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REDUCTION OF THYROXINE AND RELATED COMPOUNDS ON SILVER
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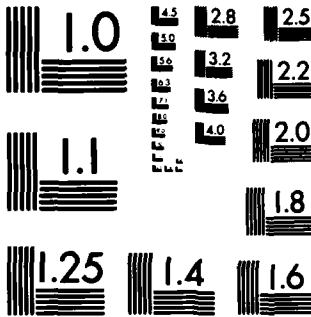
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SECURITY CLASSIFICATION OF THIS PAGE (When Data Entered)

REPORT DOCUMENTATION PAGE		READ INSTRUCTIONS BEFORE COMPLETING FORM
1. REPORT NUMBER SUNYBUF/DC/TR-19	2. GOVT ACCESSION NO.	3. RECIPIENT'S CATALOG NUMBER
4. TITLE (and Subtitle) Reduction of Thyroxine and Related Compounds on Silver		5. TYPE OF REPORT & PERIOD COVERED
		6. PERFORMING ORG. REPORT NUMBER
7. AUTHOR(s) Mizuho Iwamoto, Andrew Webber and R.A. Osteryoung		8. CONTRACT OR GRANT NUMBER(s) N00014-79-C-0682
9. PERFORMING ORGANIZATION NAME AND ADDRESS Department of Chemistry State University of New York at Buffalo		10. PROGRAM ELEMENT, PROJECT, TASK AREA & WORK UNIT NUMBERS NR-051-715
11. CONTROLLING OFFICE NAME AND ADDRESS Office of Naval Research Chemistry Program Arlington, VA 22217		12. REPORT DATE April, 1984
		13. NUMBER OF PAGES 29
14. MONITORING AGENCY NAME & ADDRESS (if different from Controlling Office)		15. SECURITY CLASS. (of this report) Unclassified
		15a. DECLASSIFICATION/DOWNGRADING SCHEDULE
16. DISTRIBUTION STATEMENT (of this Report) Approved for Public Release: Distribution Unlimited		
17. DISTRIBUTION STATEMENT (of the abstract entered in Block 20, if different from Report) DTIC ELECTE SEP 5 1984 S D		
18. SUPPLEMENTARY NOTES Prepared for Publication in Analytical Chemistry B		
19. KEY WORDS (Continue on reverse side if necessary and identify by block number) Thyroxines; Silver electrodes; Catalysis		
20. ABSTRACT (Continue on reverse side if necessary and identify by block number) The reduction of thyroxine (T_4), liothyronine, diiodothyronine, diiodotyrosine and moniodotyrosine has been studied at silver rotating disk electrodes in 0.10 M NaOH. All compounds give one reduction wave; the potential for the reduction of T_4 on silver is about one-half volt more positive than on mercury, where it reduces stepwise. The reduction is shown to be convective diffusion-controlled at the rotating silver disk electrode. Potential step and coulometric experiments are		

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OFFICE OF NAVAL RESEARCH
Contract N00014-79-C-0682
Task No. NR-051-715

TECHNICAL REPORT NO. 19

Reduction of Thyroxine and Related
Compounds on Silver

by

Mizuho Iwamoto, Andrew Webber and Robert A. Osteryoung

Prepared for Publication

in

Analytical Chemistry

Department of Chemistry
State University of New York at Buffalo
Buffalo, New York 14214

April, 1984

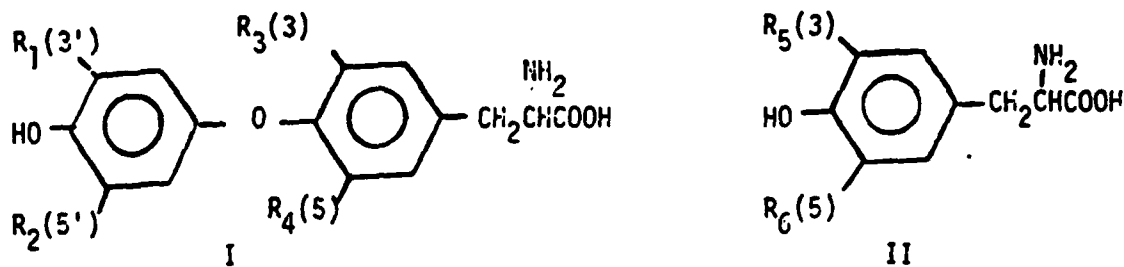
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ABSTRACT

The reduction of thyroxine (T_4), liothyronine, diiodothyronine, diiodotyrosine and monoiodotyrosine has been studied at silver rotating disk electrodes in 0.10 M NaOH. All compounds give one reduction wave; the potential for the reduction of T_4 on silver is about one-half volt more positive than on mercury, where it reduces stepwise. The reduction is shown to be convective diffusion-controlled at the rotating silver disk electrode. Potential step and coulometric experiments are employed to show that, in the case of T_4 , the reduction is an eight-electron process which results in cleavage of four iodine atoms from the T_4 molecule. Detection limits for these compounds are reported.

Iodoamino acid derivatives of thyronine and tyrosine including thyroxine (T_4), liothyronine (T_3), diiodothyronine (T_2), diiodotyrosine (Ty_2) and monoiodotyrosine (Ty_1) are important biological components produced in the thyroid gland.



I Thyroxine (T_4): $R_1=R_2=R_3=R_4=I$

Liothyronine (T_3): $R_1=R_3=R_4=I, R_2=H$

3',3,5-triiodo-thyronine

3,5-diiodo-thyronine (T_2): $R_3=R_4=I, R_1$ and $P=H$

II 3,5-diiodo-tyrosine (Ty_2): $R_5=R_6=I$

3-iodo-tyrosine (Ty_1): $R_5=I, R_6=H$

Various biological and chemical methods proposed for determination of T_4 have been critically examined [1] and are generally very complicated. For example, chemical methods are usually based on measuring the organically combined iodine. In view of the unsatisfactory nature of these methods, the polarographic behavior of T_4 and related compounds has been studied and used to determine those compounds [2-4]. Recently differential pulse polarography has been applied to the determination of T_4 and T_3 [5,6].

