Electrochemical analysis of the triarylimidazole-type organic redox catalysts: chemical stability and homogeneous electron transfer kinetics for the oxidation of 4-methoxybenzyl alcohol

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Abstract:

Triarylimidazoles have emerged as novel and useful organic redox catalysts as a result of their straightforward synthesis and tunable oxidation potential. Herein we describe an investigation of the effects of supporting electrolyte and solvent on the chemical reversibility of the triarylimidazole redox couple. Next, the homogeneous electron transfer rate for three triarylimidazole mediators toward the oxidation of 4-methoxybenzyl alcohol was estimated using cyclic voltammetry. The results indicate that the concentration and composition of the conducting salts, especially of the anion, affect the electrochemical performance of the triarylimidazole. Kinetic studies reveal that the smaller the peak potential difference between a mediator and the substrate, the larger the catalytic current and the pseudo first-order homogeneous rate constant.

Key words: triarylimidazoles; triarylamines; redox catalyst; homogeneous electron transfer.

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Introduction

Electron transfer reactions have attracted considerable attention in organic synthesis, in the study of biological process, and in the development of energy storage devices, etc [1]. Electron transfer can be initiated thermally (homogeneous and heterogeneous) [2], photochemically [3-4], electrochemically [5-6], and through the use of solvated electrons [7]. In electrochemically initiated processes, the electron is added to or removed from the substrate, leading to the formation of a reactive ion radical and its subsequent chemical transformation(s). Electroorganic synthesis constitutes one of the most promising and environmentally friendly approaches to organic synthesis [8-9]. The electron transfer between an electrode and a reactant can be carried out either directly or indirectly. In the former, the redox reaction of interest occurs at the electrode, while the latter uses an electron transfer redox catalyst to achieve homogeneous electron transfer [10-12].

An ideal redox catalyst for an electrochemical oxidation displays a peak potential that is less positive than that of the substrate, exhibits fast heterogeneous electron transfer kinetics at the electrode, and a fast homogeneous electron transfer between the oxidized form of the redox catalyst and the substrate. In addition to these kinetic factors, the thermodynamic stability of the redox catalyst in both its oxidized and reduced forms toward the species present in the reaction media is essential. A reversible cyclic voltammogram, wherein the ratio of peak currents ($I_p^{\text{Ox}}/I_p^{\text{Red}}$) is unity and remains so even after repetitive scans, provides an indicator of its chemical stability

Redox catalysts come in many varieties including inorganic ions, organometallic complexes and neutral organic compounds. Tris(4-bromophenyl)amine (TBPA) represents the most popular organic oxidative mediator (Figure 1) [13-16]. In this context, we have recently developed a series of triarylimidazole based organic redox mediator (Figure 1) and have discovered that they can be applied to the activation of benzylic C-H bonds, transforming benzyl alcohol or benzyl ether to the corresponding aldehyde, ketone or benzoate [17-20]. In addition, they have been used to achieve a

ring-opening/Friedel-Crafts heteroarylation reaction of chalcone epoxides by electrochemically **in situ generated** triarylimidazole cation radical [21].

In this work, the electrochemical performance of triarylimidazole-type redox catalysts in different supporting electrolytic systems was investigated and compared with that of TBPA under identical conditions. Kinetic analysis of the electrocatalytic oxidation of 4-methoxybenzyl alcohol with three different triarylimidazoles was also explored. Our intent and goal is to further improve our understanding of triarylimidazole chemistry and provide useful guidelines for its continued application in electroorganic synthesis.

Figure 1. Structures of TBPA and triarylimidazole-type organic redox catalysts

2. Experimental

2.1. Materials

2-(4-Bromophenyl)-1-methyl-4,5-diphenyl-1H-imidazole (**1a**), 2-(4-methoxyphenyl)-1-methyl-4,5-diphenyl-1H-imidazole (**1b**), 2-phenyl-1-methyl-4,5-diphenyl-1H-imidazole (**1c**) and 2-(4-trifluoromethylphenyl)-1-methyl-4,5-diphenyl-1H-imidazole (**1d**) were synthesized according to known procedures [18]. Other chemicals and solvents were commercially available and used without further purification.

