

The Determination of Chemical Kinetics Constant of Triphenyltin(IV) *p*-hydroxybenzoate Using Cyclic Voltammetry

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Abstract

The determination of chemical kinetics constant of triphenyltin(IV) *p*-hydroxybenzoate by the use of cyclic voltammetry has been performed. The compound used was previously synthesized and well characterized and has been applied as anticorrosion inhibitor. The determination of kinetic constants of this compound will be useful to assess future reactivity through the value of forward chemical reaction rate constant (k_f). In this study, carbocation intermediate was produced by oxidizing the compound, which will then react chemically with nucleophilic solvent. The measurement of standard solution triphenyltin(IV) *p*-hydroxybenzoate was at concentration of 0.8 mM in the water system: DMSO (3:1) was monitored by cyclic voltammetry with the condition of a potential windows of 700 mV to 1400 mV; potential scan rate variation (v) at intervals of 100 mV: 100-1000 mV/sec; the working electrode of gold (Au), reference electrode platinum (Pt) and the reference electrode of silver (Ag); and supporting electrolyte solution of sodium chloride 0,02 M. To obtain the value of the following chemical reaction rate constant of triphenyltin(IV) *p*-hydroxybenzoate on the cyclic voltammogram, we used digital simulation method using Polar 5.8.3 software. The results showed that the rate of subsequent chemical reactions constant compound triphenyltin(IV) *p*-hydroxybenzoate was a function of the potential scan rate, $k_f = 3.45 v + 0.45$ ($r = 0.994$) with a slope value of $(k_f/v) = 3.45/V$. The type of chemical reaction mechanisms occurred in around the working electrode surface following the E_qC_i .

Keywords: forward chemical reaction rate constant, triphenyltin(IV) *p*-hydroxybenzoate, cyclic voltammetry

1. Introduction

Organotin compound is characterized by having at least one direct bond between carbon of organic ligand to a metal center tin. Organotin compounds are found as mono, di, tri and tetraorganotin depending on the alkyl or aryl attached to the Sn center [1,2]. Variety of anions such as chloride, oxide, hydroxide, carboxylate and thiolate has been found to form the compound in organotin(IV) [1].

Organotin(IV) compounds are known to have many biological activities. The biological activity of this compound is determined by the number of organic ligands attached to the metal center Sn [1].

The interests in research of organotin(IV) compounds are not only because of the chemical properties and their interesting structure [2,3], but also their uses which increase as these compounds and their derivatives have been widely used and known in many biological activity tests such as anticancer and antitumour [4-8], antiviral [9], antibacterial [10,11], antifungal [12-15], and anticorrosion [16-20].

The syntheses of the derivatives of triphenyltin(IV) *o*-, *m*-, and *p*-hydroxybenzoate have previous been reported [7,8]. These compounds have also been tested biologically for anticancer and anticorrosion [7]. Triphenyltin(IV)-*p*-hydroxybenzoate has been tested as anticorrosion inhibitor towards the hard rolled plate (HRP) steel, in concentration of 100 ppm, it gave percentage efficiency inhibition (%EI) of 80.41% [21]. This compound was prepared by the reaction of triphenyltin(IV) hydroxide and *p*-hydroxybenzoic acid with methanol as solvent and temperature reaction of 60°C and reflux times of 4 hours similar to other compounds previously prepared [7,8,14-17]. The structure of this compound is shown in Figure 1.

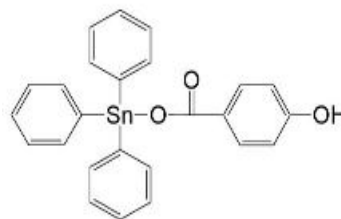


Fig. 1: Structure of triphenyltin(IV) *p*-hydroxybenzoate

Based on the use this compound in many biological tests, it is important to determine the rate of alkylation of this compound to evaluate its use and its danger in the environment. One of the parameters that can be used quantitatively is forward chemical rate constant (k_f). The analytical method applies to calculate the value of k_f of a compound is cyclic voltammetry [22]. Cyclic voltammetry

is one of electroanalytical techniques used widely in the chemical research. This method is used in the electrochemical reaction to obtain the stabilization of reaction product [22].

