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Cathodic Cleavage of Some Aryl Phenacyl Sulfides

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The electrolytic reduction of some aryl phenacyl sulfides in aqueous ethanol and anhydrous acetonitrile solutions has been investigated by means of polarography and controlled potential electrolysis. Dc polarograms of these compounds exhibit two waves in all solutions studied, the first of which corresponds to a one-electron and a two-electron transfer depending upon the absence and presence of proton donor. The electrode reaction taking place at the first reduction step involves cleavage of the carbon-sulfur bond, resulting in formation of acetophenone and the corresponding thiols in good yields even in an acetonitrile solution containing no proton donor. The second reduction step corresponds to the reduction of the acetophenone produced.

The electrolytic desulfurization of organosulfur compounds has attracted considerable attention because most of them are valuable synthetic precursors. β-Keto sulfoxides,[1–3] for instance, are electrochemically reduced by cleavage of a carbon-sulfur bond with formation of methyl ketones and thiol derivatives. The other organosulfur compounds such as β-hydroxy sulfones,[4,5] sulfoxides,[6] and sulfides,[7] vinyl sulfones,[8] sulfoxides,[9] and sulfides,[10] and alkyl imidazolyl sulfoxide[11] and sulfides[11,12] are also electrochemically reduced to afford the corresponding desulfurated compounds.

With the consumption of small quantities of electricity compared with the case of electrolytic reduction of β-keto sulfoxides, β-keto sulfides will be expected to undergo the cathodic cleavage of the carbon-sulfur bond to yield the desulfurated compound, methyl ketones. Therefore, it is considered of interest to investigate electrolytic reduction of β-keto sulfides from the standpoint of the conversion of carboxylic esters to the corresponding methyl ketones, which contain one more carbon atom than the starting esters:

$$\text{Ar-S-CH}_2^-\,\text{Li}^+ + \text{PhCO}_2\text{C}_2\text{H}_5 \longrightarrow \text{Ar-S-CH}_2\text{COPh}$$

$$\xrightarrow{\text{electrolysis}} \text{PhCOCH}_3 + \text{ArSH}$$

In the present work, the electrolytic reduction of some aryl phenacyl sulfoxides was investigated in both aqueous ethanol and anhydrous acetonitrile solutions by means of polarography, coulometry, and macroelectrolysis.

Experimental

Chemicals. Phenacyl p-tolyl sulfide (**1a**), phenacyl phenyl sulfide (**1b**), and p-methoxyphenyl phenacyl sulfide (**1c**) were prepared from the corresponding lithiomethyl aryl sulfides and ethyl benzoate on the basis of the procedure described for the synthesis of aryl phenacyl sulfoxides,[13] which were identified by their physical properties and ^{1}H NMR spectra.[14] **1a**; mp 32—34 °, NMR ($CDCl_3$) δ 2.29 (3H, s, -CH_3), 4.21 (2H, s, -CH_2-), 7.04—8.09 (9H, m, aromatic). **1b**; mp 51—52 ° (lit,[15] 52—53 °), NMR ($CDCl_3$) δ 4.24 (2H, s, -CH_2-), 7.14—7.99 (10H, m, aromatic). **1c**; NMR ($CDCl_3$) δ 3.73 (3H, s, CH_3O-), 4.14 (2H, s, -CH_2-), 6.77—8.07 (9H, m, aromatic).

The aqueous alcoholic buffer solutions contained 40% (v/v) ethanol and their ionic strengths were adjusted to 0.6 M (1 M=1 mol dm^{-3}) with KCl. All buffer compounds were of reagent grade. The pH reading was taken in the aqueous alcoholic buffer solutions with a pH-meter standardized against aqueous buffer solutions. A 95% (v/v) ethanol buffer solution of pH 5.8 contained 0.12 M lithiun acetate, 0.08 M acetic acid, and 0.5 M lithium chloride. Anhydrous acetonitrile solutions were prepared from the pre-deoxygenated acetonitrile (MeCN) and tetrabutylammonium perchlorate (TBAP) or tetrabutylammonium tetrafluoroborate (TBAB) which were purified and dried as described previously.[16] The concentrations of the supporting electrolytes were 0.1 M.