Most studies on the electrochemical reduction of T₄ and related compounds have been carried out at mercury electrodes. However, the electrode reactions have not been investigated in detail. Although polarographic methods have proven to be useful for detection of T₄ and related compounds, the dropping mercury electrode (DME) is cumbersome for practical work and also poses a toxicity problem. Hence, the application of solid electrodes to detect thyroid hormones is of interest. The use of a carbon electrode as an electrochemical HPLC detector for T₄ and T₃ [7] has been reported, but involved oxidation, not reduction.

Electrochemical properties of silver are of considerable interest since the metal is widely used in a number of industrially important electrochemical and catalytic processes. Furthermore, the hydrogen overvoltage on silver is intermediate between the corresponding values for mercury and platinum. Therefore, it was expected that the reduction of organic compounds on silver could be analytically useful. Little exists in the literature involving the use of these electrodes for reductive processes; a recent paper describes the use of silver electrodes for the determination of some nitrate esters [8]. Here we report on the reduction of T₄ and related compounds at a silver electrode, particularly the silver rotating disk electrode (RDE).

EXPERIMENTAL

Chemicals

L-thyroxine (3,3',5,5'-tetraiodo-L-thyronine), liothyronine (3,3',5-triiodo-L-thyronine), 3,5-diiodo-L-thyronine and 3,5-diiodo-L-tyrosine were obtained from Sigma Chemical Co., and 3-iodo-L-tyrosine from Aldrich Chemical Co. Stock solutions of 5.0×10^{-3} in 0.1 M NaOH were prepared

for each measurement series. Analytical grade sodium hydroxide and sodium chloride was used. Stock solutions were stored in the absence of light and used within 8 hours.

Apparatus

Three silver electrodes were used for this work. One, a commercial rotating silver disk mounted on a Model ASR rotator (Pine Instrument Co., Grove City, PA) had a geometric area of 0.442 cm^2 . A coiled silver wire of area 44.6 cm^2 (284 cm long, 0.05 cm diameter) was used for controlled potential coulometry. The third silver electrode consisted of a wire sealed in epoxy (Buehler Ltd. #20-8130-032) which was sawn in half with a diamond saw to expose a circular cross-section of the wire. The other end of this silver wire had been soldered to a nut that screwed onto a connecting rod. The nut and connector were isolated from the electrolyte by a Tygon sleeve. The method of construction was taken from a recent publication [9]. A Unitron Bi 5-3214 measuring microscope was used to measure eight diameters of this silver disk ($0.5272 \pm 0.0015 \text{ mm}$) giving an electrode area of 0.00218 cm^2 . This small electrode was used for all cyclic voltammetry and pulse voltammetry. Both the large and small silver disks were polished on a Minimet polisher (Buehler Ltd.) with $0.05 \mu\text{m}$ alumina (dry powder, Type A, Fisher) prior to immersion in the electrolyte. The potential was then held at -0.8 V to condition the electrode.

All potentials were measured and are reported against a saturated calomel electrode (SCE). Solutions were deoxygenated by purging with argon. Long experiments such as coulometry were performed in darkened cells since it has been reported that thyroxine is unstable in basic media in the

presence of light [6]. An IBM 225 voltammetric analyzer was used for cyclic voltammetry and an EG&G PARC 173 potentiostat/galvanostat with an EG&G PARC 179 digital coulometer in conjunction with an EG&G PARC 175 universal programmer for all experiments with the large rotating disk electrode. Pulse voltammetry and polarography were carried out with an EG&G PARC 174 polarographic analyzer. The flow rate of the DME was 0.813 mg s^{-1} .

Controlled potential coulometry.

Controlled potential coulometry of 125 mL of 1.0 mM T_4 in 0.1 M NaOH was carried out at the large silver wire electrode at -1.2 V. The cell was placed in an ultrasonic bath to enhance the rate of transport of material to the electrode and hence increase the current. The current at -1.2 V prior to addition of T_4 was 1.18 mA and the total charge passed (72.6 C) was corrected for this, giving a net charge passed of 57.0 C. The EG&G PARC 173 and 179 were used for the coulometry and, with the EG&G PARC 175, for voltammetry at the small silver disk electrode prior and subsequent to the electrolysis. 25 mL aliquots of the electrolysis solution were titrated with 0.01 M silver nitrate solution using a Metrohm 636 titroprocessor and E635 dosimat. Both the silver nitrate solution and the electrolysis sample were brought to pH 1 with concentrated sulfuric acid prior to the titration. The silver nitrate solution was standardized against a sodium chloride solution (0.01 M).

RESULTS AND DISCUSSION

RDE voltammograms for various concentrations of T_4 in 0.1 M NaOH are shown in Figure 1. T_4 gives one well-defined wave with a half-wave potential, $E_{1/2}$, of -0.86 V. The limiting current (i_d) is proportional

to the concentration of T_4 over a range 10^{-5} - 10^{-4} M. The voltammograms for T_3 , T_2 , Ty_2 and Ty_1 are compared with that of T_4 in Figure 2. T_3 and T_2 show one reduction wave with an $E_{1/2}$ of -0.87 V and -0.86 V respectively, and are similar to that of T_4 except for the lower limiting current. The tyrosines Ty_2 and Ty_1 , give smaller, drawn-out waves with $E_{1/2}$ values of -1.00 V and -0.99 V.

The concentration dependence of the limiting currents for the five compounds is shown in Figure 3. $E_{1/2}$ and i_d at the Ag RDE are listed in Table I. As can be seen from Table I and Figure 3, the current ratio among T_4 , T_3 and T_2 is approximately 4:3:2, and the ratio between Ty_2 and Ty_1 is 2:1. The results suggest that the reduction current depends on the number of iodine atoms in each molecule.

