

Electrochemical Oxidation of Sulfinic Acids: Efficient Oxidative Synthesis of Diaryl Disulfones

Davood Nematollahi,^z Mahsa Joudaki, Sadegh Khazalpour, and Firozeh Pouladi

Faculty of Chemistry, Bu-Ali Sina University, Hamedan 65178-38683, Iran

Electrochemical oxidation of sulfinic acids has been studied in aqueous solutions using cyclic voltammetry, controlled-potential coulometry, chronoamperometry and chronocoulometry methods. The results indicate that the oxidation of sulfinic acids is an irreversible one-electron transfer process. Our data also show that the electrogenerated sulfonyl radicals undergo a dimerization reaction to form disulfone derivatives. The present work has led to the development of a facile and environmentally friendly electrochemical method for the synthesis of diphenyl disulfone derivatives. (© 2017 The Electrochemical Society. [DOI: 10.1149/2.1111706jes] All rights reserved.

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Electrochemistry is a powerful tool for the synthesis of organic compounds. It can be used for Michael addition reaction,¹⁻³ Diels– Alder reaction,⁴ functional-group interconversion,^{5,6} installation of heteroatom moieties,⁵ C-C coupling reactions,^{7,8} dimerization,⁹ trimerization¹⁰ and polymerization.¹¹ Diphenyl disulfones are already utilized in several chemical reactions as reagent for selective cleavage of methylprenyl (2,3-dimethylbut-2-en-1-yl), prenyl (3-methylbut-2-en1-yl), and methallyl (2-methylallyl) ethers,¹² and as catalyst for isomerization of alkenes,^{13,14} chemoselective cleavage of methyl-substituted allyl ethers,¹⁵ photopolymerization of vinyl monomers,¹⁶

Several methods have been reported for the synthesis of diphenyl disulfone derivatives, including the oxidation of benzensulfinic acid by KMNO₄,¹⁷ and Cobalt(III),¹⁸ oxidation of 1,2-bis-(benzenesulfonyl)hydrazine by NaOCl in CHCl₃,¹⁹ thermal reaction of benzene and sulfur dioxide in the presence of benzoyl peroxide,²⁰ decomposition of phenylphenylsulfonyl diimide in p-xylene,²¹ oxidation of diphenyl disulfide by hydrogen peroxide,²² oxidation of N,N'-bis(benzenesulfonyl) hydrazide by sodium hypochlorite²³ or nitric acid,²⁴ reaction of sodium benzenesulfinate and benzenesulfonyl chloride,²⁵ and reduction of benzenesulfonyl chloride by samarium²⁶ or lithium.²⁷ However, these methods have the following disadvantages such as low yield, poor purity, lack of easy availability/preparation of the starting materials, tedious work-up, heavy metal pollution, strongly acidic media and safety problems. These disadvantages have motivated us to develop a green protocol for the synthesis of diphenyl disulfones by electrochemical oxidation of aryl sulfinic acids in aqueous solution. This work leads to a straight-forward methodology for the synthesis of diphenyl disulfones by an environmentally friendly method in ambient conditions and in an undivided cell.

The second objective of this study is to report the electrochemical behavior and electrochemical parameters (diffusion coefficient, *D*, surface excess, Γ , and average area, σ) of the sulfinic acids by using of cyclic voltammetry, chronoamperometry and chronocoulometry methods.

Experimental

Apparatus and reagents.—Cyclic voltammetry, chronoamperometry and chronocoulometry were performed using a Zahner pp201 potentiostat/galvanostat. Macro-scale electrolysis and controlledpotential coulometry were carried out using a Behpajooh C 2056 potentiostat. The glassy carbon disk (1.8 mm diameter) was used as the working electrode in the voltammetry experiments and a platinum wire was used as the counter electrode. The working electrode used in controlled-potential coulometry and macroscale electrolysis was an assembly of two ordinary carbon plates (20 mm length, 10 mm width and 40 mm height), and a large stainless steel gauze cylinder (25 cm² area) constituted the counter electrode. The glassy carbon electrode potentials were measured *versus* Ag/AgCl (from AZAR electrode) and reported *versus* SHE. The electrochemical synthesis was performed

^zE-mail: nemat@basu.ac.ir

under both controlled-potential and galvanostatic conditions in an undivided cell equipped with a magnetic stirrer. All experiments were carried out at a temperature of $25 \pm 1^{\circ}$ C. Melting points of the products were determined in open capillary tubes and are uncorrected. IR spectra (KBr) were recorded on Perkin–Elmer GX FT-IR spectrometer. ¹H and ¹³C NMR spectra were recorded on BRUKER Ultrashield 400 spectrometer operating at 400 and 100 MHz, respectively. Mass spectra were recorded on a HP 5973 GC-MS instrument operating at an ionization potential of 70 eV.

