# *Polarographic Studies of Some Organo-sulfur Compounds. I. A. C. and D. C. Polarography of Potassium Thiobenzoate*

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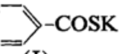
A number of the polarographic investigations of various organo-sulfur compounds have been reported. Especially thiol-type compounds such as cysteine[1] and glutathion[2] have been studied in detail, related to their reduction-oxidation systems.

Thiobenzoyl type sulfur compounds, however, have not been studied polarographically.

In this paper, the polarographic behaviors of potassium thiobenzoate (I), will be reported.



(I)

## Experiments and Results

The polarograph used was the Yanagimoto model PA-102 [D.C. & A.C. (superimposed with sinusoidal A.C. of 50 c.p.s. in frequency and of 15 mV. r.m.s. in amplitude)]. The characteristics of the dropping mercury electrode used were: $m=0.986$ mg. sec$^{-1}$, $t=4.74$ sec. (open circuit).

Synthesized pure potassium thiobenzoate (PTB) was used and its purity was tested by iodometric titration and microanalysis. All other reagents were of reagent grade.

Experiments were carried out 2 or 3 times on the same kind of sample at 25°C and the values obtained were averaged in general. The values of potentials were expressed in V. vs. S. C. E. and of currents in $\mu$℧ or in $\mu$A.

**The Influences of pH to the Limiting Currents $i_l$, the Peak Currents $i_s$ and to the Half-wave Potentials $E_{1/2}$, the Summit Potentials $E_s$.**—In the buffer solutions of pH 1.5~12.0, PTB showed three oxidation waves; some of them are shown in Fig. 1.

The relationships of pH to $i_l$, $i_s$ and $E_{1/2}$, $E_s$ are shown in Table I, Figs. 2 and 3.

The first wave had a half-wave potential very close to the second, while the third occurred at more negative potentials.

The D. C. wave heights of the 1st and the 2nd waves were both independent of pH, but the 3rd

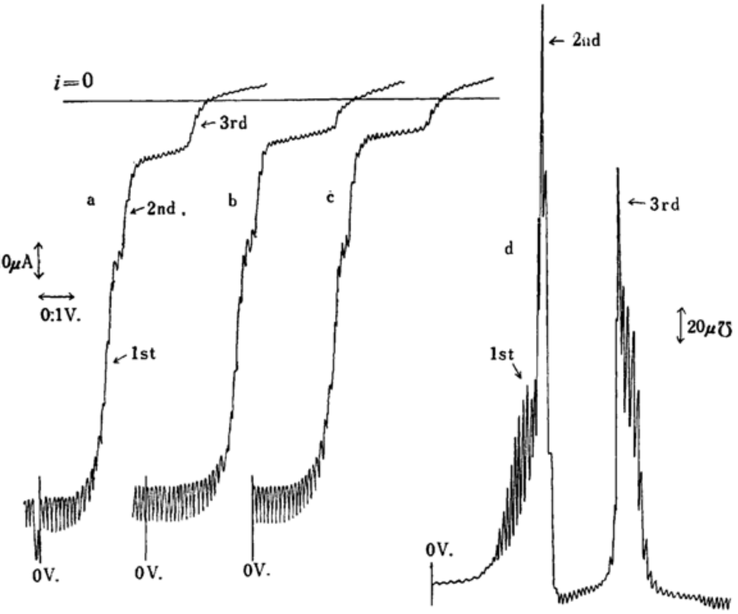


Fig. 1. Typical polarograms of PTB. a: D. C. pH=1.5, b: D. C. pH=5.0, c: D. C. pH=10.0, d: A. C. pH=10.0, [PTB]=$0.5\times10^{-3}$ mol./l., at 25°C. The solutions were air-free. Damping (D. C.)=50$\mu$F, capacitance (A. C.)=0$\mu$F.

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[1] I. M. Kolthoff and J. J. Lingane, "Polarography", Interscience Publishers, New York (1952), p. 779.

[2] I. Tachi et al., *J. Agr. Chem. Soc. Japan* (*Nippon Nogei-Kagaku Kaishi*), 25, 278, 281, 325 (1952).