2.2. Instruments

Cyclic voltammograms were recorded at room temperature using a Princeton Applied Research Model 273A Potentiostat/Galvanostat equipped with electrochemical analysis software and a conventional three-electrode cell. A glassy carbon (GC) disk electrode (ca. $\phi = 3$ mm) or a Pt disk electrode (ca. $\phi = 1$ mm) was used as the working electrode and a Pt wire as the counter electrode. Ag/AgNO₃ (0.1 M in CH₃CN) was used as a reference electrode. All electrodes for CV experiments were purchased from CH Instruments, Inc. USA.

The working electrodes were carefully polished on a polishing pad before each experiment using a fine mesh alumina slurry, and then ultrasonically rinsed with acetone. All solutions were degassed by sparging dry nitrogen through the solution for 10 min prior to conducting each electrochemical experiment; a nitrogen atmosphere was maintained throughout. In each measurement, the three electrodes were fixed in place, and were not allowed to be disturbed in any manner.

3. Results and discussion

3.1 The effects of supporting electrolyte on the chemical stability of triarylimidazole-type mediator

While supporting electrolytes are designed to be stable and inert to reactions with the substrate and mediator, ion pairing with the oxidized or reduced forms of the mediator may influence its electrochemical behavior. Among other things, the degree of ion pairing ought to differ with concentration and the nature of the supporting electrolyte. For triarylimidazole redox couple, its oxidized form is cation radical and reduced form is neutral molecule. As a result, stronger ion pairing effect ought to occur between supporting electrolyte and its oxidized form than with reduced form.

To explore the nature of these effects, cyclic voltammograms of mediator **1a** (2.0 mM) in CH₃CN were recorded using LiClO₄, *n*-Bu₄NClO₄ (TBAClO₄), *n*-Bu₄NPF₆ (TBAPF₆), Et₄NBF₄ (TEABF₄) and LiN(CF₃SO₂)₂ (LiTFSI) as supporting electrolytes. For comparison, 2.0 mM solution of TBPA was also investigated under the same conditions. For ease in visualizing the change of the reduction peak current from one run to the next, the observed current was normalized to the peak current for oxidation, i_p^{ox} ; thus the ordinate is illustrated as i/i_p^{ox} . The results illustrated in Figure 2, clearly reveal that there are dramatic differences between the behavior of the two types of mediators. It was observed that the electrochemical performance and chemical reversibility of the triarylimidazole mediator **1a/1a⁺** redox couple depends upon the composition of supporting electrolyte, while that of TBPA is essentially independent of the supporting electrolyte (compare the upper and bottom of Fig. 2).

Figure 2. Cyclic voltammograms of 2.0 mM triarylimidazole **1a** (upper) and TBPA (bottom) in N₂-saturated solution of 0.2 M (a) LiClO₄, (b) TBAClO₄, (c) TBAPF₆, (d) TEABF₄, and (e) LiTFSI in CH₃CN using a GC working electrode, Pt wire counter and Ag/AgNO₃ (0.1 M in CH₃CN) reference; scan rate: 200 mV s⁻¹.

The oxidized forms of TBPA and triarylimidazole-type redox catalysts are cation radicals and will therefore pair with the anion of the supporting electrolyte. When LiClO₄ was used as a supporting electrolyte, the anodic to cathodic peak current ratio,