4-Toluenesulfinic acid (**TS**), benzenesulfinic acid (**BS**), 4chlorobenzenesulfinic acid (**CS**) and methansulfinic acid (**MS**) were reagent-grade materials from Aldrich. Sodium hydroxide and phosphoric acid were of pro-analysis grade from E. Merck.

Electroorganic synthesis.—An aqueous solution of phosphate buffer (ca. 80 mL, c = 0.2 M, pH = 2.0) containing 4-toluenesulfinic (**TS**) (**BS**, **CS** or **MS**) (0.75 mmol) was electrolyzed in an undivided cell at 1.1 V (1.2 V for **BS**, 1.1 V for **CS** and 1.2 V for **MS**) vs. SHE, at 25 ± 1°C. The electrolysis was terminated when the current decreased by more than 95% (after consumption of about 160 coulombs, during about 4 h). At the end of electrolysis, the precipitated solid (white color) was collected by filtration and was washed several times with cold water. After drying, the products were characterized by FTIR, NMR (¹H and ¹³C) and mass spectrometry. The galvanostatic synthesis was performed under the same experimental conditions by applying a constant current density of 0.21 mA/cm² and continued until the charge reached 73 C (1 F/mol). It should be noted that, the application of these methods to the synthesis of 1,2-dimethyl disulfone (**DPD4**), was not favorable.

4,4'-Dimethyldiphenyl disulfone ($C_{14}H_{14}S_2O_4$) (DPD1).—Isolated yield: 80%. mp 199–200°C (Lit. 211°C²⁸). ¹H NMR (400 MHz, CDCl₃) δ : 2.54 (s, 6H, methyl), 7.45 (d, J = 8, 4 Hz, aromatic), 7.86 (d, J = 8.4 Hz, 4H, aromatic); ¹³C NMR (100 MHz, CDCl₃) δ : 22.0 (C-3), 128.0 (C-2), 130.4 (C-1), 131.5 (C-5), 148.1 (C-4). IR (KBr) ν : 2929 (weak, C-H), 1588 (medium C=C), 1343 (strong S=O), 1135 (strong S=O), 1063, 807, 695, 633 cm⁻¹; MS (EI, 70 eV) (m/z) (relative intensity): 310 (M⁺⁻, 1), 155 (92), 91 (100), 65 (46), 139 (29), 77 (13), 51 (8).



1,2-Diphenyl disulfone ($C_{12}H_{10}S_2O_4$) (DPD2).—Isolated yield: 68%. mp: 190–192°C (Lit. 190–192°C,¹⁷ 193–194°C²⁸). ¹H NMR (400 MHz, CDCl₃) δ : 7.65 (t, J = 7.6, 4H, aromatic), 7.83 (t, J =7.6, 2H, aromatic), 7.97 (d, J = 7.6 Hz, 4H, aromatic); ¹³C NMR (100 MHz, CDCl₃) δ : 129.7 (C-2), 131.2 (C-1), 131.5 (C-3), 136.4 (C-4); IR (KBr) v: 1578 (medium C=C), 1448 (strong), 1349 (strong) S=O), 1330 (strong), 1307 (strong), 1140 (strong S=O), 1061, 750, 704, 678, 517 cm⁻¹; MS (EI, 70 eV) (*m/z*) (relative intensity): 282 (M⁺, 1), 141 (100), 77 (91.6), 51 (33.3), 125 (25).



4,4'-Dichlorodiphenyl disulfone ($C_{12}H_8Cl_2O_4S_2$) (DPD3).—Isolated yield: 76%. mp: 197–199°C. ¹H NMR (400 MHz, DMSO-d₆) δ : 7.39 (d, J = 8.4, 4H, aromatic), 7.60 (d, J = 8.4, 4H, aromatic); ¹³C NMR (100 MHz, DMSO-d₆) δ : 127.9 (C-2), 128.2 (C-1), 133.4(C-3), 147.7 (C-4); IR (KBr) v: 3096 (weak, C-H), 1569 (medium C=C), 1350 (strong S=O), 1138 (strong S=O), 1092, 1064, 824, 750, 565, 532, 438 cm⁻¹; MS (EI, 70 eV) m/z (relative intensity): 335 (M-15, 100), 307 (44), 289 (77), 235 (27).



