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Polarography of Dialkylthallium(III) Compounds. I. Polarography of Dibutylthallium(III) Compounds

Teisuke MURAYAMA and Kenji KIKUCHI

Department of Industrial Chemistry, Faculty of Engineering, Shizuoka University, Johoku, Hamamatsu 432

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Electrochemical reduction of three dibutylthallium(III) cations has been studied through the use of polarographic methods. Reduction at a dropping mercury electrode occurs in two steps for the di-*n*-butylthallium (DNBT) and diisobutylthallium (DIBT) cations in alkaline solutions, and for the di-*sec*-butylthallium (DSBT) cation in all pH ranges examined. The first and second waves of the DSBT cation in alkaline solutions correspond to, respectively, no-proton one-electron and two-proton two-electron processes. The DNBT and DIBT cations produce a single wave in acid solutions, consuming two protons and three electrons. On polarograms recorded with Kalousek's switching circuit a product and two kinds of intermediates were observed for the reduction of the DNBT and DIBT cations, and a product and one kind of intermediate for the reduction of the DSBT cation. A reaction scheme is proposed for the polarographic reduction of dibutylthallium cations.

Several authors have reported on the polarographic reduction of dialkyl- and diarylthallium(III) compounds. Costa studied di-*n*-alkylthallium bromides in an aqueous propanol solution,[1] and observed three waves of approximately equal heights for dipropyl- and dibutylthallium bromides. He attributed the first wave to Reaction (1) or (2), and the third to a reaction leading to the production of metallic thallium.

$$R_2Tl^+ + e \longrightarrow R_2Tl\cdot \qquad (1)$$

$$2R_2Tl^+ + 2e \longrightarrow R_2Tl\text{-}TlR_2 \qquad (2)$$

DiGregorio and Morris observed three waves for the diphenylthallium cation in aqueous solutions, and proposed a reduction mechanism including transmetallation with the electrode mercury.[2] Issleib *et al.* investigated five di-*n*-alkylthallium bromides in aqueous buffer solutions and dimethylformamide.[3] They obtained single waves in aqueous solutions with pH values below 7, and double waves in solutions with pH values above 7. The single step reduction was interpreted by them as follows.

$$R_2Tl^+ + e \longrightarrow R_2Tl\cdot \qquad (1)$$

$$3R_2Tl\cdot \longrightarrow 2R_3Tl + Tl(Hg) \qquad (3)$$

$$R_3Tl + H^+ \longrightarrow R_2Tl^+ + RH \qquad (4)$$

Results of our investigation on dialkylthallium compounds indicate that the real electrode process should be more complex than any of the above-mentioned mechanisms. The present paper reports polarographic behavior of di-*n*-butyl-, diisobutyl-, and di-*sec*-butylthallium compounds. (Hereafter these are denoted as DNBT, DIBT, and DSBT compounds, respectively.) Molar conductivity data show that dimethyl, diethyl-, and diphenylthallium hydroxides are strong electrolytes.[4] By analogy dibutyl compounds may be regarded as strong electrolytes. Hence, this paper deals with the polarography of DNBT, DIBT, and DSBT cations.

Experimental

Dibutylthallium(III) chlorides were prepared by the reaction of organomagnesium compounds with thallium trichloride as described in the literature.[5] Diethyl ether was used as alkylation solvent in the preparation of DNBT chloride, but was replaced with tetrahydrofuran in the preparation of DIBT and DSBT chlorides. Nitrates were prepared from the chlorides and silver nitrate, and recrystallized three times from aqueous methanol solution. The thallium content of the products was assayed by Goddard's method.[6] Tl %: DNBT nitrate, 52.9; DIBT nitrate, 53.1; DSBT nitrate, 53.0; Calcd., 53.7. Stock solutions of dibutylthallium nitrates were made by dissolving weighed amounts.