The dependence of the limiting current on the square root of the rotation rate for T_4 , T_3 and T_2 is shown in Figure 4. The linearity of the $i_d-\omega^{1/2}$ plots indicates that each limiting current is convective diffusion-controlled. A deviation from linearity was observed at rotation rates in excess of 3600 rpm at a scan rate of 10 mV s $^{-1}$.

A hysteresis appears on current-potential curves of T_4 at rotation rates greater than 2500 rpm at a scan rate of 10 mV s $^{-1}$ or, at a scan rate of 50 mV s $^{-1}$, for rotation rates greater than 6600 rpm (Figure 5). This phenomena could be caused by adsorption of T_4 , T_3 and T_2 at the electrode surface. Thus, the cathodic limiting current has the characteristic of convective diffusion affected by adsorption. A scan rate of 50 mV s $^{-1}$ and rotation rate of 2500 rpm were used for analytical studies of T_4 , T_3 and T_2 .

The reduction of these organic iodoamino acids on the silver RDE was

compared to that on a DME. When examined in 0.1 M NaOH at the DME, T₄ gave a series of three polarographic waves and T₃ and T₂ two waves, as shown in Figure 6. On the other hand, Ty₂ gave one wave at a much more negative potential and Ty₁ showed no wave (Figure 6). In differential pulse polarographic studies of T₄ by Holak et al [4], it was suggested that the first wave of T₄ results from cleavage of the iodide from the 5-position, the second from the cleavage of iodide from the 3' and 5' positions and the third from cleavage of iodide from the 3-position. The reduction of Ty₂ to tyrosine on mercury occurs at more negative potentials [10].

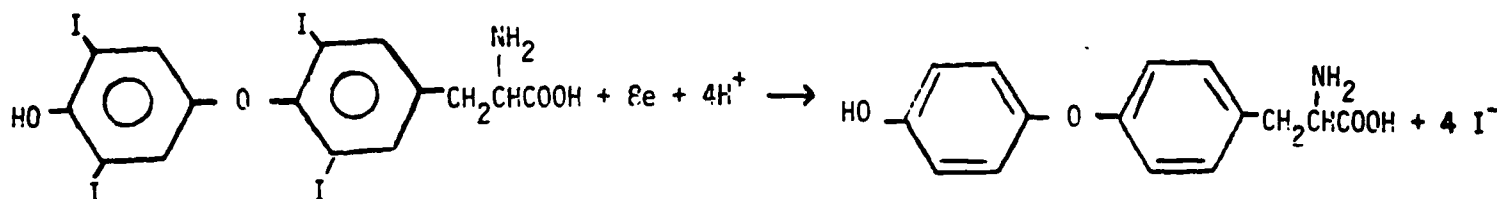
Comparison of the behavior of these compounds on silver and at the DME (Figure 2 and 6) can be summarized as follows:

1. The thyronines T₄, T₃ and T₂ are reduced in one step on a silver electrode, but stepwise at a DME.
2. All the iodoamino acids are reduced at more positive potentials on silver than on mercury. Even Ty₁, which does not give a reduction wave on mercury, is reduced on silver.
3. The total current at both electrodes depends on the number of iodine atoms in each molecule .

Reduction of thyroxine.

Since T₄ is the most biologically important compound we chose to investigate it further. The DC polarographic limiting current of T₄ is diffusion-controlled at the DME. Assuming an eight-electron reduction for the total wave height [3], the Ilkovic equation [11] gives a value for the diffusion coefficient of T₄ of $3.3 \times 10^{-6} \text{ cm}^2 \text{ s}^{-1}$ in excellent agreement with value of $3.6 \times 10^{-6} \text{ cm}^2 \text{ s}^{-1}$

estimated from the Stokes-Einstein relationship [12]. Reverse pulse polarography [13] of T₄ in 0.2 M sodium carbonate solution at a DME showed an anodic wave corresponding to the oxidation of mercury in the presence of iodide formed from the reduction of T₄ at the initial potential (-1.9 V). This data suggests that T₄ is reduced at the DME in an eight-electron process:



However, this can not, per se, be taken to apply to the reduction at a silver cathode. Indeed, the evidence for the number of electrons involved and the number of iodide ions produced at mercury is not conclusive. We therefore used RDE voltammetry, cyclic voltammetry and controlled potential coulometry to study the reduction at silver.

The value of *n* for T₄ at the silver RDE was estimated from the limiting currents at various rotation rates and the Levich equation [14]. Data were obtained at a scan rate of 10 mV s⁻¹ and the value of the diffusion coefficient was that determined from polarography at the DME. Values of *n* between 8.0 and 8.5 were obtained (Table III). Since the value of the diffusion coefficient is based on the assumption that *n* is eight for the total wave at the DME, this really means that we are assuming that *n* for the reduction of T₄ at -1.1 V at the silver RDE equals that for the

reduction at -1.9 V at the DME.

Proof that T_4 is reduced at silver electrodes to give iodide ions is presented in the cyclic voltammograms at the small silver disk electrode in Figures 7 and 8. Figure 7 a shows the diffusion-controlled irreversible reduction of T_4 (I_p vs $v^{1/2}$ at 0.878 mM T_4 , slope = $4.29 \pm 0.05 \mu A s^{1/2} v^{-1/2}$, intercept = $0.06 \pm 0.02 \mu A$) while 7b shows that no iodide is present in the bulk solution. (Iodide ions exhibit an oxidation wave at -0.15 V, due to formation of silver iodide, and a stripping peak at -0.3 V for the reduction of this silver iodide film.) Figure 7a shows that when the potential is swept to -1.2 V (i.e. reducing T_4) and then back to -0.1 V an oxidation peak and cathodic stripping peak due to the presence of iodide ions in the region of the electrode as a product of the reduction of T_4 is seen. When the following sequence of potential pulses was applied; -0.6 V, -1.2 V for t_1 , 0 V for t_2 ; a film of silver iodide was formed. The cathodic stripping peak of the silver iodide is shown in Figure 8. The silver iodide is on the electrode surface rather than distributed throughout the bulk of the electrode and thus behavior for the stripping of an insoluble compound is expected [15]. The peak height of the stripping peak is proportional to the shorter of times t_1 , and/or t_2 (when $t_1 = 30$ s, $t_2 = 0-20$ s, I_p vs $t_2^{1/2}$ gives slope = $0.44 \pm 0.01 \mu A s^{-1/2}$, intercept = $-0.02 \pm 0.03 \mu A$, and when $t_2 = 20$ s, $t_1 = 0 - 10$ s, I_p vs $t_1^{1/2}$ gives a slope = $0.49 \pm 0.02 \mu A s^{-1/2}$, intercept = $0.01 \pm 0.05 \mu A$, concentration 0.878 mM, $v = 0.1 V s^{-1}$). This is because the amount of silver iodide formed is limited by both the amount of iodide ions formed from the reduction of T_4 during t_1 , and the proportion of the iodide ions that can form silver iodide during t_2 . If $t_1 = t_2 = t$

