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Electrochemical Oxidation of Phenylthiourea at a Platinum Electrode†

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Anodic oxidation of phenylthiourea in different aqueous media (sulphuric acid, Clarks and Lubs buffer, phosphate buffer, sodium carbonate and sodium hydroxide) at a platinum electrode using cyclic voltammetric, chronoamperometric and potentiostatic steady-state techniques indicates that phenylthiourea is oxidized irreversibly with removal of one electron. Anodic electrochemical reaction order is found to be one and the final product has been identified as a disulphide. The electron transfer step involving the formation of free radical is thus probably the rate-determining step. The data also have been utilized to evaluate the diffusion coefficients of the electroactive species under consideration in different media.

THIO compounds are known to exhibit prolific film formation during their oxidation at electrodes. In the course of our studies on the electrochemical oxidation of organic compounds employing cyclic voltammetric, chronoamperometric and potentiostatic steady-state techniques, an attempt was made to investigate the electrochemical oxidation of phenylthiourea with a view to correlating the results with those of Santhanam and Krishnan[1] obtained by controlled potential coulometric studies in our laboratory. It was shown through the above coulometric studies that phenylthiourea could be oxidized with 100% efficiency at a platinum electrode using 1*N* hydrochloric acid as the supporting electrolyte. Oxidation of phenylthiourea tried in other media, viz. Clarks and Lubs buffer, phosphate buffer and sodium hydroxide suffered from lack of 100% current efficiency and the current fall was not smooth. In the present investigation the data obtained in aqueous solutions of different *p*H values have been utilized to propose the nature and mechanism of the electrochemical oxidation of phenylthiourea and to evaluate its diffusion coefficients.

The theoretical principles and various application of the cyclic voltammetric and chronoamperometric techniques have been described in detail in the literature[2-5]. Vetter has presented a vivid description of the utility and evaluation of the electrochemical reaction orders[6].

Materials and Methods

The solutions of phenylthiourea (BDH, m.p. 154°) were prepared by dissolving it in a minimum quantity of ethanol and then making up with water. Aqueous solutions of sulphuric acid (1*N*), Clarks and Lubs (C-L) buffer (*p*H 6·3), phosphate buffer (*p*H 6·6), sodium carbonate (*p*H 11·4), sodium hydroxide (*p*H 13·0) were employed as supporting electrolytes. The preparation of the solutions of supporting electrolytes used, the instrumental details and the experimental procedures employed for the different techniques have been described in our earlier publications[7,8].

For the experiments connected with the potentiostatic steady-state technique, the standard type of apparatus with manual control of potential using a set of rheostats as recommended by Lingane was found satisfactory. A multipurpose, electrochemical instrument which could function as a polarograph, a potentiostat, a cyclic voltammeter and a galvanostat was also employed in the present work. A spiral electrode made of platinum wire of radius 0·5 mm served as a working electrode. A spiral platinum rod electrode was used as the counter electrode. Performance of the working electrode was checked by carrying out the cyclic voltammetric and chronoamperometric studies using potassium ferrocyanide as a test substance in 2*M* potassium chloride as the supporting electrolyte, in view of its known behaviour in terms of reversibility and absence of adsorption at the electrode. Chronoamperometric data of this system have been employed to evaluate the electrochemical area of the working electrode which in the present case was found to be 1·326 cm^2. Working electrode was pretreated every time before use by dipping in ethanol, heating in an alcoholic flame and washing with distilled water. A platinum gauze electrode of area 48·27 cm^2 was employed as the working electrode in the potentiostatic steady-state measurements. Saturated calomel electrode was used as the reference electrode in all the above measurements.

Results and Discussion

Cyclic voltammetric results— Cyclic voltammograms of phenylthiourea in 1*N* sulphuric acid and C-L

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buffer are presented in Fig. 1. Phenylthiourea undergoes oxidation at a platinum electrode in sulphuric acid with peak potential, $E_p = +0{\cdot}86$ V (vs SCE). The peak potential in C-L buffer is also observed at +0·86 V. In the potential range covered in both the media no cathodic peak is observed at negative potentials.