Controlled potential macroelectrolysis and coulometry as well as polarography were carried out in both aqueous ethanol and anhydrous acetonitrile solutions, using the same experimental set-up and type of procedure as in the previous papers.[2,16] A saturated calomel electrode (SCE) and a Ag/0.1 M $AgNO_3$ in MeCN electrode (Ag/Ag$^+$) were used as the reference electrodes in aqueous and nonaqueous solutions, respectively.

Results

Polarography. Results of polarography with **1a**,

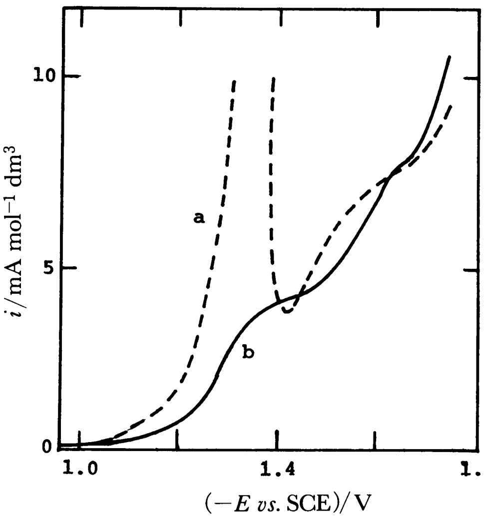

Fig. 1. Tast polarograms of phenacyl p-tolyl silfide (**1a**) in 40% ethanol buffer solution of pH 7.4 at 27 °C. (a) Without maximun suppressor, (b) in presence of 0.008% Triton X-100.

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Table 1. Polarographic data for some aryl phenacyl sulfides in 40% ethanol buffer solution of pH 7.4 in presence of 0.008% Triton X-100 at 27 °C

Substrate[a]	First wave: Half-wave potential (V *vs.* SCE)	First wave: Limiting current ($\mathrm{mA\,mol^{-1}}$)	Second wave: Half-wave potential (V *vs.* SCE)	Second wave: Limiting current ($\mathrm{mA\,mol^{-1}}$)
la	−1.29	3.7	−1.56	3.4
lb	−1.29	3.8	−1.56	3.4
lc	−1.29	3.7	−1.56	3.3

a) **la**: phenacyl *p*-tolyl sulfide, **lb**: phenacyl phenyl sulfide, **lc**: *p*-methoxyphenyl phenacyl sulfide.

lb, and **lc** in a 40% ethanol buffer solution of pH 7.4 are presented in Fig. 1 and Table 1. Figure 1 shows Tast polarograms of **la** as a representative example. The polarogram exhibited two waves with a large maximum in the absence of maximum suppressors. The addition of 0.008% Triton X-100 essentially eliminated the maximum and resulted in two well-defined waves. As can be seen from Table 1, the half-wave potentials ($E_{1/2}$) of both the first and second reduction waves of **la**, **lb**, and **lc** are independent of the Ar group of aryl phenacyl sulfides ($\mathrm{Ar{-}S{-}CH_2COPh}$). The $E_{1/2}$ of each second wave coincides with that of acetophenone in the same solution, the height of the second wave being somewhat smaller than the height of the polarographic wave of an equimolar solution of acetophenone. These suggest that the second wave is ascribed to the reduction of the acetophenone produced during the polarographic reduction. The above suggestion was confirmed by controlled potential coulometry and macroelectrolysis as will be shown later.