then the peak current is proportional to $t^{1/2}$. The $t^{1/2}$ dependence of the peak current is consistent with diffusion-control of both the reduction of T_4 and the formation of silver iodide. If the potential during t_1 is held at -0.6 V, rather than -1.3 V, so that T_4 is not reduced, no iodide is formed and no stripping peak is observed (the current is the same as the background, Figure 7b).

The stripping peak current is proportional to v (I_p vs v ; slope = $16.7 \pm 0.2 \mu A s^{-1}$, intercept = $0.001 \pm 0.02 \mu A$, concentration = 0.879 mM, $t_1 = t_2 = 30$ s) as expected for the reduction of a surface-bound species. For the reversible reduction of an adsorbed film, the difference in potentials at half the peak height equals $3.53 RT/nF$ ($90.6/n$ mV at 25° C) [15]. This gives a value for n of 0.99 ± 0.08 . The peak current is given by [15].

$$I_p = n^2 F^2 v A \Gamma / 4RT \quad (1)$$

and the charge under the peak by:

$$Q = nFA\Gamma \quad (2)$$

Combining Eqn. 1 and 2 gives:

$$I_p/Q = nFv/4RT \quad (3)$$

Using data obtained at 0.2 V s^{-1} , 2.8 mM T_4 , $t_1 = 60$ s, $t_2 = 10$ s where $I_p = 105 \mu A$ and $Q = 53.8 \mu C$, we find a value for n of 1.00 . This confirms that the stripping peak corresponds to a one-electron reduction, consistent with the reduction of silver iodide.

The value of n for the reduction of T_4 obtained from the RDE data is based on the value of the diffusion coefficient determined by polarography at the DME and assuming that n at the DME is eight. While the theoretical value of the diffusion coefficient is in excellent agreement with the

experimental value, an unequivocal method, controlled potential coulometry, was employed to determine n at a silver wire electrode. A 125 mL solution of 1.0 mM T_4 in 0.1M NaOH was reduced at -1.2V (see Experimental Section). Cyclic voltammograms were run at the small silver disk electrode before and after the electrolysis. This indicated that 57% of the T_4 had been electrolyzed. The charge passed, after allowance and correction for the background current, corresponded to a value of 8.3 for n . Cyclic voltammetry also showed that iodide ions were present in solution. From the $I_p/v^{1/2}$ ratio of the oxidation peak at -0.15V ($8.18 \pm 0.61 \mu A s^{1/2} v^{-1/2}$, $N = 5$) the concentration of iodide ions present in the electrolyte was estimated to be approximately 3.1 mM. A more accurate method was to take three 25 mL portions of the electrolyte and titrate them with a standardized silver nitrate solution. This gave a concentration of iodide of 2.172 ± 0.005 mM, corresponding to 3.80 iodide ions produced per reduced T_4 molecule. This, then confirms that T_4 is reduced at silver in an eight-electron process to give four iodide ions as depicted previously. Presumably the other thyronines undergo a similar reduction process, although additional work is required to verify this.

Finally, Table IV shows the detection limits for these compounds with the rotating silver disc electrode calculated according to the equation $C_L = (X_L - \bar{X}_B)/m$, where C_L is the detection limit, \bar{X}_B the mean value of the blank response, m the slope of the calibration curve, and X_L the smallest discernible analytical signal [16]. For the calculations in Table IV, \bar{X}_B was determined as 15×10^{-6} A for the silver disc electrode rotating at

2500 rpm in 0.1 M NaOH at -1.2 V (see Figures 1 and 2), X_L was taken as 18×10^{-6} A; i.e., a signal 3 microamperes above background could be detected. Diffusion-limited currents were measured at -1.2 V.

Conclusion.

It is clear that these compounds undergo reduction on silver in one concerted step at potentials up to one volt less negative than at mercury. This makes silver a very attractive electrode material for analytical work with these, and possibly other, organohalides. Direct determination of T_4 at the RDE down to the μM level is possible. Other methods that can be envisaged are reduction at a silver electrode to give iodide ions that are detected in a variety of ways: (a) direct voltammetry, (b) titration with silver ions, (c) oxidation, chemical or electrochemical, to iodine with spectroscopic detection, and (d) stripping voltammetry of iodide on a silver electrode. For liquid chromatography applications a coulometric cell could be used to form the iodide ions by reduction at one electrode followed by either oxidation of the iodide to iodine at another electrode prior to, for example, u.v. detection, or collection as AgI at a second in-line Ag electrode, followed by cathodic stripping. Stripping voltammetry in a flow system is feasible and sensitive, has been employed by Wang [17,18] and others [19] in flow injection analysis work, and could be employed here, as indicated above. Additional work in this area is in progress in our laboratory.

ACKNOWLEDGMENTS

The assistance of Mr. Neal Sleszynski, Dr. Marek Wojciechowski and Dr. Malcolm Carter in aspects of this work are appreciated.

CREDIT

This work was supported in part by The Office of Naval Research.