Scan technique works based on potential, move forward from the beginning to the end potential window and reverse from the end to the beginning potential window [23]. The relationship between current and voltage recorded during the process of oxidation-reduction electrolysis is called the cyclic voltammetry [23].

The forward chemical reaction constant (k_f) can be calculated in two ways, (1) using the approach of Nicholson-Shain method and using Polar 4.2 software [24]. The calculation of k_f with Nicholson-Shain method can be calculated by calculating the result of calculation value from the ratio of cathodic peak current, while the anode peak was uncorrected from experimentally voltammogram.

The calculation of k_f value with Polar 5.8.3 software can be carried out using value ratio of cathodic peak and corrected anodic peak from simulation voltammogram [25]. Thus, the aim of this research is to determine the chemical kinetics constant of triphenyltin(IV) *p*-hydroxybenzoate.

Materials and Methods

Materials

All reagents used were AR grade. High grade water, NaCl and dimethylsulphoxide (DMSO) were used as they received. Triphenyltin(IV) *p*-hydroxybenzoate was available in our laboratory previously. ER644 integrated potentiostat eDAQ with three electrode system was used where the gold as working electrode, silver wire as reference electrode, and platinum as counter electrode.

The measurement with potentiostat was performed as follows: the solution containing 2 mL triphenyltin(IV) *p*-hydroxybenzoate 0.8 mM and supporting electrolyte, 0.5 mM NaCl 0.02 M was placed in the erlenmeyer 2.5 mL. The cyclic voltammetry was then measured with condition set as follows:

Initial potential (E_{step})	: +700 mV
End potential (E_{end})	: +1400 mV
Temperature	: 25°C
Working electrode	: Gold (Au)
Auxillary electrode	: Platinum (Pt)
Reference electrode	: Silver (Ag)
Potential scan rate (v)	: varies for every 100 mV/s from 100 to 1000 mV/s

Characterization of reactions mechanism (E_xC_x)

The electrochemical reaction of alkylating substance which followed by the chemical reaction of carbocation formed will be attacked by nucleophil in the solution (acetonitril) with certain forward chemical rate (k_f), when the potential scan rate reverse, it can be reduced reversely on the cathode shown by the presence of cathodic peak current (i_{pc}).

The electrochemical reaction occurred on the surface of electrode was followed by chemical reaction. The

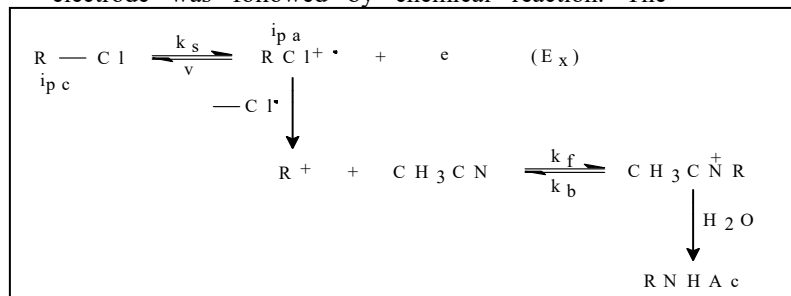


Fig. 2: Reaction model of electrochemical reaction (E_x) and chemical reaction (C_x) of halide compound oxidized in the solvent.

The characteristic of electrochemical reaction can be known from the constant value of standard heterogen electron transfer, while the characteristic of chemical reaction can be known by forward chemical reaction constant (k_f) and reverse chemical reaction constant (k_b) [26].

The reaction mechanism which occurs on the surface of working electrode is E_xC_x . The types of electrochemical reaction mechanism (E_x) on the surface of electrode are reversible (r), quasi reversible (q) and irreversible (i). In this work, the characterization of x on electrochemical reaction (E_x) is determined by calculating k_s using Polar 5.8.3 Software with the following condition [27]:

- (1) r (reversible), if $k_s > 0.3 v^{1/2}$ cm/s
- (2) q (quasi-reversible), if $k_s > 2.5 \times 10 v^{1/2}$ cm/s
- (3) i (irreversible), if $k_s < 2.5 \times 10 v^{1/2}$ cm/s

The values of potential scan rate ($v^{1/2}$) were taken from experiment.