I_p^{Ox}/I_p^{Red} , for the **1a** /**1a**⁺ couple was 1.04, and displayed a chemically reversible behavior (curve a), indicating that LiClO₄ is able to stabilize the cation radical of **1a**. As expected, replacement of LiClO₄ by TBAClO₄ is of little consequence, having no effect on the peak potentials and only a slight decrease of cathodic peak current. Clearly, the nature of the cation of the supporting electrolyte has little influence upon the chemical reversibility of the redox couple (curve b). The anion of the supporting electrolyte, however, plays a significant role. For example, when the supporting electrolyte was changed from TBAClO₄ to TBAPF₆, the peak potential and current for **1a** changed dramatically. The cathodic peak potential for **1a**⁺ shifted to 0.85 V, 24 mV positive of that recorded with TBAClO₄. In addition, the cathodic current decreased from 59 μA to 44 μA (curve c). A similar tendency is also observed when one compares the electrochemical behavior of **1a** in CH₃CN with LiClO₄ and TEABF₄ as supporting electrolytes (curve a vs curve d). For instance, in the case of TEABF₄, the CV of **1a** is irreversible, the reduction current disappears, and a negative shift of the oxidation peak potential occurs, from 0.91 V with LiClO₄ to 0.88 V with TEABF₄ (curve d). Furthermore, the chemical reversibility of **1a**/**1a**⁺ couple is lost completely when LiTFSI serves as the supporting electrolyte (curve e). Together, these results show that the cation radical of triarylimidazole, **1a**⁺, is less stable when using TBAPF₆, TEABF₄ or LiTFSI than when using supporting electrolytes having perchlorate as the counter anion, and the losing of chemical stability may stem from the decomposition of **1a**⁺ itself, or a reaction with residual water in the supporting electrolyte system or with oxygen in air. In addition, it is worth pointing out that the reversible CV of **1a** only substantiate that the **1a**/**1a**⁺ redox couple is chemically stable on the CV time scale, which does not assure that they are chemically stable under a long time scale of preparative electrolysis. In fact, we have found that mediator **1a** decomposed slowly when the solution of **1a** was electrolyzed preparatively at 0.92 V (vs 0.1 M Ag/AgNO₃ in CH₃CN), the peak potential of **1a** obtained from CV analysis under the identical conditions wherein, however, the CV of **1a** exhibits best chemical reversibility.

For comparison, the CVs of TBPA in CH₃CN with different supporting electrolytes were also recorded. As shown in Figure 2 (bottom), no obvious variation was observed for TBPA with all supporting electrolyte tested, except for a small negative shift of peak potentials in the case of LiTFSI. These observations clearly indicate that the choice of supporting electrolyte does not influence the electrochemical behavior of TBPA, an outcome that may stem from the high stability of TBPA⁺⁺ in the electrolytic medium.

The supporting electrolyte dependence of the chemical reversibility of **1a/1a⁺⁺** couple was further confirmed by comparing the anodic to cathodic peak current ratios. As summarized in Table 1, when LiClO₄ was used as the supporting electrolyte, I_p^{Ox}/I_p^{Red} was 1.04, very close to unity, indicating good chemical reversibility. Upon changing to TBAClO₄, the value increased to 1.13, and to 1.45 when TBAPF₆ served as the supporting electrolyte. The reduction current disappears completely in the cases of TEABF₄ and LiTFSI. Once again, the results show that in order to achieve better chemical reversibility of **1a/1a⁺⁺** couple, it is preferable to use LiClO₄ as the supporting electrolyte.

Table 1. Anode to cathode peak current for **1a** in different supporting electrolytes ^a

entry	supporting electrolyte	I_p^{Ox} (μA)	I_p^{Red} (μA)	I_p^{Ox}/I_p^{Red}
1	LiClO ₄	72	69	1.04
2	TBAClO ₄	67	59	1.13
3	TBAPF ₆	64	44	1.45
4	TEABF ₄	66	—	—
5	LiTFSI	112	—	—

^a Conditions: GC working electrode, Pt wire counter and Ag/AgNO₃ (0.1 M in CH₃CN) reference electrode; scan rate: 200 mV s⁻¹, support electrolyte (0.2 M) and **1a** (2.0 mM).

3.2 The effects of supporting electrolyte concentration on the chemical

stability of triarylimidazole-type mediator

Given the concentration dependence of ion pairing, one can envision that the concentration of the supporting electrolyte will also affect the chemical reversibility of the redox catalyst. Figure 3 illustrates the CV curves of **1a** recorded at different concentrations of TBAPF₆ in CH₃CN (upper). Note that both the oxidation and reduction peak currents decrease as the concentration of TBAPF₆ increases. For example, in a solution containing 0.05 M TBAPF₆, the anodic peak current is 68 μ A; it decreases to 48 μ A when the concentration of TBAPF₆ is increased to 0.5 M. Simultaneously, the cathodic peak current decreases 2.2-fold, from 59 μ A to 27 μ A, when the concentration of TBAPF₆ is increased to 0.5 M from 0.05 M. In addition, chemical reversibility also decreases as the concentration of TBAPF₆ increases. For example, the I_p^{Ox}/I_p^{Red} value increases from 1.16 at 0.05 M, to 1.45 at 0.2 M, and 1.77 at 0.5 M.