TABLE I. THE VARIATION OF $i_l$, $i_s$ and $E_s$, $E_{1/2}$ WITH pH
[PTB] = $0.5\times10^{-3}$ mol./l., measured at 25°C

| pH | Buffer | $i_l$, μA | | | $i_s$, μ℧ | | | $-E_{1/2}$, V. vs. S. C. E. | | | $-E_s$, V. vs. S. C. E. | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | $i_l^1$ | $i_l^2$ | $i_l^3$ | $i_s^1$ | $i_s^2$ | $i_s^3$ | $E_{1/2}^1$ | $E_{1/2}^2$ | $E_{1/2}^3$ | $E_s^1$ | $E_s^2$ | $E_s^3$ |
| 1.5 | A | 0.730 | 0.283 | 0.139 | 128 | 313 | 309 | 0.188 | 0.256 | 0.435 | 0.215 | 0.260 | 0.434 |
| 2.5 | A | 0.725 | 0.285 | 0.113 | 112 | 298 | 283 | 0.219 | 0.291 | 0.487 | 0.241 | 0.291 | 0.489 |
| 3.2 | B | 0.723 | 0.289 | 0.100 | 106 | 285 | 266 | 0.235 | 0.300 | 0.520 | 0.255 | 0.310 | 0.526 |
| 4.0 | B | 0.730 | 0.291 | 0.090 | 109 | 295 | 266 | 0.243 | 0.308 | 0.534 | 0.257 | 0.309 | 0.526 |
| 5.0 | B | 0.728 | 0.290 | 0.085 | 114 | 310 | 261 | 0.250 | 0.320 | 0.542 | 0.258 | 0.305 | 0.525 |
| 6.0 | C | 0.727 | 0.298 | 0.090 | 114 | 305 | 247 | 0.250 | 0.314 | 0.536 | 0.258 | 0.305 | 0.526 |
| 7.5 | C | 0.737 | 0.291 | 0.090 | 113 | 303 | 260 | 0.250 | 0.314 | 0.533 | 0.258 | 0.307 | 0.526 |
| 9.0 | D | 0.738 | 0.290 | 0.098 | 114 | 292 | 237 | 0.250 | 0.312 | 0.524 | 0.259 | 0.308 | 0.529 |
| 10.0 | E | 0.741 | 0.291 | 0.100 | 113 | 290 | 244 | 0.250 | 0.310 | 0.516 | 0.258 | 0.310 | 0.529 |
| 12.0 | E | 0.735 | 0.299 | 0.100 | 111 | 295 | 240 | 0.250 | 0.309 | 0.519 | 0.258 | 0.312 | 0.528 |

A: 0.1 M $CH_3COOH$-$HCl$, B: 0.1 M $CH_3COOH$-$CH_3COONa$, C: 0.1 M $KH_2PO_4$-$Na_2HPO_4$,
D: 0.1 M $Na_2B_4O_7$-$HCl$, E: 0.1 M $Na_2B_4O_7$-$NaOH$.

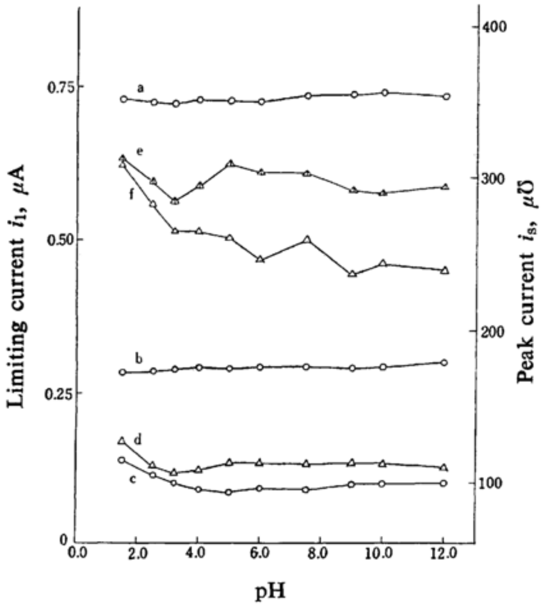


Fig. 2. The relation of $i_s$ and $i_l$ to pH.
a: D. C. 1st wave d: A. C. 1st wave
b: D. C. 2nd wave e: A. C. 2nd wave
c: D. C. 3rd wave f: A. C. 3rd wave
[PTB] = $0.5\times10^{-3}$ mol./l., at 25°C

seemed to be fairly affected with pH in very acidic solutions.