Supporting electrolytes used were a mixture of 0.02 M sulfuric acid and 0.15 M sodium sulfate (pH 2.01), acetate buffers (pH 3.94—5.95), phosphate buffers (pH 6.34—7.64), and ammonia buffers (pH 8.71—10.16). The ionic strength of the test solutions was controlled to 0.5 with sodium sulfate by reason of solubility of dibutylthallium salts. Gelatin was used as maximum suppressor.

All solutions were prepared with redistilled water.

Test solutions were degassed with nitrogen and thermostated at 25.0±0.1 °C.

The dropping mercury electrode (DME) had the following characteristics (in 0.17 M sodium sulfate solution at zero applied potential *vs.* SCE and at mercury pressure of 800 mm): rate of flow of mercury (m), 1.401 mg/s; drop time (τ), 4.96 s; $m^{2/3}\,\tau^{1/6} = 1.64$.

The cell used was of a beaker type with a Hume and Harris type salt bridge.[7] The original design of the bridge uses an intermediate agar plug saturated with potassium chloride, of which contamination causes precipitation of dibutylthallium chloride from the test solution. To avoid this difficulty the agar plug was prepared with 1 M potassium nitrate, and its nitrate ions were replaced by sulfate ions by standing the plug in a saturated potassium sulfate solution.

DC polarograms were obtained with a Yanagimoto PB-105 polarograph operated manually. The bridge of the instrument was calibrated by a precise potentiometer. All potentials were corrected for the internal resistance (*iR* drop) across the cell. A simple switching circuit was used in place of Kalousek's commutator.[8] AC polarograms were recorded with a Yanagimoto PA-102 polarograph. To minimize cell impedance, the AC voltage was applied through an auxiliary platinum electrode which connected with an SCE and the positive terminal of the polarograph through a 300 μF capacitor. Coulometry was accomplished according to the method proposed by De Vries and Kroon.[9]

Results and Discussion

DC polarograms of dibutylthallium compounds exhibit slight but persistent maxima. It needed 0.05%

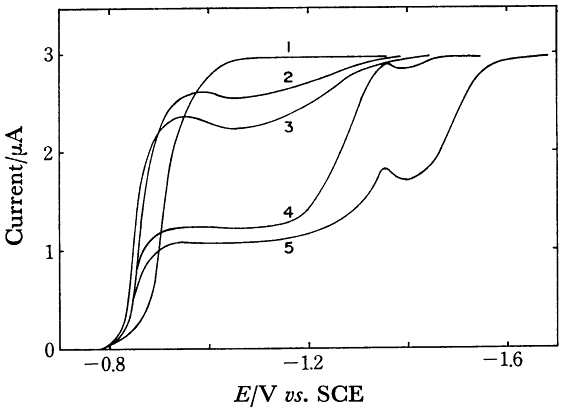

Fig. 1. Polarograms of DNBT nitrate. Concentration of DNBT nitrate, 0.410 mM. pH: 1, 5.20; 2, 6.99; 3, 7.64; 4, 8.71; 5, 10.16.

Table 1. Variation of the half-wave potential of DNBT nitrate with concentration and mercury pressure

pH	$C^{a)}$ (mM)	$h_{Hg}^{b)}$ (mm)	$-E_{1/2}^{c)}$ vs. SCE (V)
5.20	0.205	800	0.925
	0.307	800	0.917
	0.410	400	0.909
	0.410	500	0.911
	0.410	600	0.912
	0.410	700	0.913
	0.410	800	0.914
	0.410	900	0.917
	0.614	800	0.903
9.58	0.102	800	0.880
	0.205	800	0.860
	0.307	800	0.852
	0.410	800	0.844
	0.614	800	0.837

a) Concentration of DNBT nitrate. b) Height of mercury column. c) Since the second wave was accompanied by a maximum, only the half-wave potential of the first wave is shown.

gelatin to suppress them. Accordingly all polarograms shown in the present paper were measured in the presence of 0.05% gelatin. The polarographic behavior of DNBT nitrate is illustrated in Fig. 1. The compound shows a reduction wave with the half-wave potential of *ca.* −0.91 V *vs.* SCE in the range of pH 3—6. The half-wave potential changes by varying concentration of DNBT nitrate as shown in Table 1. This indicates that the reversible electron transfer step is followed by a multimolecular reaction. When the pH increases above 6, the half-wave potential shifts to positive and the rising part of the wave becomes steeper. This behavior is unlike that observed for other organic compounds. It implies that a species of which existence is favorable in acid solutions hinders the easiest reaction route, and that the reduction takes place through a route with higher energy as the pH is lowered below the optimum value.