A similar trend is observed with LiClO₄ (bottom, Fig. 3), while the degree of change is less than with TBAPF₆. It was found that the anodic peak current decreased to 62 μ A from 73 μ A when the concentration of LiClO₄ increased from 0.05 M to 0.5 M. Since the viscosity of the solution increases when the concentration of supporting electrolyte increases, we suggest that the decrease in current described above is a consequence of a reduction in the diffusion rate of **1a** to the electrode surface. In addition, over the concentration range from 0.05 M to 0.5 M, the higher the concentration of the supporting electrolyte, the less chemically reversible the redox couple. Therefore, we conclude that lower concentrations of LiClO₄ in CH₃CN are preferable in order to stabilize the cation radical of **1a**.

Figure 3. CVs of triarylimidazole **1a** (2.0 mM) in 0.05 M, 0.2 M and 0.5 M of TBAPF₆ (upper) and LiClO₄ (bottom) supporting electrolyte in CH₃CN using GC working electrode, Pt wire counter and Ag/AgNO₃ (0.1 M in CH₃CN) reference electrode; scan rate: 200 mV s⁻¹.

3.3 The effect of solvent on the chemical reversibility of triarylimidazole-type mediator

Solvent also affects the performance of a redox mediator. Our prior work has shown that the CV of triarylimidazoles in *protic* solvent, such as methanol, is chemically irreversible [17], which indicates that the cation radical of triarylimidazole

in methanol is not stable and engages in chemical reaction on the timescale of the measurement. We therefore **selected** to investigate the electrochemical behavior of triarylimidazole **1a** in *aprotic* solvents. As shown in Figure 4, I_p^{Ox}/I_p^{Red} for **1a** in CH₃CN was close to unity (1.09), whereas no cathodic current was observed when CH₃NO₂ was used as the solvent. Moreover, the anodic current of **1a** in CH₃NO₂ was only 3 μ A. The significant solvent effect indicates that nitromethane is not a suitable solvent for triarylimidazole mediated electrochemical reactions.

For comparison, voltammograms of TBPA in the two solvents were also measured. A reversible CV was observed in acetonitrile with an 88 mV peak potential difference, nearly the theoretical value for a single electron transfer. In contrast, quasi-reversibility is observed in nitromethane and is accompanied by a peak potential difference of 142 mV; thus the electrochemical **reversibility** of TBPA in CH₃NO₂ lowered. Additionally, owing to the higher viscosity of CH₃NO₂, the magnitude of the peak current for TBPA is less than in CH₃CN. For example, the oxidation peak current of TBPA decreased from 54 μ A to 38 μ A, and the reduction peak current from 47 μ A to 34 μ A.

Figure 4. CVs of triarylimidazole **1a** (2.0 mM) and TBPA (2.0 mM) in 0.05 M LiClO₄ in different solvents using GC working electrode, Pt wire counter and Ag/AgNO₃ (0.1

M in CH₃CN) reference; scan rate: 100 mV s⁻¹.

