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Electrochemical Studies of TEMPO Substituted α, β-Unsaturated Esters

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Abstract

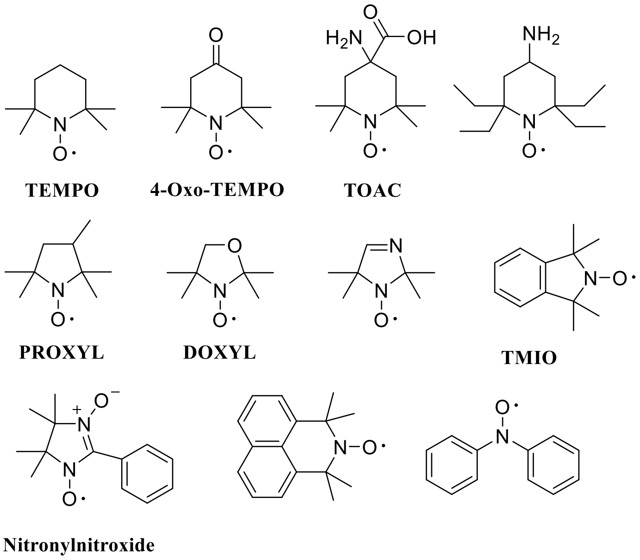
Electrochemical properties of novel α,β -unsaturated ester compounds bearing 2,2,6,6-tetramethylpiperidine-N-oxyl were studied. Synthesis of the compounds were realized with basic aldehydes and malonic acid by Knoevenagel-Doebner reaction followed by the esterification of the compounds with 4-hydroxy-2,2,6,6-tetramethylpiperidine-N-oxy by Steglich reactions with high yields. Also, poly(2,2,6,6-tetrametylpiperidine-N-oxy-4-yl 3-(thiophene-3-yl)acrylate) synthesis and characterization are given. Afterwards, electrochemical properties were studied by cyclic voltammetry in order to determine the diffusion coefficient (Do) and standard electron-transfer rate coefficients (ko).

Keywords: Nitroxide, Ester, Diffusion, Rate Coefficient

INTRODUCTION

Nitroxide is a stable radical compound used in many applications. The presence of sp^3 carbon groups attached to carbon atoms vicinal to nitrogen provides a perfect stability to nitroxide compounds by generating steric hindrance. Also, the significant properties of nitroxides originates from the three electron π bond forming the overlapping of the $2p_z$ orbitals of oxygen and nitrogen atoms (Volodarsky, 1994).

There are many variations of nitroxide species illustrated in Scheme 1 (Ouari, 2021). There are many nitroxide containing organic molecules. Among them, 2,2,6,6-tetramethylpiperidine-N-oxy (TEMPO) is mostly known and mostly used in many applications.



Scheme 1. Some nitroxide bearing organic molecules

Organic radical batteries bearing nitroxide abstracted to organic backbone, nitroxide-mediated living free radical polymerization (NMP), nitroxide spin labels, spin probes and radicals in-vivo spectroscopy and imaging are the best known applications of nitroxides. Because of their ability to interact with free radicals, they have been used for many years as biophysical tools (Soule, 2007).

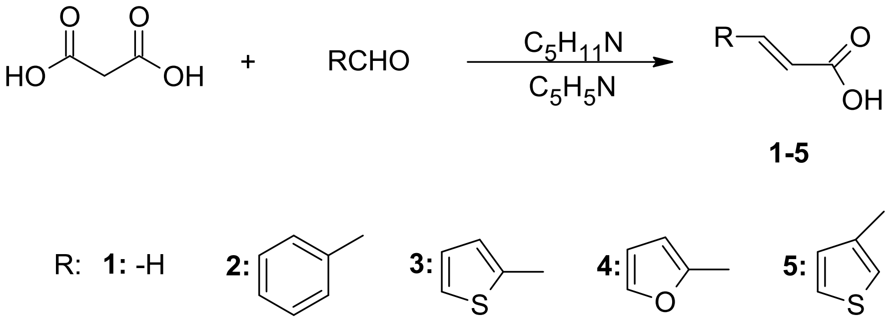
This article aims to investigate the electrochemical properties of nitroxide bearing ester compounds having aromatic and heteroaromatic substituents by cyclic voltammetry in order to determine the diffusion coefficient (D_o) and standard electron-transfer rate coefficients (k_o). Also, the synthesis and characterization data of the molecules are explained. So far, these compounds are not presented in the literature. These compounds have the potential to be used in Li-ion batteries as redox shuttles in electrolyte. However, diffusion coefficients and electron transfer-rate coefficients are not investigated. Therefore, we consider that this study to be important.