The ratio of the first wave-height to the second one for all three sulfides are approximately 1, indicating that each first wave corresponds to a two-electron transfer process. This was also supported from the polarographic result of phenacyl phenyl sulfoxide[2]: This sulfoxide gives two waves with the wave-height of approximately 2:1, $E_{1/2}$ of the second wave coincides with that of **lb**, and the ratio of the first wave-height of the sulfoxide to that of **lb** is approximately 2. Furthermore, a two-electron transfer process was supported by the coulometric experiment as will be shown later. The first wave for **la** was found to be diffusion-controlled as evidenced from the linear plots of the limiting current (i_l) against the square root of the height of the mercury head. Moreover the average temperature coefficient was of the order of 2%/°C as for a diffusion-controlled process. The other substrates, **lb** and **lc**, are also inferred to give diffusion-controlled waves from analogy with **la** with regard to the polarographic behavior.

Figure 2 shows the dependence of $E_{1/2}$ and i_l, on pH for the first wave of **la**, where polarograms were measured in 40% ethanol buffer solutions containing 0.008% Triton X-100. The values of i_l were substantially pH-independent. On the other hand, a plot of $E_{1/2}$ against pH gave two straight-line segments, the intersection of which corresponded to approximately pH 7. Similarly the pH-dependence of $E_{1/2}$ and i_l of the second wave is shown in Fig. 3, together with that of acetophenone in the same solutions. The $E_{1/2}$ of the second wave of **la** coincided with that of acetophenone over the whole pH region, but i_l of the second wave was significantly smaller than that of acetophenone.

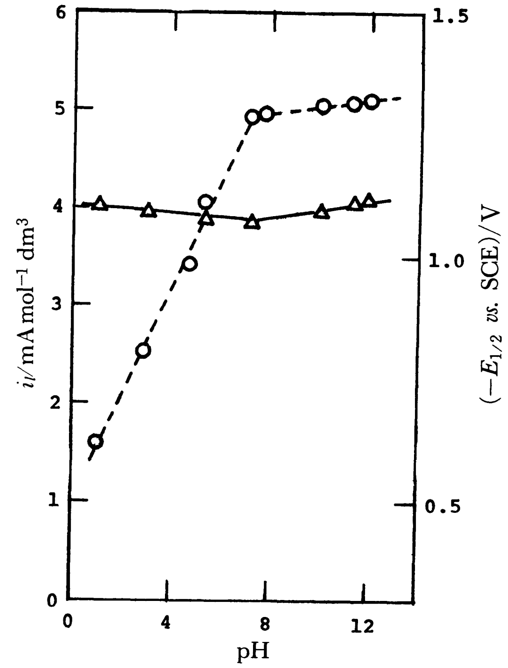


Fig. 2. Dependence of limiting current (——) and half-wave potential (----) on pH for first wave of **la** in 40% ethanol buffer solution containing 0.008% Triton X-100 at 27 °C.

Figure 4 shows typical Tast polarograms of **la** in MeCN containing 0.1 M TBAP, in the absence and presence of phenol as a proton donor. In the absence of the proton donor, **la** gave two waves with the wave-height ratio of approximately 3:1, the value of $E_{1/2}$ of the first wave indicating that **la** is easier to reduce than alkyl phenyl sulfides bearing no carbonyl group.[17] The addition of phenol caused both wave-heights to increase. The dependence $E_{1/2}$ and i_l of the first wave on phenol concentration is presented in Fig. 5, in which the values of i_l of di-*p*-tolyl disulfide also is included. As shown in Fig. 5, the $E_{1/2}$ was independent of the phenol concentration, but the i_l increased with an increase in the phenol concentration and reached twice of the original value when the molar ratio of phenol