The wave splits into two at about pH 7 when the pH is increased. Although the total height of waves remains unchanged the height of the first wave decreases with increasing pH, and at pH 10 it becomes almost a third of the wave height in acid solutions. The second wave is accompanied by a maximum, even in the presence of 0.05% gelatin. The wave height in acid solutions and the total wave height in neutral and alkaline solutions increase in proportion to the concentration of DNBT nitrate and to the square root of the height of mercury column. This indicates that the limiting currents are controlled by diffusion. The variation of the half-wave potential with the mercury pressure is included in Table 1.

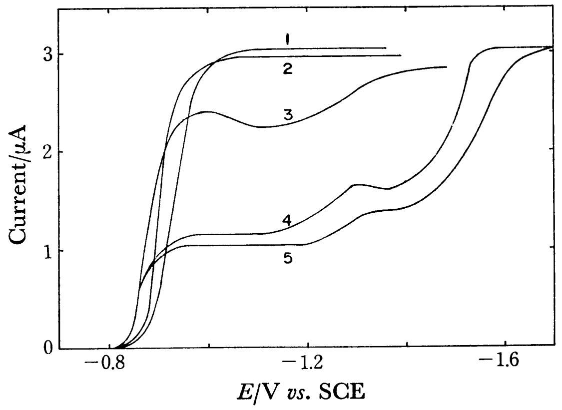

Fig. 2. Polarograms of DIBT nitrate. Concentration of DIBT nitrate, 0.421 mM. pH: 1, 4.56; 2, 6.34; 3, 7.64; 4, 8.71; 5, 10.16.

Table 2. Variation of the half-wave potential of DIBT nitrate with concentration and mercury pressure

pH	$C^{a)}$ (mM)	$h_{Hg}^{b)}$ (mm)	$-E_{1/2}^{c)}$ vs. SCE (V)
5.20	0.103	800	0.983
	0.206	800	0.966
	0.309	800	0.945
	0.412	400	0.917
	0.412	500	0.918
	0.412	600	0.919
	0.412	700	0.920
	0.412	800	0.921
	0.412	900	0.923
9.58	0.103	800	0.902
	0.206	800	0.880
	0.309	800	0.870
	0.412	800	0.864
	0.618	800	0.846

a) Concentration of DIBT nitrate. b) Height of mercury column. c) Since the second wave was accompanied by a maximum, only the half-wave potential of the first wave is shown.

The behavior of DIBT nitrate is much the same as that of DNBT nitrate. Figure 2 shows typical polarograms of the compound, and Table 2 the variation of the half-wave potential.

Figure 3 shows polarograms of DSBT nitrate, which undergoes a two-step reduction in all pH ranges examined. While the half-wave potential of the first

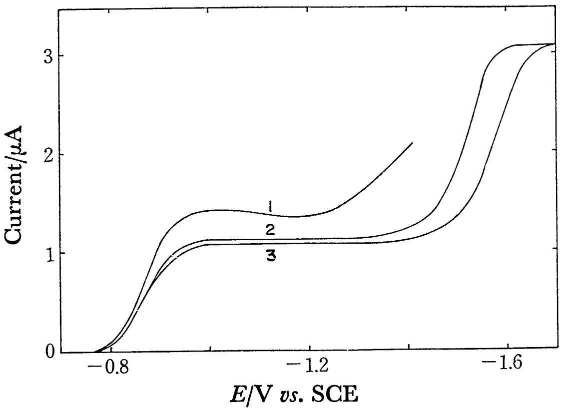

Fig. 3. Polarograms of DSBT nitrate. Concentration of DSBT nitrate, 0.424 mM. pH: 1, 3.94 (the second wave is overlapped by the hydrogen wave); 2, 8.71; 3, 10.16.