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Figure Captions

1. Limiting current of T₄ during cathodic polarization at various concentrations.
Solutions: a) 9.6×10^{-5} , b) 7.7×10^{-5} , c) 3.9×10^{-5} ,
d) 2.0×10^{-5} , e) 1.0×10^{-5} M T₄ in 0.1 M NaOH; $\omega = 2500$ rpm,
 $\nu = 50$ mV s⁻¹.
2. Current-potential curves of T₄, T₃, T₂, Ty₂ and Ty₁ on silver RDE in 0.1 M NaOH; $\omega = 2500$ rpm, $\nu = 50$ mV s⁻¹.
a) T₄, 7.7×10^{-5} M, b) T₃, 6.0×10^{-5} M, c) T₂, 5.0×10^{-5} M, d) Ty₂, 7.5×10^{-5} M, e) Ty₁, 5.0×10^{-5} M, f) background.
3. Concentration dependence of the limiting current of T₄(-o-), T₃(-Δ-), T₂(-□-), Ty₂(-●-) and Ty₁(-▲-); $\omega = 2500$ rpm, $\nu = 50$ mV s⁻¹, E = -1.2V vs SCE.
4. Dependence of limiting current on the square root of rotation rate; T₄(o,●), T₃(Δ,▲), T₂(-□-, -■-); in 1.0×10^{-4} M at a rate of 50 mV s⁻¹ (o, Δ, and □); in 5.0×10^{-5} M at a rate of 10 mV s⁻¹ (●, ▲, and ■); E = -1.12 V vs SCE.
5. Cathodic polarization curves of T₄ at various rotation rates.
A: 5.0×10^{-5} M T₄ at a scan rate of 50 mV s⁻¹, B: 1.0×10^{-4} M T₄ at a scan rate of 50 mV s⁻¹.

6. Polarograms of 1 mM iodoamino acids in 0.1 M NaOH

a) T₄, b) T₃, c) T₂, d) Ty₂, e) Ty₁

Scan rate = 2 mV s⁻¹, drop time 1 s.

7. Voltammetry in 0.1 M NaOH at the small silver disk electrode. (†)

indicates initial potentials. 0.2 V s⁻¹. (a) With 2.89 mM T₄ present, (b) background.

8. Voltammetry of 2.89 mM T₄ in 0.1 M NaOH at the small silver disk electrode. Potential sweep was begun at -0.6 V and then swept to -1.2 V, held there for 10 s, stepped to -0.1 V, held there for 10 s and finally swept to -0.5 V at 0.2 V s⁻¹.

Table I. Half-wave potentials and limiting currents of 5.0×10^{-5} M iodoamino acids in 0.1 M NaOH at a silver RDE

	T_4	T_3	T_2	T_{Y2}	T_{Y1}
$E_{1/2}^a$	-0.66	-0.87	-0.86	-1.00	-0.99
$i/\omega^{1/2}^b$	1.71	1.15	0.73	0.60	0.36

a: V vs. SCE, at a scan rate of 50 mV s^{-1} .

b: $\mu\text{A rpm}^{-1/2}$, average value obtained at various rotation rates at scan rate of 10 mV s^{-1} .

Table II. Polarographic half-wave potentials and limiting currents of 1 mM iodoamino acids in 0.1 M NaOH ^a

		1st wave	2nd wave	3rd wave	total i_d
T ₄	$E_{1/2}$	-1.19	-1.37	-1.73	9
	i_d	2.8	3.6	2.6	
T ₃	$E_{1/2}$	-1.23	-----	-1.67	6.3
	i_d	2.7		3.5	
T ₂	$E_{1/2}$	-----	-1.35	-1.68	5.0
	i_d		2.5	2.5	
Ty ₂	$E_{1/2}$	-----	-----	-1.82	3.1
	i_d			3.1	
Ty ₁	$E_{1/2}$	-----	-----	-----	-----
	i_d				

a: $E_{1/2}$, V vs SCE; i_d , μ A.

Table III

n-Values from the Levich Equation for Reduction of T_4 in 0.1N NaOH

ω /rpm	$\omega^{1/2}$	$I_d/\mu A$	n
2500	16.18	83	8.0
1600	12.94	68	8.2
900	9.71	51	8.2
400	6.47	35	8.5

$$A = 0.442 \text{ cm}^2$$

$$\nu^{1/6} = 2.15 (\text{cm}^2 \text{ s}^{-1})^{1/6}$$

$$C = 5.0 \times 10^{-5} \text{ M}$$

$$D = 3.3 \times 10^{-6} \text{ cm}^2 \text{ s}^{-1}$$

$$\text{Average } n = 8.22 \pm 0.21$$

Table IV

Detection Limits of T_4 and Related Compounds

	T_4	T_3	T_2	Ty_2	Ty_1
m (A/mol)	1.90	1.30	0.90	0.68	0.32
C_L ($\times 10^{-6}M$)	1.6	2.3	3.3	4.4	9.4

