 × 10^{-4} M).

Acetonitrile (Aldrich spectroscopic quality, <0.02% water content) was distilled over P2O5 in dry argon.

Supporting electrolytes:
- n-Bu4NBF4 (Aldrich, purity >99%) was recrystallized from water and dried by gentle heating under reduced pressure (0.05 Torr) prior to use.
- LiPF6 (Aldrich, 98%) was stored in a glove box and used without purification.
- NaClO4 (Aldrich spectroscopic quality, <0.02% water content) was dried at 100 °C for 6 h under reduced pressure (5–10^{-2} Torr).

Voltammetric experiments were performed with AutoLab PGSTAT100 Potentiostat, in a three-electrode cell of 10 ml with a Pt disk working electrode (an active surface area of 0.077 cm²), 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 Bu4NBF4 in acetonitrile. The experiments with LiPF6 were performed in a glove box and referenced against anhydrous 0.01M Ag+ /Ag reference electrode (E1/2(Fc+/Fc) = +83 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 diarylaminal/diarylnitroxide cycling is not feasible. The limiting step is oxygenation of diarylaminal 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 O2 or hydrogen peroxide precludes the targeted oxygenation process. Some other favorable competing transformations of the intermediate species (C-N and C-C couplings, intramolecular 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'-\(1,5\)\(\text{Bu}_2\)Ph\(_2\)NO\(^-\)) influences reversibility of neither oxidation nor reduction of the nitroxide, only anodic shift of the formal reduction potential is observed. Thus, 4,4'-\(1,5\)\(\text{Bu}_2\)C\(_6\)H\(_2\)NO 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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