Unlike in the case of thiourea[9], two anodic peaks are observed for this compound in phosphate buffer, sodium carbonate and sodium hydroxide (Fig. 2). The influence of concentration and sweep rate on the above two peaks has been investigated in order to characterize them. The diffusion peak has been stated to be relatively predominant at low sweep rates and the adsorption at lower concentrations[5]. The peaks observed are found to possess the following properties: (i) The second peak is relatively predominant at lower concentrations. Figure 3 gives the cyclic voltammograms for phenylthiourea in sodium carbonate for concentrations 1·4 m*M* and 2·8 m*M*. From the peaks occurring at +0·60 V in both the cases, the one observed at 1·4 m*M* is relatively predominant. (ii) At low sweep rates, the first peak is predominant. The second peak becomes prominent as the sweep rate increases. In Fig. 4 the cyclic voltammograms in sodium carbonate at 0·05 V sec^{-1} and 0·14 V sec^{-1} are presented. At a sweep rate 0·5 V sec^{-1} the diffusion peak occurring at +0·3 V is more prominent as compared to the adsorption peak at +0·60 V, while at 0·14 V sec^{-1}, the adsorption peak occurring at +0·62 V is predominant as compared to the corresponding peak at 0·05 V sec^{-1}. Thus the peaks occurring at +0·58 V (vs SCE) in the phosphate buffer, at +0·30 V in sodium

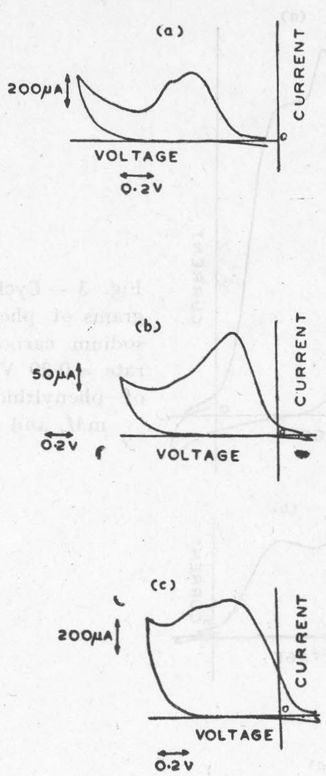


Fig. 2 — Cyclic voltammograms of phenylthiourea in (a) phosphate buffer, (b) sodium carbonate, and (c) sodium hydroxide [Conc. of phenylthiourea and sweep rate in (a), (b) and (c) respectively are: 1·4 m*M*, 0·04 V sec^{-1}; 4·1 m*M*, 0·05 V sec^{-1} and 2·8 m*M*, 0·22 V sec^{-1}]