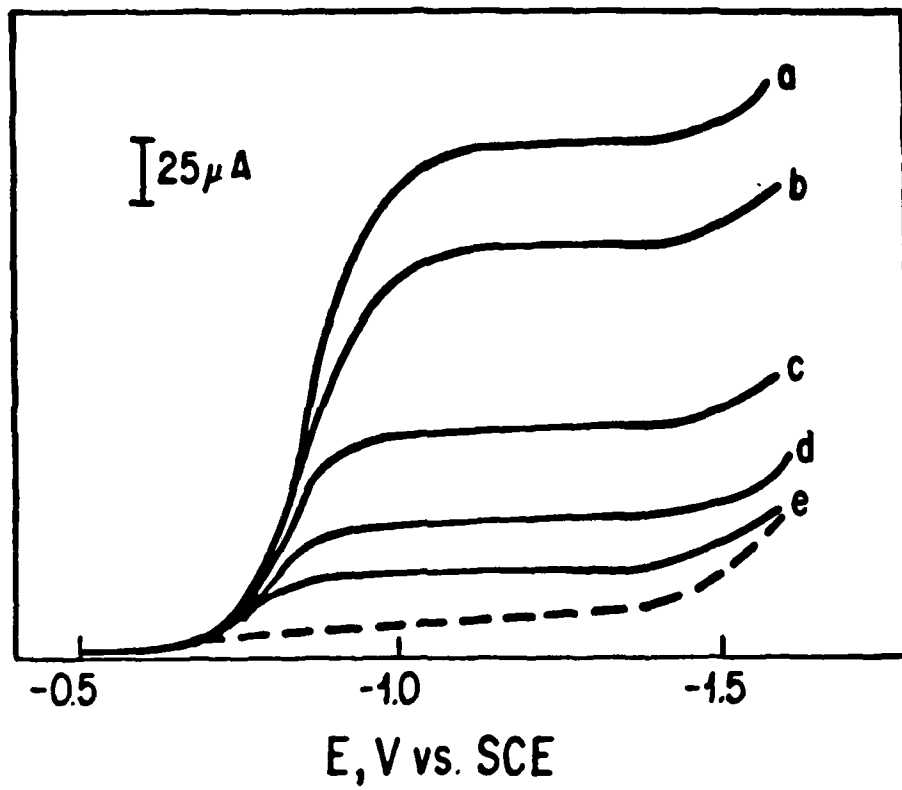


Figure 1

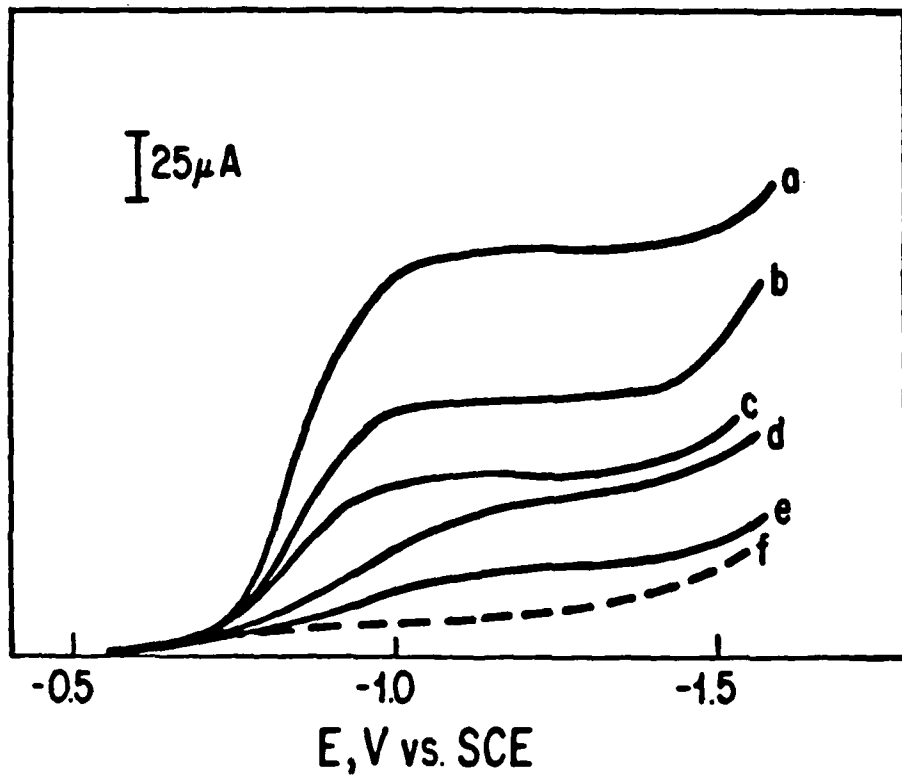


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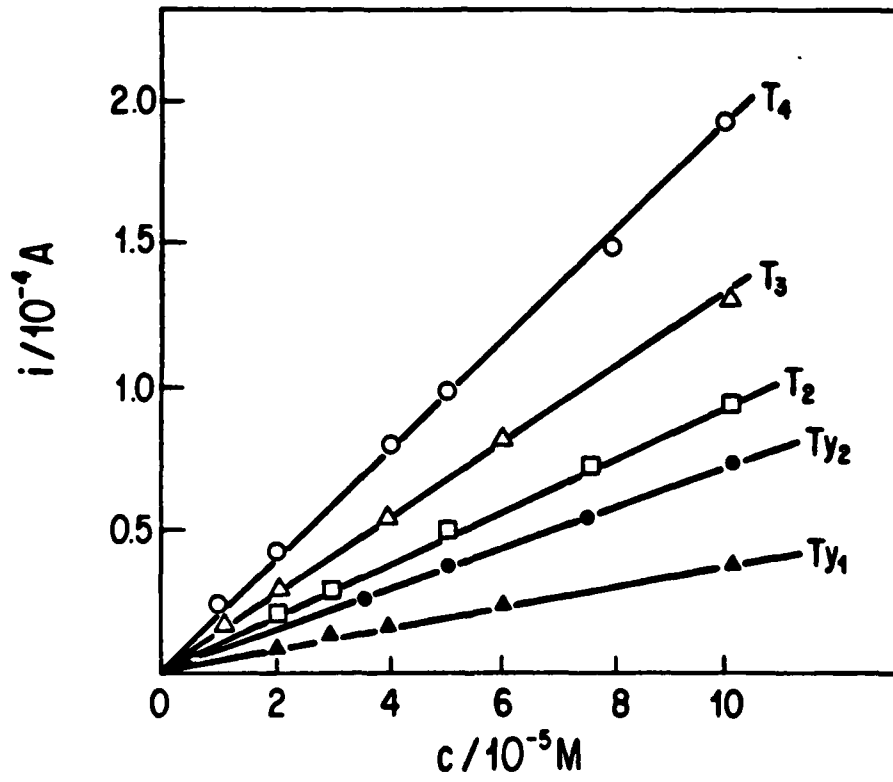