In A. C. polarography, the 2nd and the 3rd waves showed very large peak current in comparison with the 1st; the pH-dependence of them, however, was almost the same as that of the D. C. waves.

As shown in Fig. 3, the negative shift of $E_{1/2}$ and $E_s$ of 1st and 2nd waves with pH increase was observed in more acidic conditions than pH 3.5 and in the more basic region they were both independent of pH.

A theoretical equation[2] of the reversible oxidation wave of sulfhydryl compounds to the corresponding disulfides was expressed in Eq. 1;

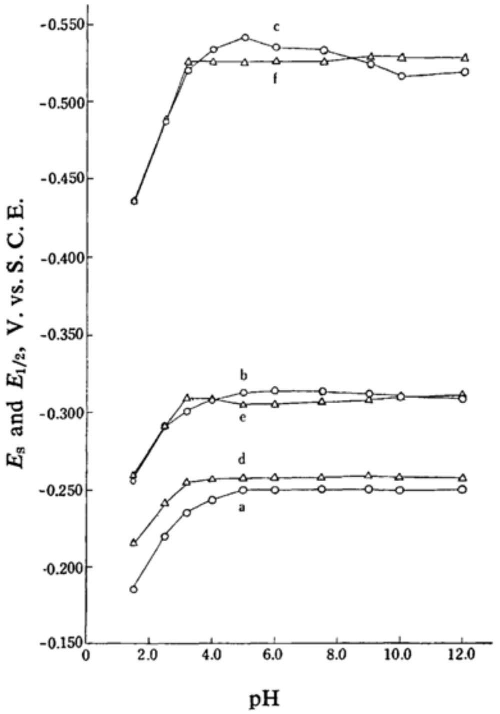


Fig. 3. The relation of $E_s$ and $E_{1/2}$ to pH.
a, b, c: D. C. 1st, 2nd and 3rd wave respectively
d, e, f: A. C. 1st, 2nd and 3rd wave respectively
[PTB] = $0.5\times10^{-3}$ mol./l., at 25°C.

$$E=E_0+(\boldsymbol{RT}/\boldsymbol{F})\ln[\mathrm{H}^+]-(\boldsymbol{RT}/2\boldsymbol{F})\ln(i_\mathrm{d}-i)^2/i+(\boldsymbol{RT}/2\boldsymbol{F})\ln(K\mathrm{D}_\mathrm{red}/2\mathrm{D}_\mathrm{ox}^{1/2}) \tag{1}$$

then half-wave potential $E_{1/2}$ was in Eq. 2;

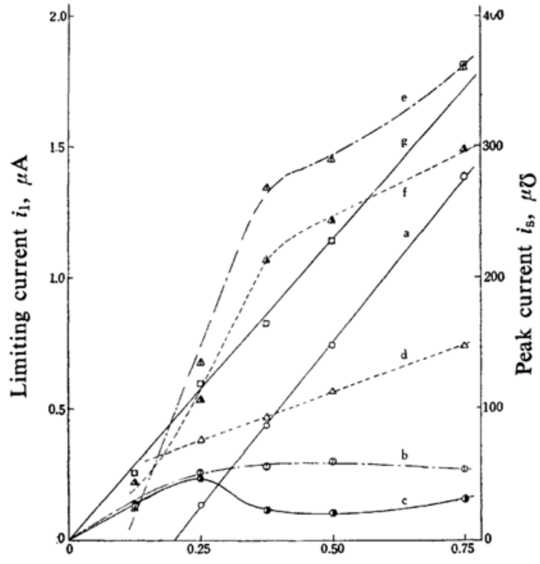
$$E_{1/2}=E_0+(\boldsymbol{RT}/\boldsymbol{F})\ln[\mathrm{H}^+]-(\boldsymbol{RT}/2\boldsymbol{F})\ln(i_\mathrm{d}/2+(\boldsymbol{RT}/2\boldsymbol{F})\ln(K\mathrm{D}_\mathrm{red}/2\mathrm{D}_\mathrm{ox}^{1/2}) \tag{2}$$

where $K$ is a dissociation constant.

According to Eq. 2, under the conditions of constant concentration and moreover of $[H^+] \gg K$, the half-wave potential may shift to more negative potentials, but of $[H^+] \ll K$, it may be independent of pH values.