wave does not change to any noticeable extent, its limiting current decreases as much as a fifth of the wave height at pH 4 as the pH increases from 4 to 8.7. Further increase of pH, however, does not produce any appreciable change on the wave height. The limiting current of the first wave and the total wave height in alkaline solutions are in proportion to the concentration of DSBT nitrate and to the square root of the height of mercury column. This implies that the limiting currents of the first and second waves are diffusion currents. Table 3 shows the variation of the half-wave potential.

Table 3. Variation of the half-wave potential of DSBT nitrate with concentration

pH	$C^{a)}$ (mM)	$-E_{1/2}{}^{b)}$ vs. SCE (V)
5.20	0.106	0.878
	0.212	0.878
	0.318	0.874
	0.424	0.870
	0.636	0.874
9.58	0.106	0.872
	0.212	0.866
	0.318	0.865
	0.424	0.860
	0.636	0.858

a) Concentration of DSBT nitrate. b) Since the second wave was not well-defined, only the half-wave potential of the first wave is shown. The height of mercury column was 800 mm.

Electrocapillary curves of DNBT, DIBT, and DSBT nitrates indicate that these compounds are not adsorbed to any appreciable extent on the surface of DME.

The pH dependency of the polarograms suggests that hydrogen ions participate in the electrode processes. Amperometric titrations were carried out to establish the relation between the number of hydrogen ions and the number of electrons consumed in the electrode reaction. Figure 4 shows the change of the polarogram of DNBT nitrate during the titration with 2.02 mM sulfuric acid. The supporting electrolyte is 0.167 M sodium sulfate. The current at potentials corresponding to the limiting current region of the second wave remains unchanged until the concentration of hydrogen ions reaches a certain value, then increases from there on. The titration curve is shown in Fig. 5, where the current is measured at a potential of the limiting current region of the second wave. A similar change in the polarogram was observed for DIBT nitrate.

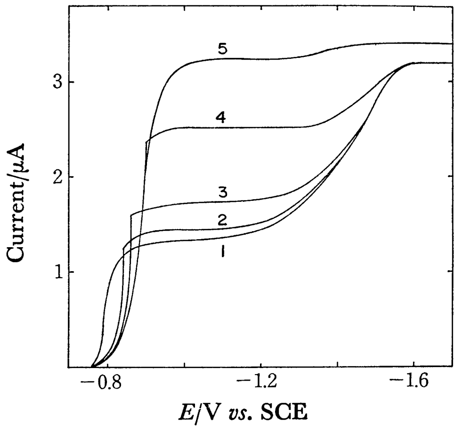

Fig. 4. Variation of the polarogram of DNBT nitrate during the titration with 2.02 mM sulfuric acid. The current was corrected for volume change. Original concentration of DNBT nitrate, 0.410 mM. Original volume of the solution, 25 ml. Supporting electrolyte, 0.167 M sodium sulfate. Volume of sulfuric acid, added: 1, 0 ml; 2, 0.5 ml; 3, 1.0 ml; 4, 2.0 ml; 5, 3.1 ml.

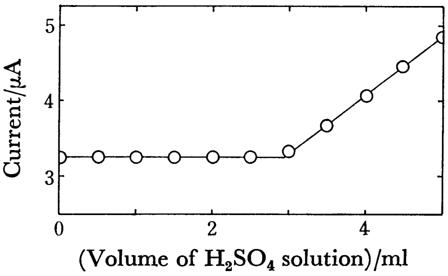

Fig. 5. Amperometric titration curve of 25 ml of 0.410 mM DNBT nitrate with 2.02 mM sulfuric acid. Titrated at −1.60 V vs. SCE.