Results and Discussion

Mechanistic studies.—The cyclic voltammetry of 4-toluenesulfinic acid (**TS**) ($pK_a = 1.55$),²⁹ benzenesulfinic acid (**BS**) ($pK_a = 1.45$),²⁹ 4-chlorobenzenesulfinic acid (**CS**) ($pK_a = 1.15$)²⁹ and methansulfinic acid (**MS**) ($pK_a = 2.28$)³⁰ was carried out in aqueous phosphate buffer (c = 0.2 M, pH = 2.0). Under these conditions, all cyclic voltammograms exhibited one well defined oxidation peak. No peaks were observed on the reverse scan, showing the irreversibility of the electrode process (Fig. 1). The effect of potential scan rate (from 10 to 1000 mV s⁻¹) on the cyclic voltammograms of **TS** is



Figure 2. Cyclic voltammograms of **TS** (0.5 mM) at various scan rates. Scan rates from (a) to (g) are: 10, 50, 100, 200, 500, 750 and 1000 mV/s, respectively at glassy carbon electrode, in aqueous phosphate buffer (c = 0.2 M, pH = 2.0). Temperature = $25 \pm 1^{\circ}$ C.

presented in Fig. 2 which confirms the irreversibility of the electrode process.

The electrochemical oxidation of **TS** has also been studied at various pH values (Fig. 3). As can be seen, the peak potential does not change in the studied rang of pH (from 2 to 10), which confirms the lack of participation of proton in the oxidation of **TS**.

In order to obtain the data from a *long-time-window method* (LTWM),³¹ controlled-potential coulometry was performed in an aqueous phosphate buffer (c = 0.2 M, pH = 2.0), containing **BS**



Figure 1. Cyclic voltammograms of 4-toluenesulfinic acid (TS), benzenesulfinic acid (BS), 4-chlorobenzenesulfinic acid (CS) and methansulfinic acid (MS) (5.0 mM) at glassy carbon electrode. Solvent = aqueous phosphate buffer (c = 0.2 M, pH = 2.0) and scan rate = 100 mV/s. Temperature = 25 ± 1 °C.

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Figure 3. Cyclic voltammograms of TS (5 mM) at different pH values (1.1, 2.0, 3.1, 4.3, 5.1, 6.0, 7.1, 7.9, 9.0 and 10.0). Scan rate 100 mV/s. Temperature $= 25 \pm 1^{\circ}$ C.

(0.75 mmol) at 1.2 V versus SHE. The monitoring of electrolysis progress by cyclic voltammetry shows that during electrolysis, the anodic peak decreases and disappears with the consumption of 1.1 electrons per **BS** molecule (Fig. 4).

Cyclic voltammetric and coulometric behavior of the studied sulfinic acids accompanied by spectroscopic data (¹H NMR, ¹³C NMR, FTIR and MS) of the products allow us to propose an $E_{irr}D$ (E_{irr} : *electron transfer* and *D*: *dimerization reaction*) mechanistic scheme for the electrochemical oxidation of sulfinic acids (Scheme 1).

According to Scheme 1, the first step in the synthesis of **DPD**, is electrochemical generation of sulfonyl radical. The formation of sulfonyl radical by electrolytic oxidation of sodium sulfinates previously reported by Little-Zeng and Zha-Wang.^{32,33}

Chronoamperometric studies.—These studies were also carried out to determine the diffusion coefficient of **TS**, **BS**, **CS** and **MS** at 1.2 V against SHE (Fig. 5). It should be noted that, a mixture of water (phosphate buffer, c = 0.2 M, pH = 2.0)/ethanol (50/50, v/v)



Figure 4. Cyclic voltammograms of **BS** (0.75 mmol) during controlledpotential coulometry at 1.2 V vs SHE after consumption of: (a) 0 (b) 10, (c) 30, (d) 50, (e) 70 and (f) 80 coulombs in aqueous phosphate buffer (c = 0.2 M, pH = 2.0). Scan rate: 100 mV/s .Temperature = 25 $\pm 1^{\circ}$ C.