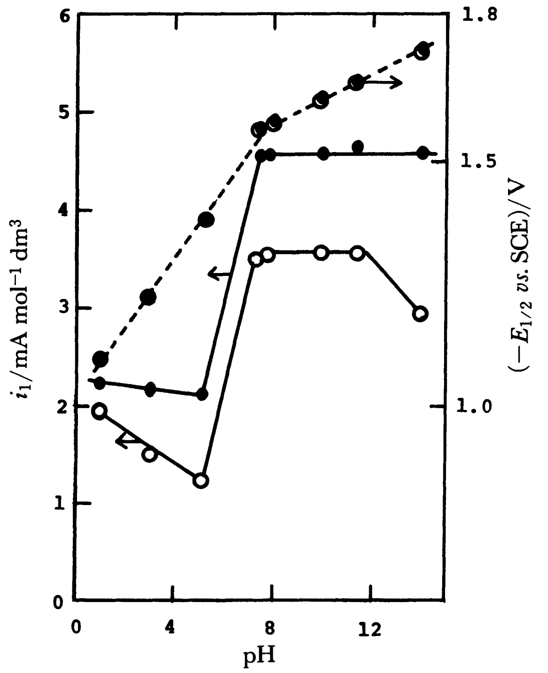


Fig. 3. Dependence of limiting current (——) and half-wave potential (----) on pH in dc polarography in 40% ethanol buffer solution containing 0.008% Triton X-100 at 27 °C.
○: Second wave of **1a**, ●: Wave of acetophenone.

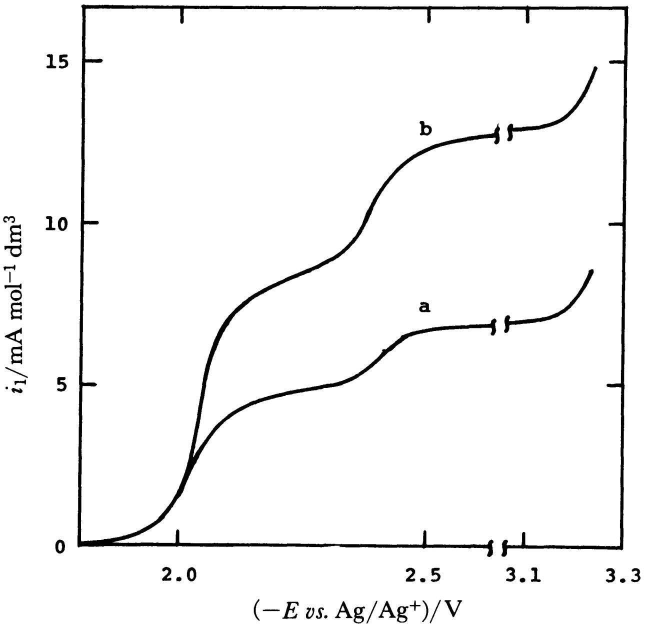


Fig. 4. Effect of phenol on Tast polarogram of **1a** in acetonitrile containing 0.1 mol dm^{-3} TBAP at 27 °C. Molar ratio of phenol/**1a**: (a) 0, (b) 2.0.

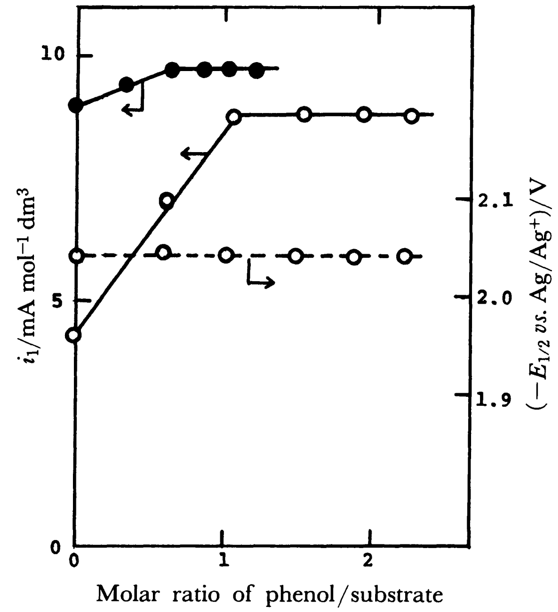


Fig. 5. Dependence of limiting current (——) and half-wave potential (----) on phenol concentration.
○: First wave of **1a**, ●: Wave of di-*p*-tolyl disulfide.