Experimental section

All the compounds were purchased from Merck and used without further purification. The IR spectra of all the compounds synthesized in this study were recorded with a Perkin-Elmer Spectrum 100 device at a resolution of 4 cm^{-1} in the range of 600-3600 cm^{-1} using anhydrous KBr disc. ^1H-NMR and ^{13}C-NMR spectra were recorded in Bruker 500 brand FT-NMR spectrometer with $CDCl_3$ as solvent and using TMS standard. Mass spectra were taken on TRACE DSQ Thermofinnigan and Agilent 5975C GC/MSD spectrometer using EIS method. Electrochemical tests of prepared half-cells were recorded using Princeton Applied Research (PAR) VersaSTAT MC 4-channel potentiostat/galvanostat. Thermogravimetric analyzes of synthesized polymers were recorded in Mettler-Toledo TGA-851 device at 5°C/min. The melting points of the synthesized molecules were determined using the Buchi brand melting point device. The molecular weights of the polymers were recorded in an Agilent 1100 GPC instrument (mobile phase: THF), with a flow rate of 0.4 mL/min. Charge/discharge processes of the prepared cells were performed using the chronopotentiometry method in a Potentiostat/Galvanostat device. All cells were prepared in Etelux Lab2000 and Vigor 1500GS brand GloveBox.

Synthesis of the acid compounds (2-5)

A 50 mL piridine solution of malonic acid (0.2 mol, 20.8 g), corresponding aldehyde (0.1 mol) and and piperidine ($C_5H_{11}N$, 1 mL) were prepared. The solution is heated by stirring up to 90-95°C and then reflued 5 minutes. Afterwards, the solution is cooled and diluted with water and to this solution HCl is added dropwise (Scheme 2).



Scheme 2. Synthesis of the unsaturated acid compounds

Cinnamic Acid (2)

Yield: 91% (13.47 g). mp: 132-135°C. IR, ν_{max}: 1620 (C=C), 1690 (C=O), 2400-300 (COOH) cm^{-1}. ^{1}HNMR (500 MHz, $CDCl_3$) δ: 6.50 (d, *J* = 15 Hz, 1H), 7.29-.760 (m, 5H, ArH), 7.85 (d, *J* = 15 Hz, 1H), 11.32 (s, 1H). MS (APCI, 100eV) m/z (%): 148 ($[M]^+$), 147 ($[M – H]^+$), 131 ($[M – OH]^+$), 103 ($[M – CH_3O]^+$), 91 ($[PhCH_2]^+$), 77 ($[Ph]^+$). Anal. calc. for $C_9H_8O_2$ (148 g/mol): C 72.96; H 5.44; Found: C 73.05; H 5.39.

3-(Thiophene-2-yl)acrylic acid (3)

Yield: 80% (12.32 g). mp: 145-148°C. IR (KBr disk): 1620 (C=C), 1700 (C=O), 2410-3000 (COOH). ^{1}H-NMR (500MHz, $CDCl_3$): 6.26 (d, *J* = 15 Hz, 1H), 7.09 (m, 3H, ArH), 7.90 (d, *J* = 15 Hz, 1H), 9.91 (s, 1H). MS (m/z): 154 ($[M]^+$), 137 ($[M – OH]^+$), 121 ($[M – SH]^+$), 109 ($[M – CH_3O]^+$). Anal. calc. for $C_7H_6SO_2$, (154 g/mol) C 54.53; H 3.92; S 20.80. Found: C 54.49; H 3.88; S 20.87.