Results and Discussion

The results of cyclic voltammetry of the compound tested are shown in Figure 3 and the data of measurement peak current (i_p) and peak potential (E_p) obtained from the

voltammogram of the triphenyltin(IV) *p*-hydroxybenzoate solution are presented in Table 1.

No	Scan rate (mV/s)	i_p blank (μ A)	i_p standard (μ A)	E_p blank (volt)	E_p standard (volt)
1	100	19.87	22.64	1.006	1.134
2	200	28.98	50.09	1.034	1.134
3	300	33.07	59.48	1.05	1.18
4	400	36.29	67.33	1.064	1.224
5	500	39.07	72.91	1.074	1.254
6	600	41.28	77.64	1.08	1.28
7	700	42.97	80.02	1.08	1.294
8	800	45.19	84.95	1.09	1.32
9	900	47.41	90.65	1.094	1.344
10	1000	49.06	94.85	1.104	1.364

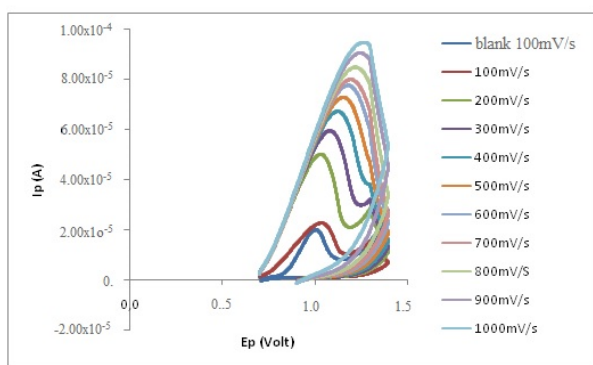


Fig. 3: The voltammogram of blank 100 mV/s and triphenyltin(IV) *p*-hydroxybenzoate 0.8 mM by varying the scan rate potential with cyclic voltammetry

Based on the data on Table 1, the increase of i_p was affected by the potential scan rate. The higher the speed of potential scan rate, the higher the current produced. The measurement of blank solution was also taken in order to ensure that its value of peak potential measured different to the value of peak potential from the standard solution measured [24].

The Analysis of Cyclic Voltammogram of triphenyltin(IV) *p*-hydroxybenzoate using Polar 5.8.3 Software

The parameter values of cyclic voltammogram obtained from the experiment was used as the reference for simulation with Polar 5.8.3 Software. The parameter values that affect the form of simulation cyclic voltammogram were constant of standard heterogen electron transfer (k_s), diffusion coefficient (D), standard potential cell (E°), potential scan rate (v), electron transfer coefficient (α), and forward chemical rate constant (k_f). The simulation was conducted by varying the parameters on the Polar 5.8.3 Software, so it will affect the high of

peak current and potential peak produced (Figure 4) [24, 25].

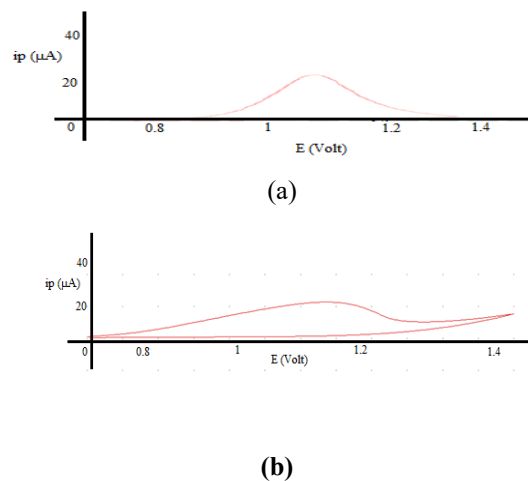


Fig. 4. Cyclic voltammogram of (a). Simulation with scan rate of 100 mV/s (b). experiment with scan rate of 100 mV/s

Table 2 presents the values of k_s , D, α , E° and k_f on the kinetic menu. The matching of parameter values of anodic peak current and anodic peak potential on the voltammogram of experiment data and simulation are presented in Table 2.