When DSBT nitrate was titrated by the acid, the height of the first wave increased a little (by about a fourth of the initial height) at first and then remained unchanged, unlike that of the first wave of DNBT and DIBT nitrates. The hydrogen wave appeared at potentials between the first and second waves, and grew with increasing concentration of hydrogen ions, consuming the second wave. The titration curve is given in Fig. 6, where the current is measured at a potential of the limiting current region of the second wave.

The concentration of hydrogen ions at the end point, C_h, is related with the concentration of the dibutylthallium compound, C, by

$$I_hC_h = \frac{n_h}{n}IC \qquad (5)$$

where I is the diffusion current constant of the dibutylthallium compound, I_h the diffusion current constant of hydrogen ions, n the number of electrons involved in the electrode process, and n_h the number of hydrogen

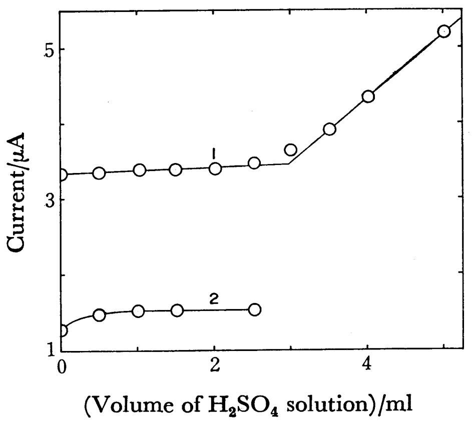

Fig. 6. Amperometric titration curves of 25 ml of 0.424 mM DSBT nitrate with 2.02 mM sulfuric acid. Curve 1, titrated at −1.80 V *vs.* SCE, of which potential lies in the limiting current region of the second wave. Curve 2, titrated at −1.10 V *vs.* SCE, of which potential lies in the limiting current region of the first wave.

ions consumed.[10] Values of the ratio n_h/n, calculated with Eq. (5) from observed values, are: 0.6_9 for DNBT nitrate, 0.6_9 for DIBT nitrate, and 0.7_2 for DSBT nitrate.

Coulometry was used for determination of the n value of DNBT nitrate reduction. The supporting electrolyte used is a mixture of 0.09 M sodium chloride and 0.01 M hydrochloric acid, where DNBT nitrate undergoes the single step reduction. A value of $n=3.0_2$ was obtained for the reduction. The n values of other reduction waves were estimated by comparison of the respective diffusion currents with the limiting current of DNBT nitrate in acid solutions.

Based on values of n and n_h/n, it was concluded that single step reductions of DNBT and DIBT nitrates in acid solutions are two-proton three-electron processes. The same reasoning was applied to the two-step reduction of DSBT nitrate. Besides, the inspection of the behavior of the first and second waves during the titration with sulfuric acid revealed that in unbuffered solutions all hydrogen ions are consumed by the electrode reaction of the second wave except a quite small fraction to be consumed by that of the first wave. Taking this and the change of height of the first wave with pH into consideration, it was concluded that the first and second waves of DSBT nitrate in alkaline solutions correspond to, respectively, no-proton one-electron and two-proton two-electron processes. In acid and neutral solutions a proton-consuming reaction proceeds to some extent at potentials of the first wave.

Figure 7 shows polarograms of DNBT nitrate recorded with Kalousek's circuit. This compound in acid solutions gives an only anodic wave at −0.4 V *vs.* SCE, of which the potential coincides with that of the anodic wave of thallium amalgam. Hence, thallium amalgam is one of the reduction products of DNBT nitrate in acid solutions where the single wave is observed on the DC polarogram. The DC polarographic wave splits into two at about pH 7 as the pH increases. Three anodic waves appear in the solution of pH 6.99 when the constant auxiliary potential (CAP) is controlled to be equal to a potential in the limiting current region of the first wave on the DC polarogram. The first and third anodic waves (counting from negative potentials to positive) decrease in height and disappear as the CAP successively becomes more negative. The second anodic wave is the dissolution wave of thallium amalgam. At pH 9.58 DNBT nitrate produces two anodic waves, namely, the first and second waves, the former disappearing with negative shift of the CAP to a potential corresponding to the limiting current region of the second wave on the DC polarogram.