3.4 Kinetic analysis for the electrocatalytic oxidation of 4-methoxybenzyl alcohol using different triarylimidazoles

In order to further investigate the catalytic efficiency of triarylimidazole for the indirect anodic oxidation of benzyl alcohols [20], and to compare them with the widely used TBPA, we recorded the cyclic voltammograms of triarylimidazole **1a** in LiClO₄/CH₃CN, the electrolyte-solvent system of choice, in the absence and presence of 4-methoxybenzyl alcohol. As shown in Figure 5, **1a** exhibits an oxidation peak at 0.92 V (vs 0.1 M Ag/AgNO₃ in CH₃CN) and a peak current of 47 μA (curve a). In the presence of 4-methoxybenzyl alcohol, the peak current increased to 131 μA, a ~2.8-fold increase (curve b). Since the peak potential of 4-methoxybenzyl alcohol occurs at 1.26 V (vs 0.1 M Ag/AgNO₃ in CH₃CN), the enhancement appearing at 0.92 V is attributed to a catalytic current that arises from regeneration of **1a** following a homogeneous electron transfer between **1a**^{•+} and 4-methoxybenzyl alcohol. Under identical conditions, the peak current for TBPA increased from 51 μA to 67 μA, an ~1.31-fold enhancement, the smaller value reflecting a reduced homogeneous electron transfer efficiency when compared with the triarylimidazole **1a**^{•+}. Considering the fact that peak potential of **1a** is 0.92 V (vs 0.1 M Ag/AgNO₃ in CH₃CN), while that for TBPA appears at 0.79 V, we speculate that the diminished catalytic efficiency may arise from a smaller potential difference between **1a** and 4-methoxybenzyl alcohol (ΔE 0.34 V) compared with the substrate and TBPA (ΔE 0.47 V). Regardless of its origin, we see here that the smaller the potential difference between redox catalyst and the substrate, the greater the catalytic efficiency.

Figure 5. Cyclic voltammograms of triarylimidazole **1a** and TBPA in 0.05 M LiClO₄/CH₃CN in the presence of 4-methoxybenzyl alcohol and 2,6-lutidine using GC as working electrode, Pt wire counter and Ag/AgNO₃ (0.1 M in CH₃CN) reference. Scan rate: 100 mV/S. (a): triarylimidazole **1a** (2.0 mM). (b): **1a** (2.0 mM) and 4-methoxybenzyl alcohol (80 mM) and 2,6-lutidine (200 mM). (c): TBPA (2.0 mM); (d): TBPA (2.0 mM) and *p*-methoxybenzyl alcohol (80 mM) and 2,6-lutidine (200 mM).

To further investigate the correlation of potential difference between the mediator and substrate with the homogeneous electron transfer rate, the CV response of three triarylimidazole mediators, **1b**, **1c** and **1d** was recorded in the absence and presence of excess 4-methoxybenzyl alcohol and 2,6-lutidine. As shown in Figure 6, reversible chemical behavior is observed for all three triarylimidazoles (curve a) and, as we have noted previously, their oxidation peak potentials vary as a function of the electronic character of the substituent appended to the aryl ring. For example, the peak potential for the phenyl substituted imidazole **1c** (X = H) is 0.87 V (vs 0.1 M Ag/AgNO₃ in CH₃CN). When H is replaced by an electron-donating methoxy group the value shifts to 0.75 V for **1b**, and to 0.99 V when an electron-withdrawing trifluoromethyl group is present (**1d**, X = CF₃).

Figure 6. Cyclic voltammograms of 2.0 mM **1b** (I; X = OMe), **1c** (II; X = H) and **1d** (III; X = CF₃) in the absence (a), and presence (b), of 80 mM 4-methoxybenzyl alcohol and 200 mM 2,6-lutidine in N₂-saturated LiClO₄/CH₃CN supporting electrolyte using glassy carbon working electrode, Pt wire counter and Ag/AgNO₃ (0.1 M in CH₃CN) reference electrode, scan rate: 100 mV/s.

Voltammograms of the three triarylimidazoles were reacquired with 80 mM *p*-methoxy benzyl alcohol and 200 mM 2,6-lutidine present in the solution (curve b). A dramatic increase of the oxidation peak current and a disappearance of reduction peak current was observed, leading to typical sigmoidal-shaped curves, a feature that is diagnostic of an electrocatalytic process. As expected, the magnitude of the catalytic current was quite different from one triarylimidazole to another. Thus, the oxidation peak current of **1b** increased from 27.7 μA to 41.4 μA in the presence of excess 4-methoxy benzyl alcohol and 2,6-lutidine. In the case of **1c**, the current increased more than 2.4-fold from 42.9 μA to 102.4 μA. For **1d**, the peak current increased 6-fold, from 36.4 μA to 217.5 μA. The results further substantiate the idea that the smaller the potential difference between triarylimidazole and the substrate, the larger the catalytic currents.

The difference between the peak current for the triarylimidazole mediators in the presence and absence of 4-methoxybenzyl alcohol can be directly correlated to the

homogeneous electron transfer rate. In order to gain a more quantitative comparison between the different triarylimidazole mediators, additional electrochemical studies were carried out.