Table 2: The values of k_s , D, α , E° and k_f simulation result (cyclic voltammogram) using Polar 5.8.3 Software

scan rate (mV/s)	k_s (cm/s)	A	D (cm ² /s)	E° (volt)	k_f (1/s)
100	0.007	0.4	0.645	0.91000	0.69050
200	0.007	0.4	0.645	0.89000	1.18074
300	0.007	0.4	0.645	0.92500	1.62820
400	0.007	0.4	0.645	0.96000	2.01390
500	0.007	0.4	0.645	0.98500	2.41090
600	0.007	0.4	0.645	1.01000	2.77870
700	0.007	0.4	0.645	1.02000	3.22550
800	0.007	0.4	0.645	1.03800	3.57097
900	0.007	0.4	0.645	1.05900	3.85970
1000	0.007	0.4	0.645	1.07800	4.16230

Based on the data on Table 2, the values of k_f was plotted against the values of potential scan rate produced a linear curve with correlation value of more than 90% (Figure 5), which indicate that there was linearity relationship between k_f toward v .

Table 3: The matching result of E_p and i_p experimental values with E_p and i_p simulation result from Polar 5.8.3 Software with working electrode gold

Scan rate (mV/s)	E_p experiment (Volt)	E_p simulation (Volt)	i_p experiment (μ A)	i_p simulation (μ A)
100	1.134	1.134	22.64	22.64
200	1.134	1.134	50.09	50.09
300	1.18	1.18	59.48	59.48
400	1.224	1.224	67.33	67.33
500	1.254	1.254	72.91	72.91
600	1.28	1.28	77.64	77.64
700	1.294	1.294	80.02	80.02
800	1.32	1.32	84.95	84.95
900	1.344	1.344	90.65	90.65
1000	1.364	1.364	94.85	94.85

Table 4: The calculation of k_s value with Polar 5.8.3 software

No	scan rate (V/s)	k_s polar (cm/s)	$r_{0.3} v^{1/2}$ (cm/s)	Ex
1	0.1	0.007	0.0948	q
2	0.2	0.007	0.1341	q
3	0.3	0.007	0.1643	q
4	0.4	0.007	0.1897	q
5	0.5	0.007	0.2121	q
6	0.6	0.007	0.2323	q
7	0.7	0.007	0.2509	q
8	0.8	0.007	0.2683	q
9	0.9	0.007	0.2846	q
10	1.0	0.007	0.3000	q

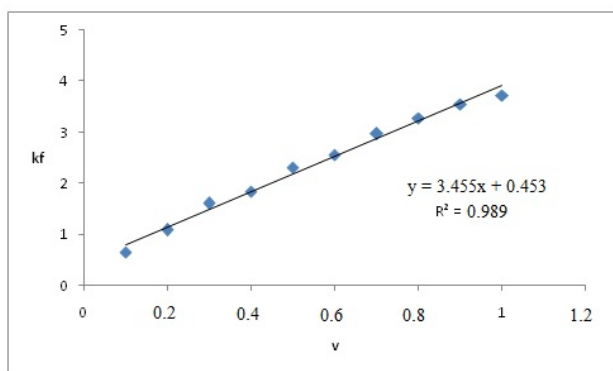


Fig. 5: Linear curve of k_f against potential scan rate (v)

Reaction mechanism (ExCx)

Based on the calculation of k_s value (Table 4), it can be concluded that $k_s > 2.5 \times 10^{-5} v^{1/2}$ cm/s, thus the electrochemical reaction of triphenyltin(IV) *p*-hydroxybenzoate followed electrochemical reaction quasi-reversible (Eq) which mean the process of electron transfer to the surface of electrode was little bit slower than the reversible condition (Er) condition [27].

On the cyclic voltammogram of triphenyltin(IV) *p*-hydroxybenzoate produced, the cathodic peak current (i_{pc}) did not appear, because the following chemical reaction occurred in one direction or irreversible (Ci) thus the k_b value on the input submenu on Polar 5.8.3 Software was filled zero [25].

CONCLUSIONS

Based on the data obtained and discussion above, it is concluded that since the cathodic peak current (i_{pc}) did not appear on the cyclic voltammogram of triphenyltin(IV) *p*-hydroxybenzoate, the reaction mechanism occurred followed the reaction mechanism of EqCi i.e. the electrochemical reaction quasi-reversible and chemical reaction irreversible.

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