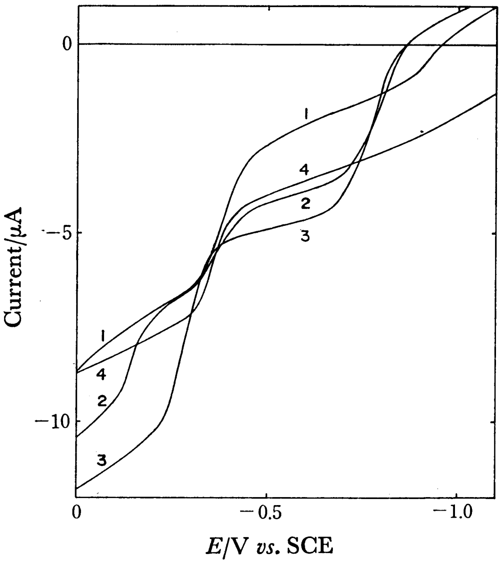

Fig. 7. Polarograms of DNBT nitrate recorded with Kalousek's circuit. Concentration of DNBT nitrate, 0.410 mM. pH and CAP (V *vs.* SCE), respectively: 1, 5.20 and −1.25; 2, 6.99 and −1.05; 3, 9.58 and −1.05; 4, 9.58 and −1.65.

DIBT nitrate produced similar polarograms when they were recorded with Kalousek's circuit.

Figure 8 shows polarograms of DSBT nitrate recorded

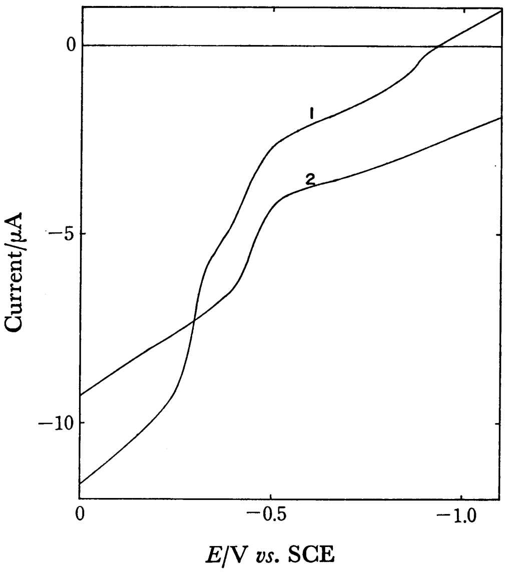

Fig. 8. Polarograms of DSBT nitrate recorded with Kalousek's circiut. Concentration of DSBT nitrate, 0.424 mM. pH and CAP (V *vs.* SCE), respectively: 1, 9.58 and −1.00; 2, 9.58 and −1.70.

with Kalousek's circuit. This compound gives two waves on the DC polarogram in all pH ranges examined. When the CAP is controlled to be equal to a potential in the limiting current region of the first wave on the DC polarogram, the compound produces two anodic waves: the dissolution wave of thallium amalgam and a wave which appears at more positive potentials and disappears with negative shift of the CAP.

The behavior of the anodic waves clearly indicates that at least two kinds of intermediates are involved in the reduction of DNBT and DIBT nitrates: one which produces the first anodic wave and of which formation does not require hydrogen ions, and the other which produces the third anodic wave and of which formation requires hydrogen ions. While the former also takes part in the reduction of DSBT nitrate (and produces the second anodic wave of this compound), participation of the latter was not proved experimentally. These conclusions were confirmed by comparison of the polarograms, recorded with Kalousek's circuit, of the three dibutylthallium nitrates in 0.167 M sodium sulfate with and without addition of sulfuric acid.