It was found that the relations shown in Fig. 3 almost completely followed Eq. 2. $K$ of PTB obtained from Fig. 3 was approximately 3.5.

In neutral buffer solutions, the solutions of PTB often came to be turbid and in acidic solutions (pH<4), A. C. polarograms had complicated forms, therefore the following experiments were carried out in basic buffer solution of pH 10.0 (0.1 M borate buffer).



Concentration, $\times 10^{-3}$ mol./l.

Fig. 4. The relation of $i_s$ and $i_l$ to the concentration.

a, b, c: D. C. 1st, 2nd and 3rd wave respectively

d, e, f: A. C. 1st, 2nd and 3rd wave respectively

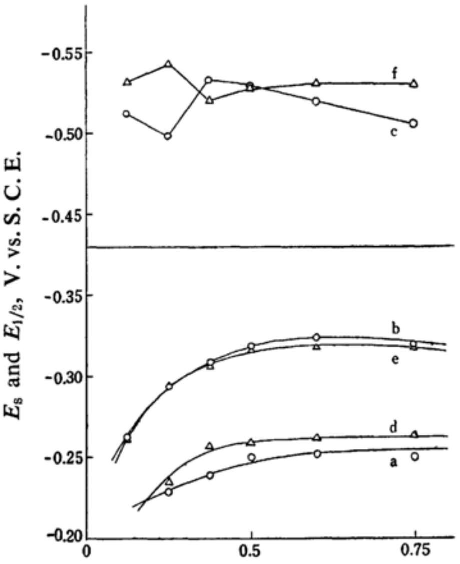
g: D. C. total wave (1st+2nd+3rd)

Supporting electrolyte is 0.1 M borate buffer pH 10.0.

**The Relations of the Concentrations of PTB to $i_l$, $i_s$ and $E_{1/2}$, $E_s$.**—In the cases where there was diffusion or kinetic currents, good linearity was generally found between concentrations and wave heights. A linear relation was observed for the 1st wave, but it did not pass the zero point. Better linearity was found for the total wave as shown in Fig. 4.

Saturation phenomena were found for the 2nd and the 3rd waves of both D. C. and A. C. polarograms.

The relations between $E_{1/2}$, $E_s$ and $C$ were shown in Fig. 5. A negative shift of $E_{1/2}$ and $E_s$ of the 1st and 2nd waves was observed, while the 3rd seemed to be independent of the concentrations.



Concentration, $\times 10^{-3}$ mol./l.

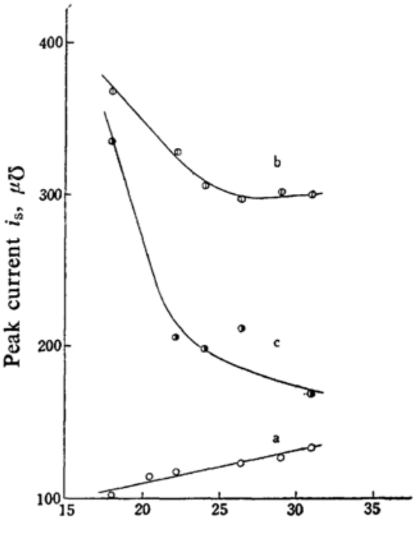
Fig. 5. The relation of $E_{1/2}$ and $E_s$ to the concentrations.

a, b, c: D. C. 1st, 2nd and 3rd wave respectively

d, e, f: A. C. 1st, 2nd and 3rd wave respectively

Supporting electrolyte is 0.1 M borate buffer pH 10.0.

In Eq. 2, it was shown that at constant pH, the half-wave potentials may shift to more negative potentials with concentration increase. The behaviors of the 1st and the 2nd waves seemed to coincide approximately with the theory.



Temp., °C

Fig. 6. The relation of $i_s$ to temperature.
a: 1st, b: 2nd, c: 3rd wave.
[PTB]=$0.5 \times 10^{-3}$ mol./l. in 0.1 M borate buffer pH 10.0.

**The Influences of Temperature upon $i_1$, $i_s$ and $E_{1/2}$, $E_s$.**—Very different results were obtained in D. C. and A. C. polarograms. In D. C., all temperature coefficients of the first, the 2nd and the 3rd were 2.15, 0.74 and 3.51% respectively, but in A. C., only the 1st had the positive coefficient of 1.94% and the others showed negative values as shown in Fig. 6.