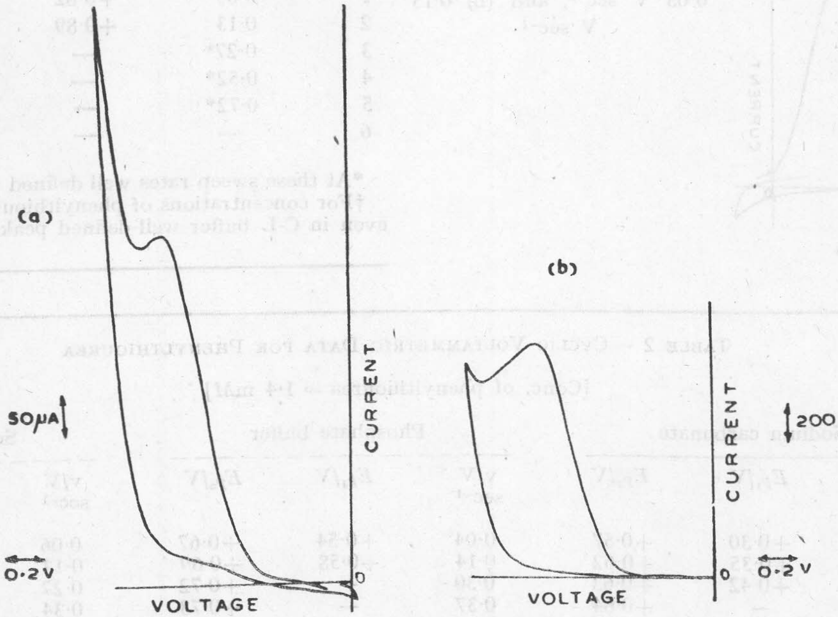


Fig. 1 — Cyclic voltammograms of phenylthiourea in (a) sulphuric acid and (b) Clarks and Lubs buffer [Conc. of phenylthiourea in (a) 4·1 m*M*, and in (b) 9·9 m*M*; sweep rate in (a) 0·05 V sec^{-1}, and in (b) 0·04 V sec^{-1}]

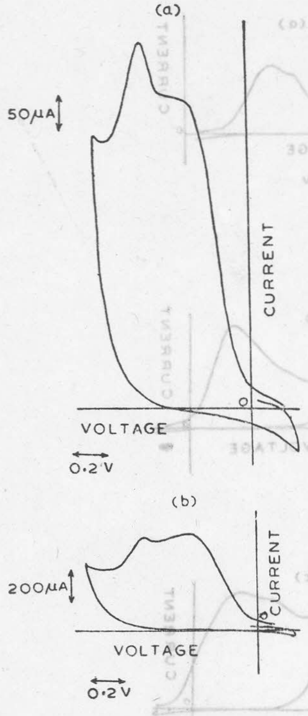


Fig. 3 — Cyclic voltammograms of phenylthiourea in sodium carbonate at sweep rate = 0·29 V sec^{-1} [Conc. of phenylthiourea: (a) 1·4 mM, and (b) 2·8 mM]

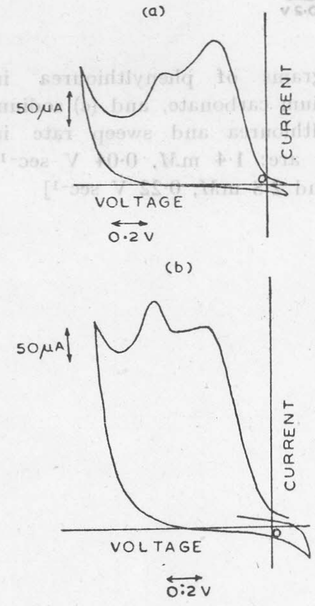


Fig. 4 — Cyclic voltammograms of phenylthiourea (1·4 mM) in sodium carbonate at sweep rate (a) 0·05 V sec^{-1}, and (b) 0·15 V sec^{-1}

carbonate and at +0·27 V in the sodium hydroxide (Fig. 2) are characterized as diffusion peaks. The adsorption peaks observed at potentials anodic to the diffusion peaks may be attributed to the strong adsorption of the reactant (phenylthiourea) on platinum electrode in these media.

E_p values are found to vary with the sweep rate and the values in sulphuric acid medium and C-L buffer are presented in Table 1. In the case of sodium carbonate, sodium hydroxide and phosphate buffer, wherein two peaks are observed, E_p values for both the peaks at different sweep rates are presented in Table 2. Potentials of both the peaks are found to shift in anodic direction. i_p versus $v1/2$plot in Fig. 5 also suggests that the oxidation of phenylthiourea in C-L buffer is diffusion-controlled[10].

i_p values for phenylthiourea in various media are presented in Table 3. Comparing these values with those obtained for thiourea[9], where one-electron oxidation has been confirmed, the number of electrons involved in the electrode process under consideration also can be taken as one. αn_a data used for the computation of i_p values have been reported earlier[11].

Chronoamperometric results — Table 4 presents the current-time data after correcting for the background current and the potential employed for chrono-

TABLE 1 — CYCLIC VOLTAMMETRIC DATA FOR PHENYLTHIOUREA

[Conc. of phenylthiourea = 5·4 mM]†

Sl No.	Sulphuric acid		C-L buffer	
	v/V sec^{-1}	E_p/V	v/V sec^{-1}	E_p/V
1	0·05	+0·82	0·04	+0·78
2	0·13	+0·89	0·14	+0·81
3	0·27*	—	0·30	+0·84
4	0·52*	—	0·35	+0·85
5	0·72*	—	0·50	+0·86
6	—	—	0·71	+0·88

*At these sweep rates well defined peaks were not formed.
†For concentrations of phenylthiourea lower than 5·4 mM even in C-L buffer well-defined peaks are not obtained.