Scheme 1. Proposed mechanism for the electrochemical oxidation of sulfinic acids.

was used as solvent in order to elimination of adsorption effects in the determination of diffusion coefficient. According to the Cottrell equation,³¹ the data show that under experimental conditions, the oxidation process (for four species, **TS**, **BS**, **CS** and **MS**) is diffusion controlled as shown by the linear relationship existing between currents and $t^{-1/2}$. The slope of the lines are a measure of the substrate concentration and increases as the concentration is increased. This technique has also been used for determining the diffusion coefficient (*D*) under mass transfer controlled conditions.³⁴ *D* can be evaluated by the several methods.³⁵ In this work, the diffusion coefficients of the studied sulfinic acids in ethanol-water were determined using potential step chronoamperometry in accordance with the Shoup and Szabo method.³⁶

The necessary equations for this method are as follows:

$$I = -4nFDcr_{\rm d}f(\tau)$$
^[1]

$$f(\tau) = 0.7584 + 0.8863 \tau^{-1/2} + 0.2146 \exp\left(-0.7823 \tau^{-1/2}\right)$$
[2]

where *D* is the diffusion coefficient, r_d is the radius of the disk electrode (0.9 mm), *n* is the number of electrons (n = 1), *c* is the initial concentration, *F* is the Faraday constant and τ is the dimensionless time parameter, given by:

$$\tau = \frac{4Dt}{r_d^2}$$
[3]

A handwritten nonlinear curve fitting function was used to fit the theoretical data (using Eq. 3) to the experimental results³⁷ The calculated diffusion coefficients for **TS**, **BS**, **CS** and **MS** are shown in Table I. The data show that, because of the structural similarity, the diffusion coefficient of the aryl sulfinic acids (**TS**, **BS** and **CS**) are close to each other and are within the range of $5.1-6.5 \times 10^{-6}$ cm² s⁻¹. However because of the smaller structure size, the diffusion coefficient of methansulfinic acid (1.5×10^{-5}) is about three times larger than that obtained for aryl sulfinic acids.

Chronocoulometry studies.—The double-potential step chronocoulograms of **TS**, **BS**, **CS** and **MS**, in aqueous phosphate buffer (c = 0.2 M, pH = 2.0), are shown in Fig. 6. As can be seen, the forward charges (Q_f) is much larger than Q_b . The charge ratios, (Q_f^{τ} - Q_b)/ Q_f at $t_r = \tau$ for **TS**, **BS**, **CS** and **MS** are 0.16, 0.10, 0.14 and 0.10 which are much lower than theoretical value of 0.586 for a reversible process, confirm the irreversible nature of the electrode process.³¹

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Figure 5. Chronoamperograms of **TS**, **BS**, **CS** (3.0, 4.0, 5.0, 6.0 and 7.0 mM) and **MS** (3.0, 4.0, 6.0 and 7.0 mM), at glassy carbon electrode, in water (phosphate buffer 0.2 M, pH 2.0)/ethanol mixture (50/50, v/v). The applied potential is ± 1.2 V vs. SHE. Inset: Variation of *I* vs. $t^{-1/2}$. Temperature = $25 \pm 1^{\circ}$ C.

In addition, this method is a useful method for the mechanistic and adsorption studies.^{38–43} In this method, the total charge (Q_t) obtained from the applied

potential have three sources of generation: the double layer charge $(Q_{\rm dl})$, the adsorption charge $(Q_{\rm ads})$ and diffusion charge $(Q_{\rm diff})$.³¹

 $Q_{\rm t} = Q_{\rm dl} + Q_{\rm ads} + Q_{\rm diff}$

Among these, $Q_{\rm diff}$ is only associated with the time as described in Eq. 5 while $Q_{\rm dl}$ and $Q_{\rm ads}$ are time independent:⁴⁴

$$Q_{\rm diff} = \frac{2nFAD_o^{1/2}C_o^*t^{1/2}}{\pi^{1/2}}$$
[5]

$$Q_{\rm ads} = nFA\Gamma_o$$
 [6]

Table I. The data obtained from Shoup and Szabo and chronocoulometry methods for electrochemical oxidation of TS, BS, CS and MS in water and water/ethanol mixture.