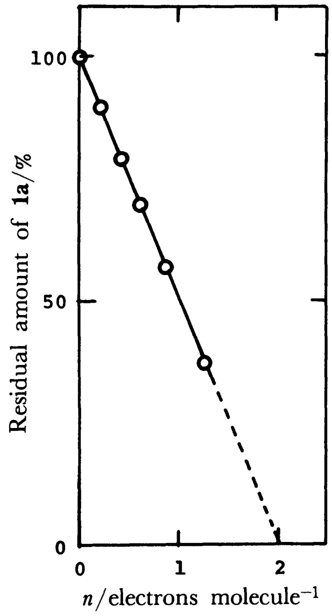


Fig. 6. Coulometric n-value of **1a** at Hg cathode of -1.35 V *vs.* SCE in 40% ethanol buffer solution of pH containing 0.008% Triton X-100 at 27 °C.

to the substrate was more than approximately 1. The electrode reaction taking place at the first wave of **1a** in anhydrous acetonitrile containing sufficient phenol is estimated to be a two-electron transfer process from comparison with the values of i_l of **1a** and di-*p*-tolyl disulfide. Thus, the first wave of **1a** in the absence of proton donors corresponds to a one-electron transfer process. Both values of $E_{1/2}$ and i_l for the second wave were dependent on the phenol concentration in the same fashion with acetophenone.

Coulometry. To determine the apparent number of electrons transfered (n-value) for the reduction of **1a**, **1b**, and **1c** under different electrolytic conditions, a series of controlled potential coulometric experiments were performed. The substrate concentrations were within the range, in which a linear i_l *vs.* concentration behavior is observed. The electrolyses were interrupted at several points and then the exhausted amounts of the substrate were monitored by means of polarography as a function of the quantity of electricity passed. Figure 6

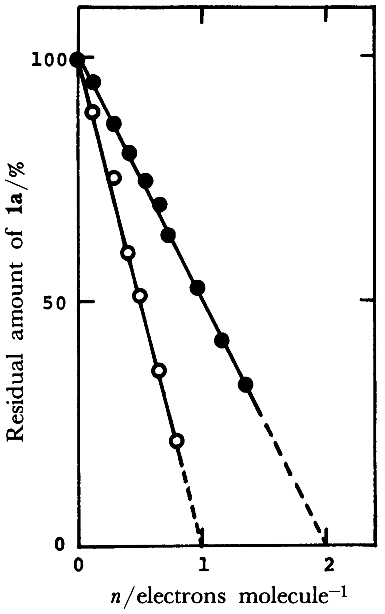


Fig. 7. Coulometric n-values of **1a** in acetonitrile containing 0.1 mol dm^{-3} TBAB at Hg cathode of −2.1 V *vs.* Ag/Ag$^+$. Molar ratio of phenol/**1a**: (○) 0, (●) 2.5.

shows a typical result of the coulometric experiment with **1a** in 40% ethanol buffer solution of pH 7.4 in the presence of Triton X-100 at a stirred mercury pool cathode. The coulometric n-value was estimated by extrapolation to be 2 electrons per molecule, which is agreement with the polarographic n-value.

Similarly typical coulometric results of **1a** at a stirred mercury pool cathode in MeCN containing 0.1 M TBAB are presented in Fig. 7, which also illustrates the effect of phenol on the n-value. Figure 7 definitely shows that the coulometric n-values in the absence and presence of phenol are 1 and 2 electron (s) per molecule, respectively. When a platinum plate electrode in place of the mercury pool was used, the same n-values were obtained.