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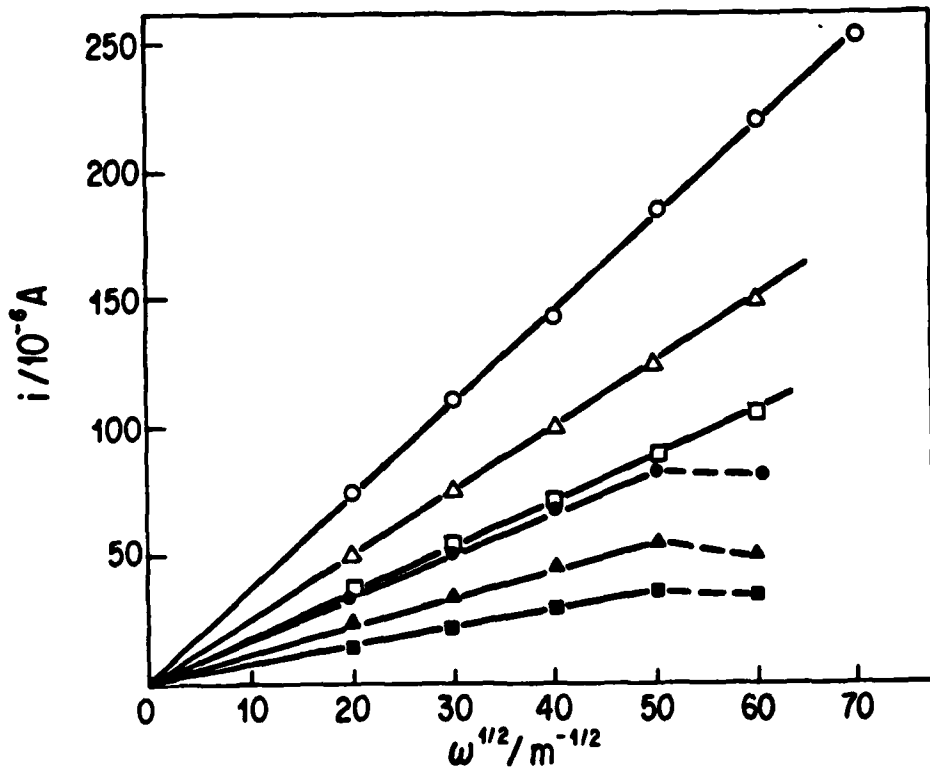


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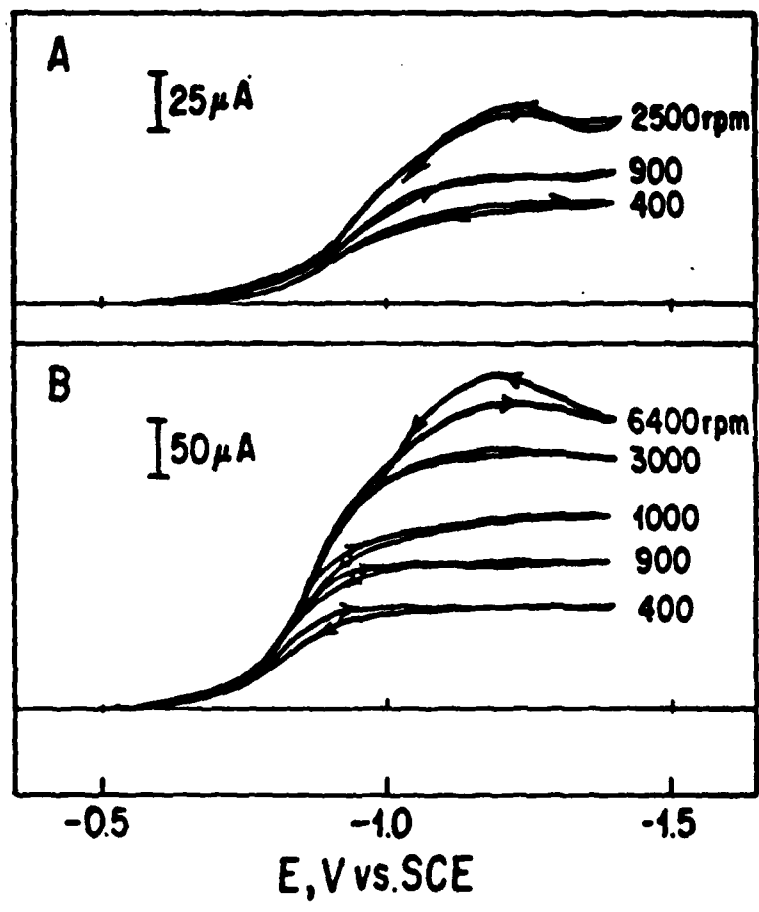
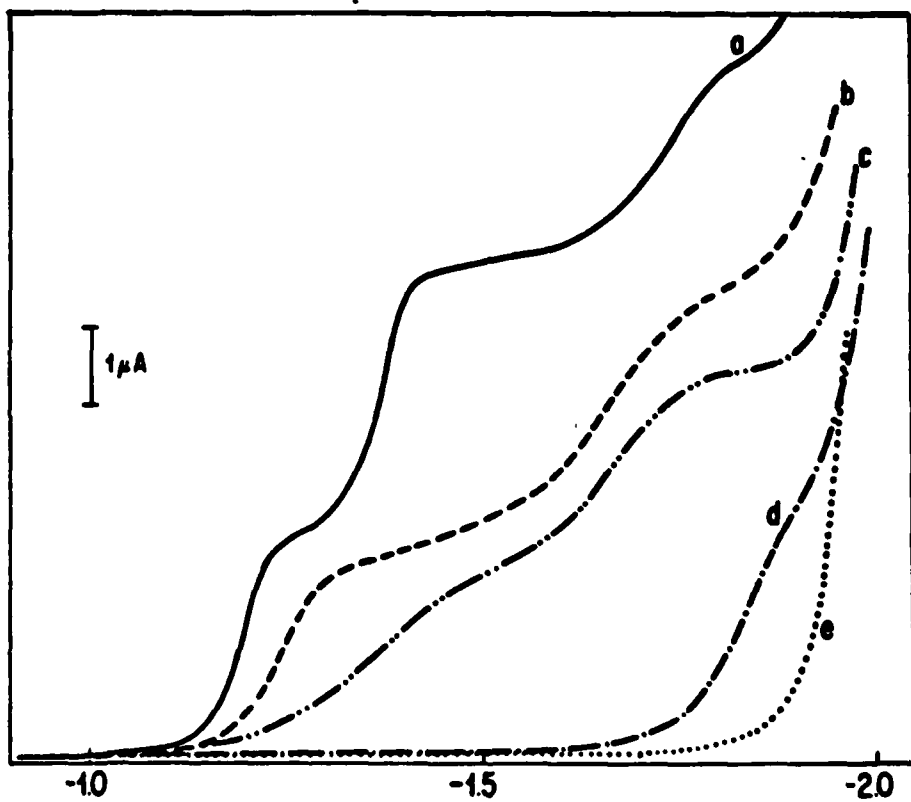