3-(Furan-2-yl)acrylic acid (4)

Yield: 85% (11.73 g). mp: 139-141˚C. IR (KBr disk): 1630 (C=C), 1710 (C=O), 2390-3000 (COOH). ^{1}H-NMR (500 MHz, $CDCl_3$): 6.33 (d, *J* = 15 Hz, 1H), 6.50 (dd, J = 8 Hz, 3 Hz, 1H, ArH), 6.68 (d, *J* = 15 Hz, 1H), 7.53 (m, 2H, ArH). MS (m/z): 138 ($[M]^+$), 121 ($[M – OH]^+$), 110, 94 ($[M – CHO_2]^+$), 82 ($[M – C_2O_2]^+$), 65, 53. Anal. calc. for: $C_7H_6O_3$, (138 g/mol). C 60.87; H 4.38. Found C 60.85; H 4.45.

3-(Thiophene-3-yl)acrylic acid (5)

Yield: % 75 (11.55 g). mp: 152-154°C. IR (KBr disk): 1620 (C=C), 1680 (C=O), 2450-3000 (COOH). ^{1}H-NMR (500MHz, $CDCl_3$): 6.31 (d, *J* = 15 Hz, 1H), 7.20 – 7.63 (m, 3H), 7.81 (d, *J* = 15, 1H), 10.88 (s, 1H). MS (m/z): 154 ($[M]^+$), 137 ($[M – OH]^+$), 112, 109 ($[M – CH_3O]^+$), 97, 82. Anal. calc. for $C_7H_6SO_2$, (154 g/mol). C 54.53; H 3.92; S 20.80. Found C 54.58; H 3.99; S 20.77.

Synthesis of the TEMPO substituted esters:

4-hydroxy TEMPO (5 mmol, 0.86 g), DMAP (1.25 mmol, 0.153 g) and DCC (5 mmol, 1.02 g) dissolved in dichloromethane at 0°C under argon under α,β-unsaturated carboxylic acid (5 mmol) is added. The mixture is stirred at room temperature for 12 hours. The solids formed at the end of the reaction are filtered off and the solution is treated with 1N HCl, then neutralized with saturated $NaHCO_3$. The organic phase is dried over Na_2SO_4 and purified on the column in a hexane/ethyl acetate solvent system.

2,2,6,6-Tetramethylpiperidine-N-oxy-4-yl acrylate (6)

Yield: 73% (0.82 g). mp: 75-77˚C. IR (KBr disk): 1420 (N-O), 1680 (C=C), 1730 (C=O), 2980 (C-H, aliphatic). MS (m/z): 226 ($[M]^+$), 212 ($[M - CH_2]^+$), 196 ($[M - C_2H_6]^+$), 154 ($[C_9H_{16}NO]^+$), 140 ($[C_9H_{18}N]^+$), 124 ($[C_9H_{16}]^+$), 109, 98, 82, 67, 55 ($[C_3H_3O]^+$). Anal. calc. for $C_{12}H_{20}NO_3$, (226 g/mol). C 63.69; H 8.91; N 6.19. Found C 63.63; H 8.82; N 6.24.

2,2,6,6-Tetramethylpiperidine-N-oxy-4-yl cinnamate (7)

Yield: 91% (1.36 g). mp: 101-105˚C, IR (KBr disk): 1470 (N-O), 1630 (C=C), 1720 (C=O), 2950 (C-H, aliphatic), 3010 (C=C, aromatic). MS (m/z): 302 ($[M]^+$), 288 ($[M - CH_2]^+$), 272 ($[M - C_2H_6]^+$), 228, 154 ($[C_9H_{16}NO]^+$), 140 ($[C_9H_{18}N]^+$), 124 ($[C_9H_{16}]^+$), 103, 91, 77 ($[C_6H_5]^+$), 58. Anal. calc. for $C_{18}H_{24}NO_3$, (302 g/mol). C 71.50; H 8.00; N 4.63. Found C 71.58; H 8.05; N 4.67.

2,2,6,6-Tetrametylpiperidine-N-oxy-4-yl-3-(thiophene-2-yl)acrylate (8)

Yield: 96% (1.48 g). mp: 102-103˚C. IR (KBr disc): 1450 (N-O), 1630 (C=C), 1720 (C=O), 2980 (C-H, aliphatic), 3020 (C=C, aromatic). MS (m/z): 308 ($[M]^+$), 294 ($[M - CH_2]^+$), 278 ($[M - C_2H_6]^+$), 154 ($[C_9H_{16}NO]^+$), 137, 124 ($[C_9H_{16}]^+$), 109, 97, 82 ($[C_4H_2S]^+$), 69, 55 ($[C_3H_3O]^+$). Anal. calc. for $C_{16}H_{22}NSO_3$, (308 g/mol). C 62.31; H 7.19; N 4.54; S 10.40. Found C 62.26; H 7.22; N 4.51; S 10.37.