Macroelectrolysis. Controlled potential macroelectrolyses of some β-keto sulfides were carried out at the plateau potential of the first wave of their polarograms, in 40% ethanol buffer solution of pH 7.4, 95% ethanol buffer solution of pH 5.8, and MeCN containing 0.1 M TBAB with and without phenol. These results are summarized in Table 2, with the coulometric n-values. In a series of macroelectrolyses, the amounts of acetophenone formed were almost equivalent to the sum of the diaryl disulfides and arenethiols and the yields of the isolated acetophenone were 66—76% under all conditions studied. As can be seen from Table 2, in aqueous ethanol solutions and anhydrous acetonitrile solution containing sufficient phenol, coulometric n-values all were close to 2 electrons per molecule, whereas the n-value was 1 electron per molecule in the acetonitrile with no proton donor. Namely, Table 2 shows the curious result that the yields of acetophenone are essentially invariable, no matter whether the n-values are 1 or 2 electrons per molecule. This implies that there is a difference between the reduction mechanisms of aryl phenacyl sulfides to acetophenone in the absence or presence of sufficient proton donor.

The data in Table 2 also show that, with regard to the yields and the coulometric n-values, the electrolytic reduction of aryl phenacyl sulfides is independent of the nature of the electrode material.

Discussion

As shown in Fig. 3, the second wave of **1a** in 40% ethanol buffer solutions gave somewhat underestimated values in wave-height over the whole pH region. This may be interpreted as follows: The electrode reaction taking place at the first wave leads to formation of phenacyl anion ($PhCOCH_2^-$) which is electroinactive. Of course, acetophenone, produced by protonation of the phenacyl anion, is electroactive so that it gives the second wave. Therefore, if all phenacyl anions produced are not protonated within a period of the polarograpic measurement, the second wave will result in a somewhat underestimated wave-height. This idea was supported by the following polarography in a 95% ethanol buffer solution of pH 5.8. As shown in Fig. 8, the polarogram of **1a** exhibited two waves, but the ratio of the second wave-height to the first one was small compared to that in the 40% ethanol buffer solu-

TABLE 2. CONTROLLED POTENTIAL MACROELECTROLYSES OF SOME ARYL PHENACYL SULFIDES ($Ar{-}S{-}CH_2COPh$) AT THE PLATEAU POTENTIAL OF THE FIRST WAVE

Substrate	Solvent	Cathode material	Mole ratio of phenol/substr.	Coulometric n-value	Products (mol%) PhCOCH$_3$	ArSH	ArSSAr[a]	Yield[b] of PhCOCH$_3$ (%)
Ar= p-$CH_3C_6H_4$	40% C_2H_5OH	Hg	0	1.9	50	50	0	66
	95% C_2H_5OH	Hg	0	2.0	56	40	4	66
	CH_3CN	Hg	0	1.0	48	15	37	69
	CH_3CN	Hg	2.6	2.0	51	10	39	67
	CH_3CN	Pt	0	1.0	47	9	44	72
	CH_3CN	Pt	2.5	2.1	55	0	45	76
Ar=C_6H_5	CH_3CN	Hg	2.3	1.8	47	5	48	67
Ar= p-$CH_3OC_6H_4$	CH_3CN	Hg	2.7	2.0	55	0	45	67
	CH_3CN	Pt	0	1.0	44	15	41	74
	CH_3CN	Pt	2.4	1.8	53	0	47	76

a) Calculated on the basis of sulfur content. b) Isolated yield.