Figure 5



E, V vs. SCE

Figure 6

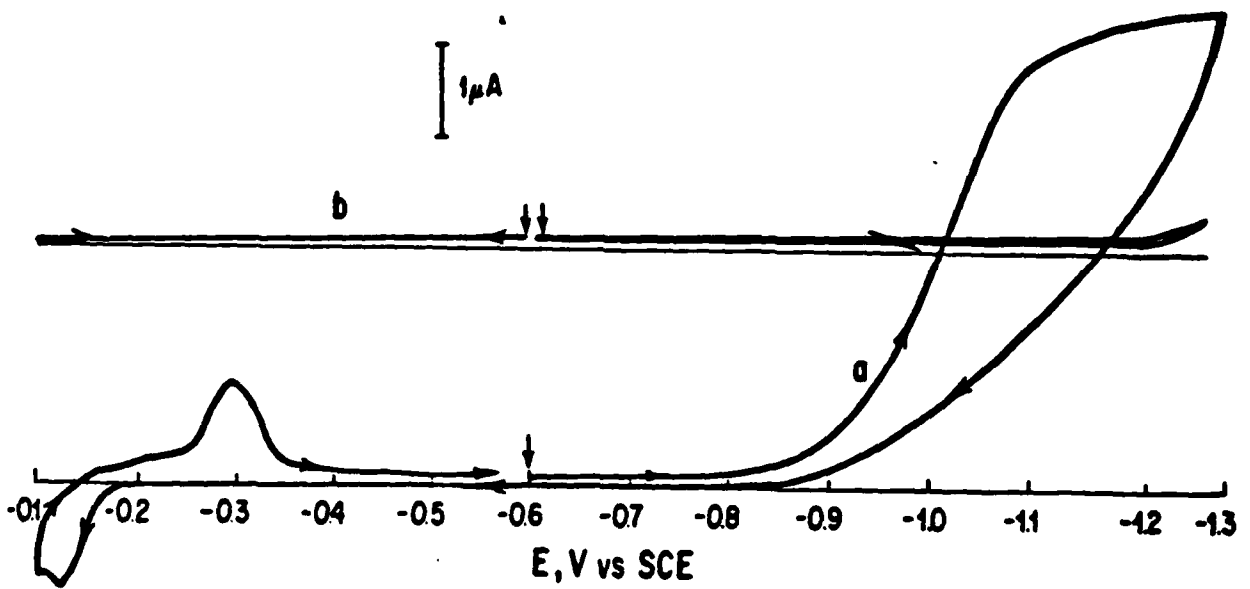


Figure 7

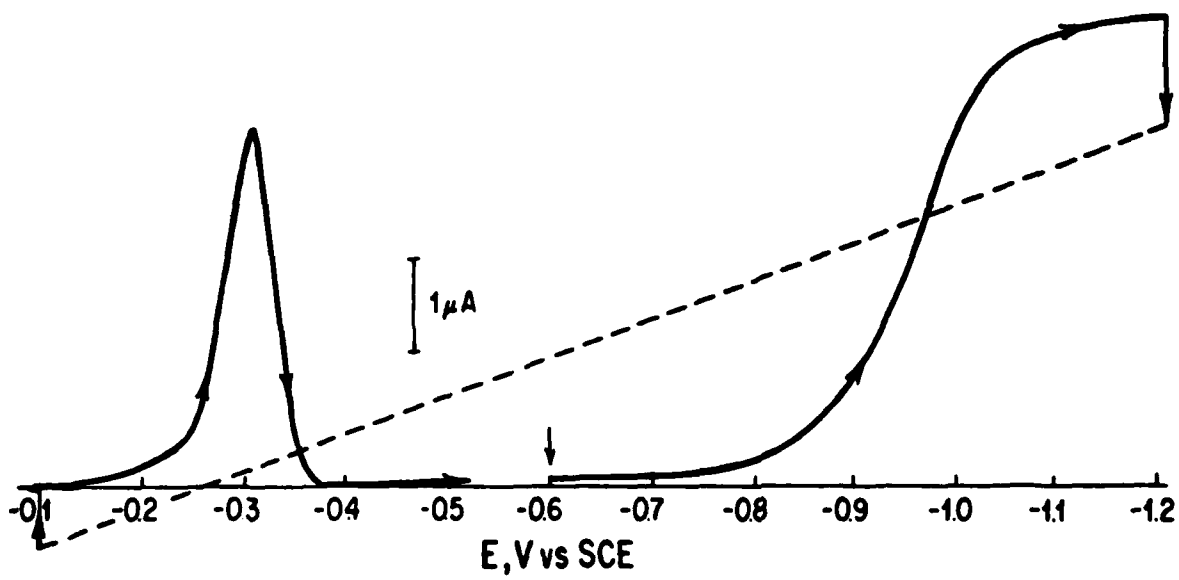


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