It could be known that the 2nd and the 3rd waves were tensammetric and the 1st was considered to contain partly the kinetics current.

As shown in Table II, both the A. C. and D. C. waves shifted to more positive potentials according to the rise of temperature.

TABLE II. THE VARIATIONS OF $E_{1/2}$ AND $E_s$ WITH TEMPERATURE

$[PTB]=0.5\times10^{-3}$ mol./l. in 0.1 M borate buffer pH 10.0

| Temp. °C | $-E_{1/2}$* | | | $-E_{1/2}$* | | |
|---|---|---|---|---|---|---|
| | $-E^1_{1/2}$ | $-E^2_{1/2}$ | $-E^3_{1/2}$ | $-E^1_s$ | $-E^2_s$ | $-E^3_s$ |
| 18.0 | 0.250 | 0.323 | 0.540 | 0.267 | 0.317 | 0.540 |
| 20.5 | — | — | — | 0.265 | 0.313 | 0.529 |
| 22.2 | 0.250 | 0.322 | 0.532 | 0.269 | 0.312 | 0.525 |
| 24.0 | 0.250 | 0.315 | 0.521 | 0.267 | 0.312 | 0.526 |
| 26.4 | 0.250 | 0.311 | 0.516 | 0.260 | 0.300 | 0.517 |
| 29.0 | 0.240 | 0.308 | 0.510 | 0.255 | 0.301 | 0.511 |
| 31.0 | 0.240 | 0.300 | 0.496 | 0.256 | 0.297 | 0.510 |

* V. vs. S. C. E.

**The Relation between the Mercury Reservoir Height $H$ and the Wave Height $i_1$ in D. C. Polarograms.** — Good linearities were obtained between $\log H$ (corrected with the reverse pressure, $3.1/(mt)^{1/3}$) and $\log i_1$. They could be written as follows:

$$\text{1st wave:} \quad i_1=H^{0.18}+K_1 \qquad \text{(I)}$$

$$\text{2nd wave:} \quad i_1=H^{0.64}+K_2 \qquad \text{(II)}$$

$$\text{3rd wave:} \quad i_1=H^{0.61}+K_3 \qquad \text{(III)}$$

$$\text{Total wave:} \quad i_1=H^{0.33}+K_4 \qquad \text{(IV)}$$

where $K_1, \cdots, K_4$ were constants.

It seemed that the 1st consisted of the two components; kinetic and diffusion currents and the two others, of diffusion and adsorption currents.

In the case of the complicated systems, the usual analysis of the relationship between $H$ and $i_1$, such as the plotting of $H^{1/2}$ against $i_1$ or $H$ against $i_1$, was considered to be less accurate than the method of the plotting of $\log H$ against $\log i_1$. In fact, the relation between $H$ or $H^{1/2}$ and $i_1$ both showed appearent linearities, so that no definite results could be obtained.

**Logarithmic Plotting.** — The relations between the applied potentials $E$ and $\log\{i/(i_d-i)\}$ and $\log\{i/(i_d-i)^2\}$ were investigated. Only the 1st wave showed good linearity of $RT/nF=28$ mV., if $E$ was plotted against $\log\{i/(i_d-i)^2\}$, the two others showed S-shaped curves, and the relations of $E$ to $\log\{i/(i_d-i)\}$ of each three waves were S-shaped too.

The 1st wave was considered to be two electrons oxidation producing one mole of the oxidation form from two moles of the reduced form.

**Electrocapillary Curve.**—When the adsorption or desorption of depolarizers takes place on the surface of D. M. E., some irregularities may be found in the electrocapillary curves.

As shown in Fig. 7, a remarkable irregularity was found from −0.65 up to 0 V. having a sharp minimum at −0.27 V.; this minimum corresponded to the 2nd wave approximately.

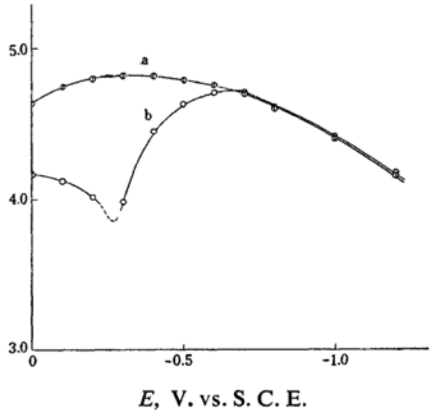


Fig. 7. Electrocapillary curves.
a: Reference pH 10.0, 0.1 M borate buffer.
b: 1 mM PTB in a.