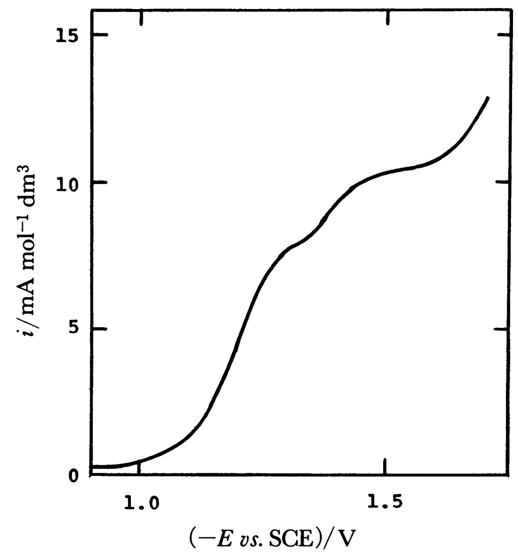


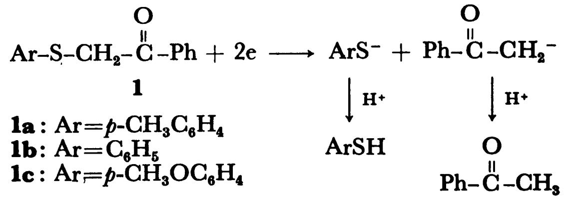
Fig. 8. Tast polarogram of **1a** in 95% ethanol buffer solution of pH 5.8 in presence of 0.008% Triton X-100 at 27 °C.

tion (curve b in Fig. 1). This can be attributed to the weakness of proton donor of the 95% ethanol solution compared to the 40% ethanol solution.

In Table 2, one is faced with the apparent paradox of the isolation of diaryl disulfides in spite of the fact that they are easily reduced to arenethiols at the potential at which the macroelectrolysis was to be run.[18] This may be resolved in terms of an air oxidation of arenethiols, *i.e.*, the thiols easily undergo an air oxidation, particularly in anhydrous media during the work-up procedure after electrolysis, resulting in formation of diaryl disulfides.

The electrolytic reduction of aryl phenacyl sulfides in the absence of proton donors afforded acetophenone and the corresponding thiols in good yields despite of the coulometric n-value of 1, suggesting that such β-keto sulfides undergo a one-electron reduction to yield phenacyl radical ($PhCOCH_2\cdot$) and the corresponding thiolate anions (ArS^-). However, the following results suggest formation of phenacyl anion rather than its radical: (1) The dimer of phenacyl radical was not detected under the present reaction conditions. (2) Phenacyl anion seems to be more stable than its radical because the phenacyl anion is stabilized through the acetyl anion in which the charge is highly delocalized onto the oxygen atom of the carboxyl group. In view of the above reasons, at the present stage, it cannot be concluded whether the electrode reaction taking place at the first wave of aryl phenacyl sulfides in MeCN containing no proton donor, involving a one-electron uptake, leads to formation of phenacyl anion or its radical.

In the sufficiently proton-donor-containing solutions such as aqueous ethanol solutions and anhydrous acetonitrile solutions containing excess phenol, the electrolytic reduction of aryl phenacyl sulfides at the first wave potential, involving a two-electron transfer, will yield phenacyl anion and the corresponding thiolate anions. Hence a plausible mechanism may be illustrated as follows:



$$\mathrm{Ar{-}S{-}CH_2{-}\overset{\overset{O}{\|}}{C}{-}Ph} + 2e \longrightarrow \mathrm{ArS^-} + \mathrm{Ph{-}\overset{\overset{O}{\|}}{C}{-}CH_2^-}$$

$$\mathrm{ArS^-} \xrightarrow{H^+} \mathrm{ArSH} \qquad \mathrm{Ph{-}\overset{\overset{O}{\|}}{C}{-}CH_2^-} \xrightarrow{H^+} \mathrm{Ph{-}\overset{\overset{O}{\|}}{C}{-}CH_3}$$

1

1a: Ar=p-$CH_3C_6H_4$
1b: Ar=C_6H_5
1c: Ar=p-$CH_3OC_6H_4$

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18) For example, $E_{1/2}$ of di-p-tolyl disulfide is 1.27 V *vs.* Ag/Ag^+ in MeCN containing 0.1 M TBAP in the presence of excess phenol.