2,2,6,6-Tetramethylpiperidine-N-oxy-4-yl-3-(furan-2-yl)acrylate (9)

Yield: 85% (1.24 g). mp: 79-82˚C. IR (KBr disc): 1420 (N-O), 1630 (C=C), 1700 (C=O), 2930 (C-H), 3020 (C=C, aromatic). MS (m/z): 292 ($[M]^+$), 278 ($[M - CH_2]^+$), 262 ($[M - C_2H_6]^+$), 154 ($[C_9H_{16}NO]^+$), 140 ($[C_9H_{18}N]^+$), 121, 109, 98, 82, 65 ($[C_4H_2O]^+$), 53. Anal. calc. for $C_{16}H_{22}NO_4$, (292 g/mol). C 65.73; H 7.58; N 4.79. Found C 65.69; H 7.55; N 4.74.

2,2,6,6-Tetrametylpiperidine-N-oxy-4-yl-3-(thiophene-3-yl)acrylate (10)

Yield: 80% (1.23 g). EN: 133-136˚C. IR (KBr disc): 1480 (N-O), 1630 (C=C), 1720 (C=O), 2950 (C-H, aliphatic), 3010 (C=C, aromatic). MS (m/z): 309 ($[M + H]^+$), 308 ($[M]^+$), 294 ($[M - CH_2]^+$), 278 ($[M - C_2H_6]^+$), 154 ($[C_9H_{16}NO]^+$), 140 ($[C_9H_{18}N]^+$), 124, 109, 98, 82 ($[C_4H_2S]^+$), 69, 58. Anal. calc. for $C_{16}H_{22}NSO_3$, (308 g/mol). C 62.31; H 7.19; N 4.54; S 10.40. Found C 62.36; H 7.14; N 4.46; S 10.35.

Poly(2,2,6,6-tetrametylpiperidine-N-oxy-4-yl 3-(thiophene-3-yl)acrylate) (11)

Iron trifluoracetate $[Fe_3O(O_2CCF_3)_6(H_2O)_3]$ catalyst was weighed at 1% mole (0.01 mmol, 0.00915 g) and placed in a Schlenk flask and dissolved in 1 mL of anhydrous acetonitrile. The monomer (1 mmol, 0.308 g) was weighed into a separate Schlenk tube and dissolved in 5 mL of anhydrous acetonitrile. N_2 gas was passed through both solutions for 30 minutes. Then the monomer solution was added to the catalyst solution and stirred at 70°C for 5 h. After completion of the reaction, it was dropped dropwise into the hexane solution and the polymer was precipitated and filtered. The obtained polymer was washed with hexane toughly and dried in a vacuum oven.

Yield: 75% (0,25 g). mp: Decomposed. FTIR (KBr disc): 1480, 1640, 1720, 2950. GPC (THF): M_n: 889 g/mol, M_w: 896 g/mol, $M_w/M_n = 1.01$.

Electrochemical measurements

All electrochemical tests were performed using a three-electrode cell assembly. The properties of active compounds vs. Ag/AgCl were investigated. Electrochemical measurements were carried out by taking the electrode working electrode containing the active substance prepared in this system and Ag/AgCl as reference and Pt wire as counter electrode. The mixture containing 80% of the organic material to be measured (**6**, **7**, **8**, **9** and **10**), 15% of carbon black and 5% of PVdF is slurry with NMP, it is applied on 10 µm thick aluminum sheets cut in 15 mm diameter and weighed followed by to be left to dry in an oven at 70°C. When the NMP has completely evaporated, it is pressed in a hot press at 80°C with and weighed again and kept in a vacuum oven at 75°C for 2 h. The electrode, which is removed from the vacuum oven, is quickly placed in an argon atmosphere controlled glove box and prepared a a test cell to be tested.