**Polarograms Obtained with a Rotating Platinum Microelectrode.**—In order to know the real oxidation potential of PTB to the disulfide form, benzoyl disulfide, a platinum electrode was employed. The polarograms obtained are shown in Fig. 8. The

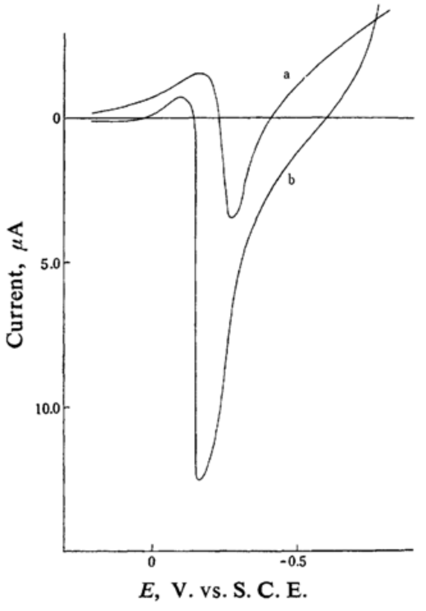


Fig. 8. Polarograms with a rotating platinum electrode. (1400 r. p. m., $\phi=0.8$ mm., $l=6$ mm. horizontal)
a: 0.5 mM, b: 1 mM PTB in a 0.1 M borate buffer (pH 10.0).

reproducibility and the reversibility of the waves, however, were inferior to those of D. M. E., but a notable peak at the potential of $-0.1\sim-0.3$ V. was recognized in every experiment.

This irreversible peak current was considered to be the oxidation wave of PTB to its disulfide, because the formations of mercury salts of PTB do not occur in the case of the oxidation reaction with Pt-electrode. It coincided with the oxidation waves obtained at D. M. E., therefore the oxidation which occurred at D. M. E. was thought to be the formation of disulfide.

## Discussion

The characteristics of the three oxidation waves of PTB are summarized as follows:

(1) The 1st wave is considered to be the diffusion current having the slight kinetic properties and to be two-electrons oxidation forming its disulfide.

(2) The 2nd and the 3rd waves are so-called tensammetric waves, owing to the adsorption or the desorption at the surface of D. M. E. and this adsorption is thought to continue during the applied potentials which change from $-0.65$ V. to more positive potentials beyond 0 V.

The oxidation of PTB takes place at $-0.5$ V. approximatly; then the adsorption of PTB to the surface of D.M.E. occurs continuously. The adsorbed PTB might be electro-inactive, so that the rise of the oxidation current is suppressed during the adsorption continuing down to $-0.3$ V. At the potential $-0.3$ V. PTB is desorbed and becomes electro-active again, therefore the oxidation current begins to increase.

The oxidation product of PTB also seems to be adsorptive to D. M. E., because the abnormal decrease of $t$ is observed at more positive potentials than $-0.3$ V. (Fig. 7).

Slight kinetic properties, described in previous sections, of the 1st wave are attributed to the continuous adsorption, desorption and oxidation of PTB and to the secondary adsorption of the oxidation product.

The whole oxidation process is expressed as follows:

$$2C_6H_5COS^- \rightleftarrows (C_6H_5COS)_2+2e$$

## Summary

The polarographically new sulfur compound, potassium thiobenzoate, was investigated, using A. C. and D. C. polarographs. Comparatively complicated three oxidation waves were observed in both polarograms.

According to the various investigations about the properties of these waves, it was found that the whole reaction was the oxidation of PTB to its disulfide, benzoyl disulfide. The 1st wave was mainly due to this oxidation reaction and the two others were mainly due to the adsorption and the desorption of PTB at the surface of D. M. E.

The reversible oxidation-reduction system consisting of PTB and benzoyl disulfide would not be expected owing to the adsorption and desorption processes that interfered with the normal oxidation of PTB to benzoyl disulfide, if the studies were done with a dropping mercury electrode.

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