[4]

sulfinic acid	$Q_{ m dl}/ m C$	$Q_{\rm ads}/{ m C}$	$\Gamma_{\rm o}/{\rm mol}~{\rm cm}^{-2}$	σ/cm ²	D/ cm ² s ^{$-1b$}	D/ cm ² s ^{$-1c$}
TS ^a	$8.3 imes 10^{-7}$	6.2×10^{-7}	$2.5 imes 10^{-10}$	$6.6 imes 10^{-15}$	9.5×10^{-7}	$5.1 imes 10^{-6}$
BS ^a	8.3×10^{-7}	5.3×10^{-7}	2.2×10^{-10}	7.6×10^{-15}	1.8×10^{-6}	6.5×10^{-6}
CS ^a	8.3×10^{-7}	6.2×10^{-7}	2.5×10^{-10}	6.6×10^{-15}	2.2×10^{-6}	5.2×10^{-6}
MS ^d	2.3×10^{-7}	3.2×10^{-7}	2.1×10^{-10}	7.7×10^{-15}	2.0×10^{-5}	2.0×10^{-5}

^aElectrode surface area is 0.0256 cm².

^bCalculated by chronocoulometry method in water.

^cCalculated by Shoup and Szabo method in water/ethanol (50/50, v/v) mixture.

^dElectrode surface area is 0.014 cm².



Figure 6. Double-step chronocoulograms of **TS**, **BS**, **CS** and **MS** (5 mM) at glassy carbon electrode, in aqueous phosphate buffer (c = 0.2 M, pH 2.0). (50/50 v/v). When the potential is stepped from +1.2 V to +0.70 V vs. SHE. Inset: Variation of Q vs. $t^{1/2}$ (a) in the presence of sulfinic acid and (b) in the absence of it (supporting electrolyte). Temperature = $25 \pm 1^{\circ}$ C.

$$Q_{\rm t} = Q_{\rm dl} + nFA\Gamma_o + \frac{2nFAD_o^{1/2}C_o^*t^{1/2}}{\pi^{1/2}}$$
[7]

where: Γ_o (surface excess) is the amount of adsorbed sulfinic acid (mol cm⁻²). The plots of Q_t vs. $t^{1/2}$ (Anson plots) are also shown in Fig. 6 (curves a). According to Eq. 7, the intercept of an Anson plot can be used for calculating the sum of Q_{dl} and Q_{ads} . In this regard by subtracting Q_{dl} from intercept, the Q_{ads} could be calculated.^{38,39} A general method for the determination of Q_{dl} is established based on the chronocoulometry of the supporting electrolyte alone.³¹ The chronocoulogram of sulfinic acids in aqueous solution containing aqueous phosphate buffer (c = 0.2 M, pH = 2.0) were also recorded under the same conditions as those described above. The plots of the total charge (Q_t) vs. $t^{1/2}$ are shown in Fig. 6 (curves b). In the next step, the calculated Q_{ads} is used for the calculation of Γ_o using Eq. 6.

The slope of the Anson plot can be used for calculating the diffusion coefficient. The calculated values for Γ_o and D for **TS**, **BS**, **CS** and **MS**, are shown in Table I. As can be seen, because of the structural similarity between the studied aryl sulfinic acids (**TS**, **BS** and **CS**), the calculated Γ_o and D for these compounds are close to each other (except **MS**). However, the calculated values for D by this method have significant differences in comparison with the Shoup and Szabo method. The most important factor for the difference in the calculated diffusion coefficients, is related to differences in the types of solvents. The solvent used in the Shoup and Szabo method is a mixture of water/ethanol (50/50, v/v), while, water was used as solvent in chronocoulometry experiments. The presence of ethanol (50/50, v/v) in the water/ethanol mixture decreases the hydrogen bonding ability of the solvent to interact with sulfinic acids,^{45,46} which leads to increase in diffusion coefficient (*D*).^{47,48} The chronocoulometry method was also used to determine the average area, σ (cm²) occupied by a molecule of adsorbed sulfinic acid. The average area occupied by a molecule of sulfinic acid was calculated by:⁴⁹

$$\sigma = \frac{1}{N_A \Gamma_0}$$
[8]

where, N_A is Avogadro's constant. The calculated σ , $Q_{dl and} Q_{ads}$, are shown in Table I.