TABLE 2 — CYCLIC VOLTAMMETRIC DATA FOR PHENYLTHIOUREA

[Conc. of phenylthiourea = 1·4 mM]

Sl No.	Sodium carbonate			Phosphate buffer			Sodium hydroxide		
	v/V sec^{-1}	E_{p_1}/V	E_{p_2}/V	v/V sec^{-1}	E_{p_1}/V	E_{p_2}/V	v/V sec^{-1}	E_{p_1}/V	E_{p_2}/V
1	0·05	+0·30	+0·57	0·04	+0·54	+0·67	0·06	+0·18	+0·57
2	0·15	+0·35	+0·62	0·14	+0·58	+0·69	0·13	+0·20	+0·57
3	0·29	+0·42	+0·63	0·30	—	+0·72	0·27	+0·24	+0·58
4	0·35	—	+0·64	0·37	—	+0·73	0·34	—	+0·60
5	0·50	—	+0·67	0·54	—	+0·74	0·46	—	+0·62
6	0·72	—	+0·69	0·71	—	+0·76	0·70	—	+0·62

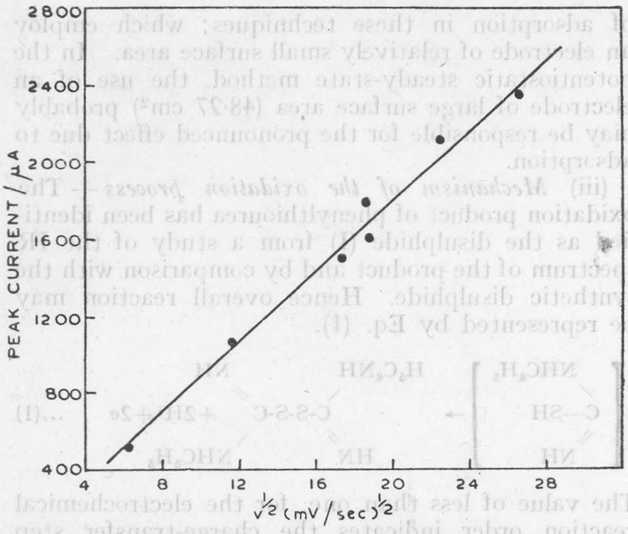


Fig. 5 — i_p versus $v^{1/2}$ plot for phenylthiourea (5·4 mM) in Clarks and Lubs buffer

TABLE 3 — i_p VALUES FOR PHENYLTHIOUREA IN VARIOUS MEDIA

Sl No.	Medium	Sweep rate/ V sec^{-1}	[Phenylthiourea] mM	Current μA	$i_p/(V^{1/2}C)$
1	Sulphuric	0·05	2·9	295	501
	acid	0·13	4·2	720	497
2	C-L buffer	0·14	5·4	1060	530
		0·30	7·7	2100	496
3	Phosphate	0·14	1·4	165	317
	buffer	0·04	2·8	117	214
4	Sodium	0·05	1·4	160	527
	carbonate	0·29	2·7	400	272
5	Sodium	0·05	1·4	215	631
	hydroxide		2·8	245	366

amperometry. The current in the case of sulphuric acid and C-L buffer decays with time smoothly and reaches a steady-state value. In the other media, the current falls after an initial rapid rise to a lower steady-state value. The $it^{1/2}$ versus t plots, presented in Fig. 6, show that in the case of sulphuric acid, the plot is almost horizontal and in C-L buffer, the plot is linear with a positive slope. The fall of current in both the cases may be taken to conform to ideal Cottrell's behaviour. For other media, linear plots with negative slopes are obtained suggesting complications due to adsorption.