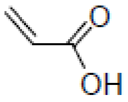
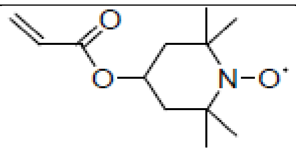
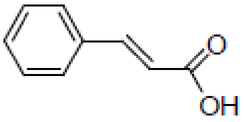
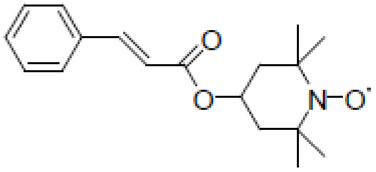
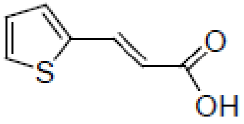
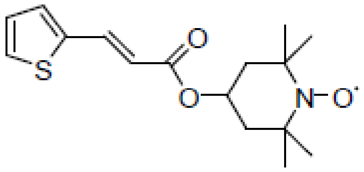
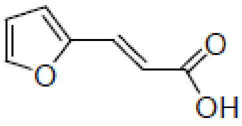
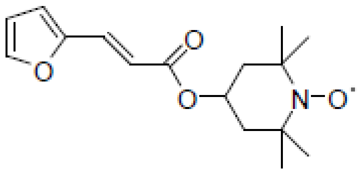
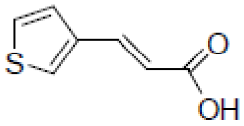
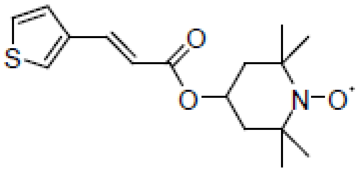
RESULT AND DISCUSSION

Synthesis of the compounds

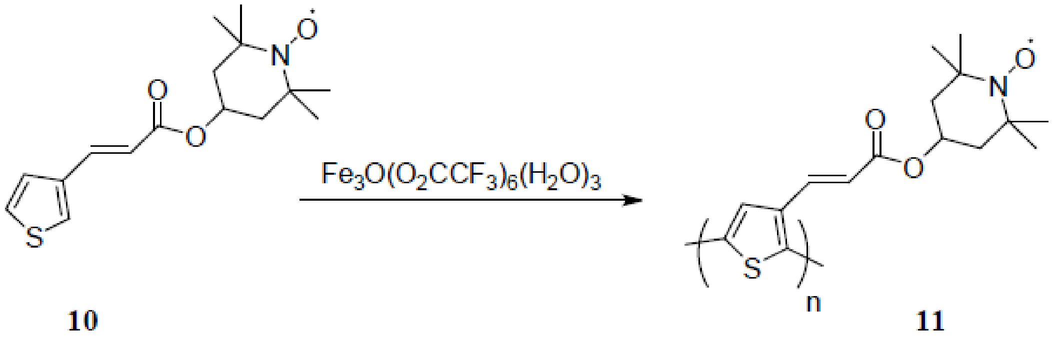
The synthesis of α,β-unsaturated acid derivatives compounds **1-5** was carried out by the Knoevenagel-Doebner Reaction (Scheme 1) (Yılmaz, 2016). Reaction yields were found to be 91% for compound **2**, 80% for **3**; 85% for **4** and 75% for **5**. The synthesized α,β-unsaturated carboxylic acid compounds **1-5** were esterified with 4-hydroxy TEMPO using

Dicyclocarbodiimide (DCC) and N,N-dimethylaminopyridine (DMAP) at low temperature (0-5°C) by Steglich reaction. In Table 1, the reaction product compounds **6-10** and their yields are given. Compounds were synthesized as a single product with high yields by the Steglich reaction. Product yields were calculated after the crude products were passed through column chromatography. Characterization of the compounds **6-10** obtained was carried out using FTIR and MS. However, the presence of free radicals in these compounds prevents the taking of ^{1}H-NMR of these compounds. It has been reported in the literature that NMR spectra can be obtained by reducing compounds to hydroxyl amine with isoascorbic acid in order to obtain ^{1}H-NMR (Nakahara, 2002). Within this method, compounds **6-10** are reduced to hydroxyl amine, but since the reaction is an equilibrium reaction; thus, ^{1}H-NMR results could not be obtained due to the fact that it turns back to nitroxide in a short time.

Table 1. The yields of the compounds **1-5** and **6-10**.