Electrochemical synthesis.—The applicability of the two electrochemical methods, controlled-potential and galvanostatic methods for the synthesis of disulfone derivatives was assessed. In controlled-potential methods, in an undivided cell by applying appropriate potential (1.1-1.2 V vs. SHE) (see Experimental section), the dimers **DPD1-3** were successfully synthesized with yields of 68–80%.

To develop our method, we also synthesized dimers **DPD1-3** under galvanostatic conditions. The galvanostatic method was performed under similar conditions as those described for controlled-potential synthesis. In this method, the effects of two important factors, current density and charged passed on product yield were studied. The



Figure 7. The effect of (a) current density (charged passed is equal to the theoretical one, 1.0 F/mol) and (b) charged passed on the yield of **DPD1**.

current density is one of the most important factors affecting the purity and yield. In this work, the current was changed from 0.05-1.07 mA/cm², whereas the other parameters, which are similar to those of the controlled-potential method. Figure 7a displays the effect of current density on the yield of **DPD1**. It shows that, the product yield increases with increasing current density up to 0.21 mA/cm² and then decrease.

The product yield also depends on the quantity of charge passed. The effect of charge passed at current density 0.21 mA/cm² was studied in the range of 1 (theoretical amount) to 3 F/mol (Fig. 7b). As can be seen, the product yield decreases with increasing charge passed from theoretical value. This can be attributed to the occurrence of side reaction(s) after consumption of 1 F/mol electricity.

Conclusions

This paper have two aspects, which are as follows: (1) new insights into the electrochemical oxidation of sulfinic acids in aqueous solutions and (2) the electrochemical synthesis of some diphenyl disulfones via a facile and environmentally friendly electrochemical method. To attain the first goal, the electrochemical oxidation of three aryl sulfinic acids (**TS**, **BS** and **CS**) and of methansulfinic acid (**MS**) has been studied at different pH values using cyclic voltammetry, controlled-potential coulometry, chronoamperometry and chronocoulometry methods and their redox behavior were studied in detail (Scheme 1). In addition, some electrochemical parameters (diffusion coefficient, *D*, surface excess, Γ , and average area, σ) of the sulfinic acids were reported. To achieve the second goal, the obtained electrochemical data were used in the synthesis of diphenyl disulfones, **DPD1-3**. In this study, the synthesis of some diphenyl disulfones through the green and facile method was reported.