Results from the potentiostatic steady-state technique — The supporting electrolyte (100 ml) used for each run was placed in a 400 ml beaker and an equal volume put in a porous vessel of convenient size placed in the beaker. A spiral platinum rod electrode was placed outside in the solution contained in the beaker and a platinum gauze electrode in the solution in the porous vessel. After pre-electrolysis, known concentration of phenylthiourea was added to the solution in the porous vessel. With the rest potential at zero current noted, the potential of the working electrode was increased in steps of 25 mV and the current readings were taken. Log current density versus overvoltage plots in sulphuric acid are presented in Fig. 7. The charge-transfer overvoltage in this region is found to be 150-300 mV. The anodic reaction order is evaluated as 0·5. A transfer coefficient of value of 0·23 is obtained at all concentrations of thiourea in the range 0·6 to 3·5 mM. The ionic exchange current densities (Acm^{-2}) at phenylthiourea concentrations 0·6, 1·2, 2·4 and 3·5 mM are 2·327, 2·927, 4·329 and 7·185 × 10^{-6} respectively. The supporting electrolyte is 1N sulphuric acid, temp. = 28·5°, and surface area of the working electrode = 48·27 cm^2.

TABLE 4 — CHRONOAMPEROMETRIC DATA FOR PHENYLTHIOUREA

[Conc. of phenylthiourea = 1·4 mM]

Sl No.	Time sec	Current (μA)				
		Sulphuric acid	C-L buffer	Sodium carbonate	Sodium hydroxide	Phosphate buffer
1	2	164	328	90	192	16·0
2	4	136	248	42	107	6·0
3	5	108	227	34	91	3·0
4	6	100	201	26	76	0·0
5	7	94	200	25	65	0·0
6	8	90	188	22	60	−1·5
7	9	88	181	19	55	−0·5
8	11	80	167	18	44	−2·0
9	13	76	156	14	39	−4·0
10	15	70	145	11	34	−5·0
11	16	64	143	10	31	−6·0
12	18	60	137	8	29	−7·0
13	20	56	129	7	28	−7·0

Potentials employed: +0·80 V in sulphuric acid, C-L buffer, sodium carbonate and phosphate buffer; and +0·70 V in NaOH medium.

The current values measured at different potentials in the sodium hydroxide are not steady.

The following conclusions have been drawn from the present studies:

(i) *Nature of the electrode process* — The electrochemical oxidation of phenylthiourea at a platinum electrode may be characterized as an irreversible process in view of the variation of peak potential with sweep rate and the absence of a cathodic peak near about 60 mV from the anodic peak, expected if the process is to be reversible.

(ii) *Complications due to adsorption* — Phenylthiourea appears to be strongly adsorbed on platinum in sodium carbonate, phosphate buffer and sodium hydroxide media. The $it^{1/2}$ values in these media show a decreasing trend with time. The appearance of a new peak, anodic to the diffusion peak, in all these media indicates strong adsorption of the reactant on the electrode surface. Controlled potential coulometry of phenylthiourea in sodium hydroxide and phosphate buffer show that 100% current efficiency is not obtained for the same reason[1]. The fractional value (0·5) for the anodic electrochemical reaction order obtained for phenylthiourea in sulphuric acid shows the presence of adsorption even in this medium. Cyclic voltammetric and chronoamperometric results are satisfactory to some extent, possibly due to the small effect of adsorption in these techniques; which employ an electrode of relatively small surface area. In the potentiostatic steady-state method, the use of an electrode of large surface area (48·27 cm²) probably may be responsible for the pronounced effect due to adsorption.