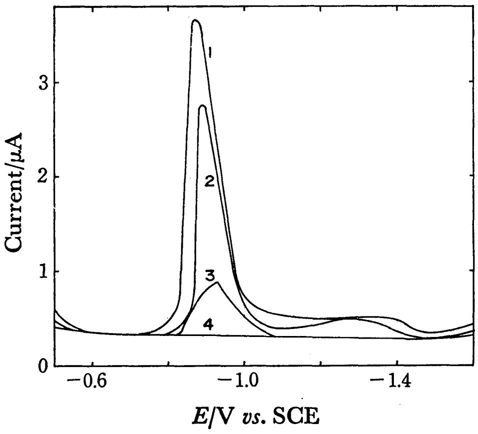

Fig. 9. AC polarograms of dibutylthallium nitrates in 0.1 M sodium hydroxide. Ionic strength was controlled to 0.5 with sodium sulfate. Curve 1, 0.410 mM DNBT nitrate; Curve 2, 0.421 mM DIBT nitrate; Curve 3, 0.424 mM DSBT nitrate; Curve 4, supporting electrolyte only.

Figure 9 shows AC polarograms of dibutylthallium nitrates in 0.1 M sodium hydroxide. It indicates that the electrode process of the first wave is most reversible for DNBT nitrate and least for DSBT nitrate. The peak heights decrease with increasing concentration of hydrogen ions, except that the peak height of DSBT nitrate does not change to any noticeable extent.

Mechanisms so far presented are not adequate enough to explain the results described above.[1-3] The following reaction scheme, accordingly, is proposed tentatively for the polarographic reduction of dibutylthallium compounds:

$$\mathrm{Bu_2Tl^+ + e \rightleftarrows Bu_2Tl} \tag{6}$$

$$\mathrm{Bu_2Tl + H^+ \rightleftarrows Bu_2TlH^+} \tag{7}$$

$$\mathrm{2Bu_2TlH^+ \longrightarrow Bu_2Tl^+ + Tl^+ + 2BuH} \tag{8}$$

$$\mathrm{Tl^+ + e \rightleftarrows Tl(Hg)} \tag{9}$$

$$\mathrm{Bu_2TlH^+ + Bu_2Tl \rightleftarrows Bu_2Tl^+ + Bu_2TlH} \tag{10}$$

$$\mathrm{Bu_2TlH + H^+ + e \longrightarrow Tl(Hg) + 2BuH} \tag{11}$$

$$\mathrm{Bu_2Tl + Hg \longrightarrow Tl(Hg) + Bu_2Hg} \tag{12}$$

$$\mathrm{Bu_2Tl + 2e \longrightarrow Tl(Hg) + 2Bu^-} \tag{13}$$

$$\mathrm{Bu^- + H_2O \rightleftarrows BuH + OH^-} \tag{14}$$

In the above scheme a sequence of Reactions (6)–(7)–(8)–(9) explains the single wave of DNBT and DIBT nitrates in solutions having pH values below 6. The regenerated ion $\mathrm{Bu_2Tl^+}$ in Reaction (8) again enters the sequence at Reaction (6). For the species $\mathrm{Bu_2TlH^+}$ it should be noted that the $\mathrm{Tl\text{-}H^+}$ bond is a one-electron bond. With increase of pH another sequence of Reactions (6)–(7)–(10)–(11) becomes favorable, and is responsible for the positive shift of the wave with increase of pH in neutral solutions. Further increase of pH, however, decreases the height of the wave by making Reaction (7) difficult to proceed. The $\mathrm{Bu_2Tl}$ molecules that are not consumed by the reaction with $\mathrm{Bu_2TlH^+}$ ions undergo transmetallation with the electrode mercury as given in Reaction (12). A two-electron reduction of the molecule is also possible by negative increase of the potential of DME. This results in a sequence Reaction (13)–(14), which corresponds to the second wave. The species $\mathrm{Bu_2Tl}$ and $\mathrm{Bu_2TlH}$ (or $\mathrm{Bu_2TlH^+}$) are responsible for, respectively, the first and third anodic waves on the polarogram recorded with Kalousek's circuit.

The equilibrium constant of Reaction (7) in the reduction of DSBT nitrate does not seem to be as large as that in the reduction of DNBT and DIBT nitrates, since DSBT nitrate gives the double wave in all pH ranges examined.

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