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References

- 1. A. Maleki and D. Nematollahi, Org. Lett., 13, 1928 (2011).
- E. Salahifar, D. Nematollahi, M. Bayat, A. Mahyari, and H. Amiri Rudbari, Org. Lett., 17, 4666 (2015).
- 3. A. Amani and D. Nematollahi, J. Org. Chem., 77, 11302 (2012).
- 4. D. Nematollahi, M. S. Workentin, and E. Tammari, Chem. Commun., 1631 (2006).
- 5. S. R. Waldvogel and B. Janza, Angew. Chem. Int. Ed., 53, 7122 (2014).
- 6. H. J. Schäfer, C. R. Chimie, 14, 745 (2011).
- M. Jamshidi, D. Nematollahi, and H. Amiri Rudbarib, J. Electrochem. Soc., 163, G145 (2016).
- D. Nematollahi, S. S. Hosseiny Davarani, and P. Mirahmadpour, ACS Sustainable Chem. Eng., 2, 579 (2014).
- H. Salehzadeh, D. Nematollahi, and M. Rafiee, J. Electroanal. Chem., 650, 226 (2011).
- 10. R. Esmaili and D. Nematollahi, *Electrochim. Acta*, 56, 3899 (2011).
- 11. J. Arjomandi, D. Nematollahi, and A. Amani, J. Appl. Polym. Sci., 131, 40094 (2014).
- 12. D. Markovic' and P. Vogel, Org. Lett., 6, 2693 (2004).
- D. Markovic', A. Varela-Alvarez, J. A. Sordo, and P. Vogel, J. Am. Chem. Soc., 128, 7782 (2006).
 - 14. D. Markovic' and P. Vogel, Angew. Chem., Int. Ed., 43, 2928 (2004).
 - D. Marković, P. Steunenberg, M. Ekstrand, and P. Vogel, *Chem. Commun.*, 2444 (2004).
 - M. Tsunooka, T. Higuchi, M. Fujii, M. Tanaka, and N. Murata, *Kogyo Kagaku Zasshi*, 73, 596 (1970).
 - 17. M. Kobayashi, K. Tanaka, and H. Minato, Bull. Chem. Soc. Jpn., 45, 2906 (1972).
 - G. C. Denzer Jr., P. Allen Jr., P. Conway, and M. van der Veen, J. Org. Chem., 31, 3418 (1966).
 - 19. A. T Maioli and J. P. Anselme, Tetrahedron Lett., 36, 1221 (1995)
 - 20. J. M. Squire and W. A. Waters, J. Chem. Soc., 2068 (1962).
 - 21. C. G. Overberger and A. J. Rosenthal, J. Am. Chem. Soc., 82, 117 (1960).
 - A. V. Anisimov, R. A. Mokhammad, A. V. Tarakanova, and S. A. Borisenkova, *Neftekhimiya*, 34, 421 (1994).
 - 3. A. Maioli and J. P. Anselme, *Tetrahedron Lett.*, 8, 1221 (1995).
 - 24. E. A. Bartmann, Synthesis, 490 (1993).
 - 25. N. Kunieda and S. Oae, Bull. Chem. Soc. Jpn., 41, 233 (1968).
 - 26. Y. Liu and Y. Zhang, Tetrahedron Lett., 44, 4291 (2003).
 - 27. I. Prokes, S. Toma, and J. L. Luche, Tetrahedron Lett., 36, 3849 (1995).
 - 28. T. P. Hilditch, J. Chem. Soc., 93, 1524 (1908).
 - 29. Y. Ogata, Y. Sawaki, and M. Isono, *Tetrahedron*, **26**, 731 (1970).
 - 30. W. Thomas, I. Bruice, and G. L. Kenyon, *J. Protein Chem.*, **1**, 47 (1982).
 - A. J. Bard and L. R. Faulkner, *Electrochemical methods*, 2nd edn., Wiley-VCH, New York, p. 479 (2001).
 - 32. P. Qian, M. Bi, J. Su, Z. Zha, and Z. Wang, J. Org. Chem., 81, 4876 (2016).
 - Y. Y. Jiang, Q. Q. Wang, S. Liang, L. M. Hu, R. D. Little, and C. C. Zeng, J. Org. Chem., 81, 4713 (2016).
 - G. Denuault, M. V. Mirkin, and A. J. Bard, *J. Electroanal. Chem.*, 308, 27 (1991).
 - 35. H. Ikeuchi and M. Kanakubo, J. Electroanal. Chem., 493, 93 (2000).
 - 36. D. Shoup and A. Szabo, J. Electroanal. Chem., 140, 237 (1982).
 - 37. S. Khazalpour and D. Nematollahi, RSC Adv., 4, 8431 (2014).
 - 38. B. Dadpou and D. Nematollahi, J. Electrochem. Soc., 163, H559 (2016).
 - 39. S. Khazalpour and D. Nematollahi, RSC Adv., 4, 8431 (2014)
 - D. Nematollahi, F. Ghasemi, M. Sharafi-Kolkeshvandi, and F. Varmaghani, J. Electroanal. Chem., 775, 299 (2016).
 - 41. D. Nematollahi, B. Feyzi Barnaji, and A. Amani, J. Sulfur Chem., 36, 1 (2015).
 - H. Beginejad, D. Nematollahi, F. Varmaghani, and H. Shayani-Jam, *Monatsh. Chem.*, 144, 1481 (2013).
 - H. Beiginejad, D. Nematollahi, M. Noroozi, and S. Lotfi, J. Iran. Chem. Soc., 12, 325 (2015).
 - 44. F. C. Anson, Anal. Chem., 38, 54 (1966).
 - T. A. Dolenko, S. A. Burikov, S. A. Dolenko, A. O. Efitorov, I. V. Plastinin, V. I. Yuzhakov, and S. V. Patsaeva, *J. Phys. Chem. A*, **119**, 10806 (2015).
 - 46. D. Nematollahi and F. Varmaghani, J. Iran. Chem. Soc., 8, 803 (2011).
 - T. M. Alligrant, J. C. Hackett, and J. C. Alvarez, *Electrochim. Acta*, 55, 6507 (2010).
 - B. Yang, L. Hoober-Burkhardt, F. Wang, G. K. Surya Prakash, and S. R. Narayanan, J. Electrochem. Soc., 161, A1371 (2014).
 - 49. D. Nematollahi and F. Gomar, J. Iran. Chem. Soc., 9, 693 (2012).