	Products 1-5	Yields (%)	Products 6-10	Yields (%)
1		-		73
2		91		91
3		80		96
4		85		85
5		75		80

Polymerization of cinnamic acid and derivatives were poor explained by Marvel and coworkers (Marvel, 1953). Even though our efforts, particularly by radical polymerization with benzoyl peroxide and 2,2’-azobis(cyclohexanecarbonitrile), we failed to polymerization of Compounds **6-9**. It was polymerized thanks to the open 2- and 5- positions of the thiophene in the synthesized compound **10**. In order to polymerize this compound, radical polymerization was tried in acetonitrile, dichloromethane, chloroform and carbon tetrachloride solvent systems together with $FeCl_3$ (Kim, 1999, Lanzi, 2002, Aydın, 2011). However, it was observed that polymerization did not occur. Besides, polymerization was tried using a catalyst. Multi-valent Fe(II)-Fe(III) trifluoracetate complex was used as catalyst (Ertürk, 2008). As a result of the reaction, polymerization was carried out with 75% efficiency (Scheme 3).



Scheme 3. Polymerization of Compound **10**

In the GPC analysis of the obtained poly(2,2,6,6-tetramethylpiperidin-N-oxy-4-yl 3-(thiophen-3-yl)acrylate) (**11**) polymer, the number average molar mass M_n = 889 g/mol and by mass. The average molar mass was determined as M_w = 896 g/mol. The heterogeneity index value (M_w/M_n) of the polymer was calculated as 1.01. However, due to the high resolution of compound **11**, no electrochemical measurement were obtained.

Determination of diffusion coefficients (D_o) and the standard rate constants (*k*)

The flow of electrons from electroactive surfaces is accompanied by the movement of counterions to maintain charge balance. Thus, distance, electron movement, shape of redox surfaces, and electronic properties of counterions and redox surfaces, and the charge balance between them all affect the permeability and electron conduction of counterions. Therefore, many studies on electroactive surfaces limit the characterization of electron flow by experimental determination of D_o.

The standard rate constants of nitroxide derivatives were calculated by Nicholson method. Nicholson assume diffusion controlled current. Also, Randles-Sevcik was applied for the calculation of Diffusion coefficient.

Various electrochemical and spectroscopic studies are carried out to determine the diffusion coefficient. Cyclic voltammetry is one of these methods. The diffusion coefficient for reversible proocesses can be determined by anodic peak current in cyclic voltammetry technique using the Randles-Sevcik Equation (1) namely,

$$i_{\mathrm{p}} = 0.4463\, n^{3/2} F^{3/2} A\, (RT)^{-1/2} D_o^{1/2} C\, v^{1/2} \qquad (1)$$

where, i_{p} is the peak current; n is the number of electrons that oxidized/reduced species; F Faraday's constant; A electrode area; R is the gas constant; T is the ambient temperature; D_{o}, diffusion coefficient; C is the concentration of the species and v is the scan rate in mV/s (Randles, 1948; Sevcik, 1948).

After taking the cyclic voltammogram of a reversible reactions (Figure 1), the peak currents are plotted against the square root of the scan rate and the diffusion coefficient is calculated from Equation 1 using the slope obtained (Figure 1). Thus, Table 2 indicates the diffusion coefficients of nitroxide compounds calculated from cyclic voltammetry by using Randles-Sevcik Equation. It is worth to mention that Shaeen *et.al.* calculated the diffusion coefficient of 4-hydroxy TEMPO itself was 1.6 x 10^{-7} cm^2/s in 50 mM ethaline solution by using Levich Equation (Shaheen, 2020).