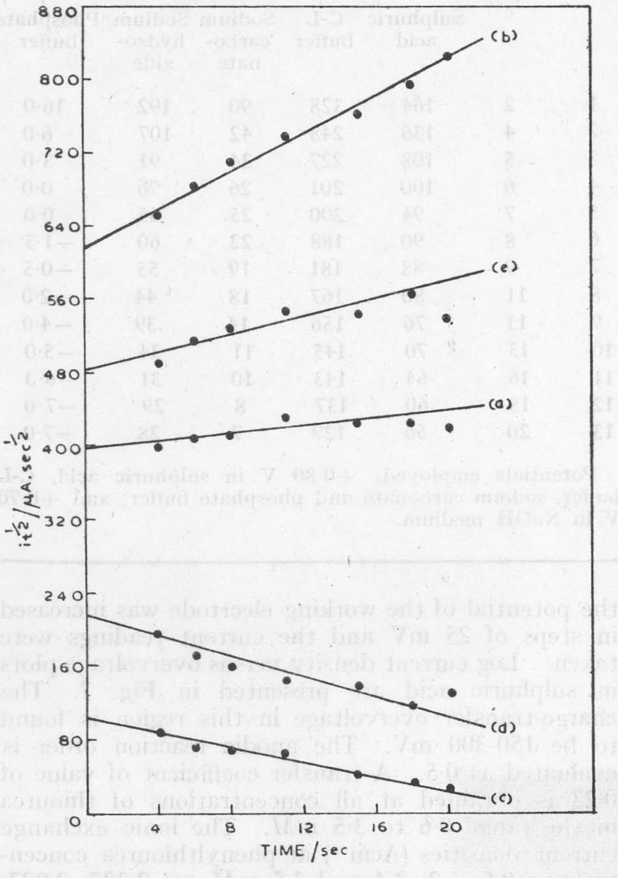
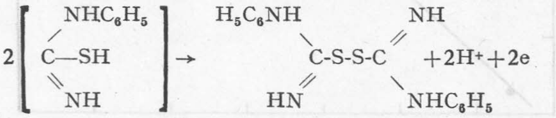


Fig. 6 — $it^{1/2}$ versus t plots for phenylthiourea (2·74 mM) in (a) sulphuric acid, (b) Clarks and Lubs buffer, (c) phosphate buffer, (d) sodium carbonate, and (e) sodium hydroxide

Fig. 7 — Log | I_+ | versus η plots for phenylthiourea in sulphuric acid at 27·5° [Phenylthiourea conc.: (a) 0·6 mM, (b) 1·2 mM, (c) 2·4 mM, and (d) 3·5 mM]

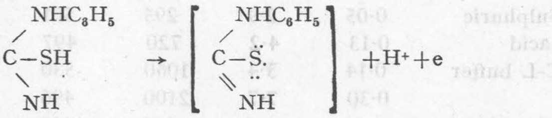
(iii) *Mechanism of the oxidation process* — The oxidation product of phenylthiourea has been identified as the disulphide (I) from a study of the IR spectrum of the product and by comparison with the synthetic disulphide. Hence overall reaction may be represented by Eq. (1).



...(1)

The value of less than one, for the electrochemical reaction order indicates the charge-transfer step to involve only one molecule of phenylthiourea. The electrochemical oxidation is found to be a one-electron process from the present cyclic voltammetric data.

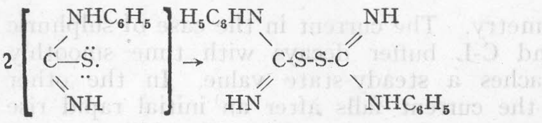
In all the supporting electrolytes employed, *n* value comes out to be 1. The oxidation process may consist of two steps (Eqs. 2 and 3): The formation of a free radical during the charge-transfer process (Eq. 2)



...(2)

The variation of the half-peak potential with *p*H (dE_p/dpH = 0·059 V for unit change of *p*H) suggests the involvements of a proton in the charge-transfer process.

The combination of free radicals to form disulphide (Eq. 3)



...(3)

The step represented by Eq. (2) is likely to be the rate-determining in the electrochemical oxidation of phenylthiourea.

(iv) *Evaluation of diffusion coefficient* — The diffusion coefficients, evaluated using the chronoamperometric results, in different media, viz. sulphuric acid, C-L buffer, sodium carbonate and sodium hydroxide are 5·89, 2·15, 1·07 and 5·54 $\times 10^{-6}$ cm² sec^{-1}. The diffusion coefficient in phosphate buffer, obtained from cyclic voltammetric results is found to be $3{\cdot}38\times10^{-6}$ cm^{-2} sec^{-1}. Since the values given above are obtained from $(it^{1/2})_0$ values which are calculated by extrapolation of $it^{1/2}$ values to zero time, they are not likely to be affected by the complications assciated with the surface state of the electrode.

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