As shown in Figure 7, the oxidation peak current, I_p^{ox} , for triarylimidazole **1c** correlates linearly with the square root of the scan rate, $v^{1/2}$, which indicates that the heterogeneous electron transfer at the anode is a diffusion-controlled process. In addition, the slope of the line being 0.5 reveals that adsorption of **1c** on the electrode does not occur. [6, 22]

Figure 7. Oxidation peak current for **1c** with the square root of scan rate. Conditions: GC working electrode, Pt wire counter and Ag/AgNO₃ (0.1 M in CH₃CN) reference electrode; scan rate range: 40-160 mV s⁻¹; 2.0 mM **1c**; N₂-saturated 0.1 M LiClO₄/CH₃CN.

For such a process, the ratio of the catalytic current to the diffusion current, I_k/I_d , is proportional to $(k_f RT/nF)^{1/2} v^{-1/2}$, wherein I_k is catalytic current, I_d the diffusion controlled current, n is number of electrons transferred, and T is the temperature [23,24]. Based on the CV data for **1c** obtained at different scan rates, a working curve of I_k/I_d vs. $(k_f RT/nF)^{1/2} v^{-1/2}$ was obtained as shown in Figure 8. From the slope of the linear plot, the pseudo first-order homogeneous rate constant of **1c** could be determined. Using identical methods and under the identical conditions, pseudo first-order homogeneous rate constants for **1b** and **1d** were also acquired and the

results are summarized in Table 2.

Figure 8. Linear plot of I_k/I_d vs. $v^{-1/2}$ of **1c** as a function of square root of the scan rate. Data was obtained from CV measurements of 2.0 mM **1c** in N_2 -saturated 0.1 M $LiClO_4/CH_3CN$. GC working electrode, Pt wire counter and $Ag/AgNO_3$ (0.1 M in CH_3CN) reference electrode; scan rate range: 40-160 $mV s^{-1}$;

Table 2. Pseudo first-order homogeneous rate constant for triarylimidazole mediator **1b**, **1c** and **1d**

Redox catalyst	E_{ox}^a (V)	ΔE_{ox}^b (V)	k_f (s^{-1})
1b (X = OMe)	0.75	0.51	0.33
1c (X = H)	0.87	0.39	10.15
1d (X = CF_3)	0.99	0.27	85.53

^a The potential is referred $Ag/AgNO_3$ (0.1 M in CH_3CN)

^b The peak potential difference between redox catalyst and 4-methoxybenzyl alcohol

The data reveals that the pseudo first-order homogeneous rate constants increase as the potential difference between the redox catalyst and 4-methoxybenzyl alcohol decreases; thus, $k_f(\mathbf{1d}) > k_f(\mathbf{1c}) > k_f(\mathbf{1b})$. For example, in the case of **1b**, ΔE_{ox} is 0.51 V, and their pseudo first-order homogeneous rate constant is measured to be 0.33 s^{-1} . When the potential difference decreases to 0.39 V (for **1c**) and 0.27 (for **1d**), the corresponding k_f increases to 10.15 s^{-1} and 85.53 s^{-1} , respectively.

Conclusion

In summary, the electrochemical performance of triarylimidazole-type redox catalysts in different supporting electrolyte and solvent systems was investigated. The results show that their current response and chemical stability differs depending upon the nature of the conducting salt and solvent, as well as the concentration of the supporting electrolyte. In contrast, only a slight change was observed for TBPA under the identical CV conditions. The best chemical stability for the triarylimidazoles could be achieved in 0.05 M LiClO₄/CH₃CN. Kinetic analysis of the electrocatalytic oxidation of 4-methoxybenzyl alcohol using different triarylimidazoles was carried out. The electrochemical catalytic efficiency was found to depend upon the peak potential difference between a redox catalyst and the substrate. The smaller the potential gap, the greater the catalytic efficiency. This observation was further confirmed by a quantitative measurement of the pseudo first-order homogeneous rate constants of three triarylimidazole-type redox catalysts in their oxidation of 4-methoxybenzyl alcohol.

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