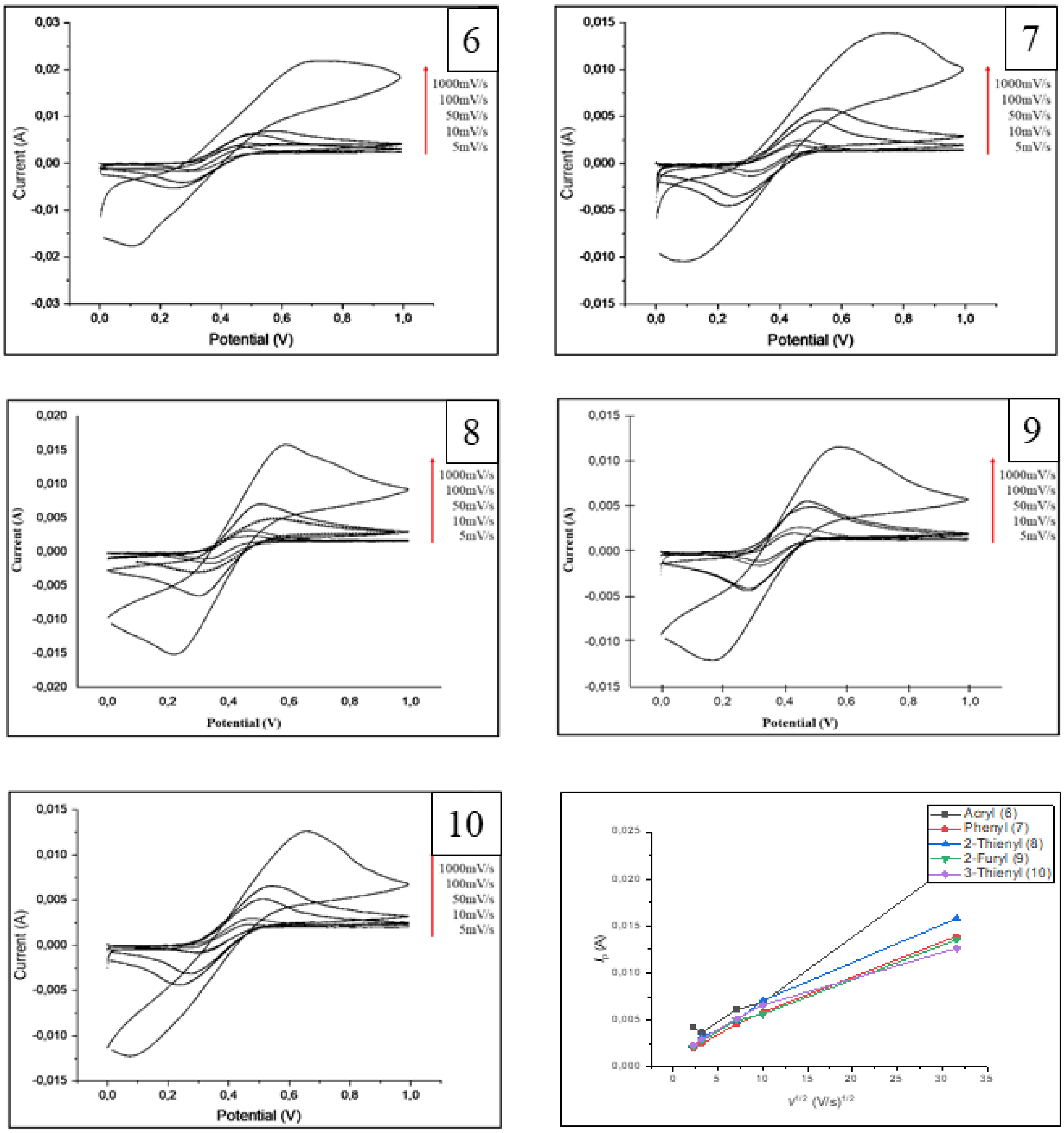


Figure 1. Cyclic voltamograms of the nitroxide compounds **6-10** and the curves of peak current to square root of scan rate

Standard electron transfer rate coefficients (k_o) were calculated by using the Nicholson curve from the cyclic voltammetry method, using the formula in Equation 2 below:

$$\psi = (\gamma^{\alpha} k_s)/(\pi n F v D_o / R T)^{1/2} \qquad (2)$$

where n is the number of electrons of the reduced/oxidized species; F is Faraday's constant; v, scan rate; D_o, diffusion coefficient (of oxidized or reduced species); R is the gas constant and T is the ambient temperature. In reversible reactions, the value of $\gamma = D_{ox} / D_{red}$ (Diffusion constant for oxidation and reduction) is taken as 1. The α value is expressed as α = (n F v) / RT. The ψ value is defined as a function of ΔEp (Nicholson, 1965). All the calculated standard rate constants for nitroxide compounds **6-10** are indicated in Table 2.

Table 2. Diffusion coefficients of the nitroxide compounds **6-10**

Nitroxide Compound	Slope	Diffusion (D_o, cm^2/s)	Standard Rate Constants (k_o, cm/s)
6	0.0017	4.72×10^{-5}	0.005
7	0.0018	3.86×10^{-5}	0.004
8	0.0023	3.86×10^{-5}	0.004
9	0.0014	3.86×10^{-5}	0.004
10	0.0018	3.34×10^{-5}	0.004

CONCLUSION

Nitroxide compound is a useful agent for many industries since it is a stable radical. Hence, it fulfills all the tasks assigned to it in every field within the highest efficiency. To date, the electrochemical properties of nitroxide ester compounds have not been reported in the literature. Therefore, this study reveals the electrochemical properties of these compounds. To compare with 4-hydroxy TEMPO itself (=1.6×10^{-7} cm^2/s), a better diffusion coefficient was obtained when 4-hydroxy TEMPO esterified with the corresponding molecules (**6**, **7**, **8**, **9**, **10**). In summary, a high diffusion coefficient values together with standard rate constants were obtained.

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REFERENCES

Aydın, M., Esat, B., Kılıç, Ç., Köse, M.E., Ata, A. and Yılmaz, F. 2011. A polythiophene derivative bearing TEMPO as a cathode material for rechargeable batteries. European Polymer Journal, 47:2283-2294.

Ertürk, E., Demir, A.S. 2008. Iron(III) trifluoroacetate[Fe(O_2CCF_3)$_3$] catalyzed epoxide opening with amines. Arkivoc, 2008 (2):160-171.

Ouari, O., Gigmes, D. 2021. Nitroxides. Chapter 1: A Brief History and Outlook of Nitroxides. 1st Ed. The Royal Society of Chemistry, London.

Kim, B., Chen, L., Gong, J. and Osada, Y. 1999. Titration behaviour and spectral transitions of water-soluble polythiophene carboxylic acids. Macromolecules, 32:3964-3969.

Lanzi, M., Paganin, L., Costa-Bizzarri, P., Della-Case, C. and Fraleoni, A. 2002. Facile synthesis of soluble multifunctional polyalkylthiophenes. Macrolecular Rapid Communications, 23:630-633.

Marvel, C.S. and McCain, G.H. 1953. Polymerization of esters of cinnamic acid. Journal of American Chemical Society, 75:3272-3273.

Nakahara, K., Iwasa, S., Satoh, M., Morioka, Y., Iriyama J. and Suguro, M. 2002. Rechargeable batteries with organic radical cathodes. Chemical Physics Letters, 359:351-354.

Nicholson, R.S. 1965. Theory and application cyclic voltammetry for measurement of electrode reaction kinetics. Analytical Chemistry, 37:1351-1355.

Randles, J.E.B. 1948. A cathode ray polarograph. Part II. The current-voltage curves. Trans. Faraday Soc., 44:327-338.

Sevcik, A. 1948. Oscillographic polarography with periodical triangular voltage. Collect. Czech. Chem. Commun., 13:349-377.

Shaheen, N.A., Ijjada, M., Vukmirovic, M.B., Akolkar, R. 2020. Mechanism of electrochemical oxidation of nitroxide radicals in ethaline deep eutectic solvent. J. Electrochem. Soc. 167:143505.

Soule, B.P., Hyodo, F., Matsumoto, K., Simone, N.L. Cook J.A., Krishna, M.C., Mitchell, J.B. 2007. The chemistry of biology and nitroxide compounds. Free Radical Biology & Medicine, 42:1632-1650.

Uçar, M., Solak, A.O., Aksu, M.L., Toy, M. 2002. Electrochemical investigation of 4-haloderivatives of N,N-dimethyl-4-aminoazobenzene. Turk. J. Chem. 26:509-520.

Volodarsky, L.B., Reznikov, V.A., Ovcharenko, V.I. 1994. Synthetic chemistry of stable nitroxides. 1st Ed. CRC Press, Boca Raton: Florida.

Yılmaz, M., Ustalar, A., Uçan B., Pekel, A.T. 2016. Regio- and diastereoselective synthesis of trans-dihydrofuran-3-carboxamides by radical addition of 1,3-dicarbonyl compounds to acrylamides using manganese(III) acetate and determination of exact configuration by X-ray crystallography. Arkivoc iv:79-91.