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ELECTROCHEMISTRY OF ORGANIC SULFUR COMPOUNDS V.[1)]

A POLAROGRAPHIC STUDY ON THE ANODIC OXIDATION OF PHENYL SULFIDES

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This paper describes a total analysis of polarograms in the oxidation of phenyl sulfides along with a discussion based on complete products analysis,[3)] since such electrochemical studies are required to establish a reliable theory on the mechanism of the anodic process.[4,5)]

Polarograms of sulfides (I, II, III, and IV) and the related products derived from the anodic oxidation were measured in an acetonitrile solution of 0.2-0.3 mM of substrate containing 0.1 M of sodium perchlorate at 20°.[6)] The half-wave potentials on polarograms and the peak potentials in cyclic voltammetry are listed in Table I. Typical polarograms of I, II, III, and IV are shown in Fig. I. The polarograms of sulfides (I, II, and III) showed marked first oxidation waves at 1.44-1.47 V vs. SCE almost independently on the structure of phenyl sulfides, however, in the absence of the sulfides no practical anodic current was observed in the range of 1.0-2.2 V in acetonitrile-sodium perchlorate. This indicates that the phenylthio group is susceptible of the initial step in the anodic oxidation.

Diphenyl sulfide (I) gave a discriminable curve (A) including three oxidation waves. The second wave at 1.71 V was found to be consistent with that of sulfonium salt (VIII), which was the major product in the oxidation of I in anhydrous condition. A shoulder wave appeared at 2.00-2.15 V[7)] would be derived from diphenyl sulfoxide (V) which was obtained in wet acetonitrile (Fig. II). In fact, addition of VIII in a sulfide (I)-acetonitrile solution resulted in increase of the diffusion current of the second wave, whereas the presence of water caused decrease of the current. Methyl phenyl sulfide (II) afforded a just similar curve (B) to that of I. The second and the third waves are almost corresponding to those of the sulfonium salt (IX) and methyl phenyl sulfoxide (VI).

In contrast with the discriminative second waves of I and II, the polarogram of benzyl phenyl sulfide (III) showed a broad second wave at 1.70–2.25 V. The wave was quite similar to the first wave of benzyl phenyl sulfoxide (VII), however, the broadness of the wave suggests that the oxidation waves derived from diphenyl disulfide (X), benzyl alcohol (XI), and benzyl acetamide (XII), all of which are products in the anodic reaction of III, may partly overlap with the second wave of III.

Phenyl triphenylmethyl sulfide (IV) afforded a simple curve (D) as compared with three phenyl sulfides (I, II, and III). Contrasting with the curves (A–C), the first wave of (D) has a gentle slope appeared at 1.4–1.8 V due to overlapping of the oxidation wave from X, since disulfide (X) is predominantly produced from the oxidation of IV, and the oxidation potential and the polarographic pattern of X are quite similar to those of the first wave of IV. It is noteworthy that the curve (D) includes no marked oxidation wave in the range of 1.7–2.1 V ascribable to the corresponding sulfoxide and sulfonium salt since disulfide (X) and triphenyl carbinol (XIII) derived from the S–C bond cleavage are major products in the anodic oxidation. As described above, the result of the polarography coincides with that of products analyses and well explains the reaction pathways of the anodic oxidation of phenyl sulfides.

Coulometry of I, II, and III by flow method[8)] at the first oxidation wave afforded the values, 1.2±0.1, 1.1±0.05, and 1.2±0.1, respectively. While measurement of diffusion limitting

Table I The Half-Wave Potential ($E_{\frac{1}{2}}$) and the Peak Potential (E_p) of Phenyl Sulfides and Related Compounds in CH_3CN-$NaClO_4$

Compound	I	II	III	IV	V	VI	VII
$E_{\frac{1}{2}}$ V vs. SCE	1.45 1.71 2.05	1.47 1.86	1.44 1.83	1.52 2.30	2.08	2.07	1.83
E_p V vs. SCE	1.50 1.75 2.06	1.44 1.83 2.27	1.49 1.95	1.56 2.32	2.07		

Compound	VIII	IX	X	XI	XII	XIII
$E_{\frac{1}{2}}$	1.67		1.52	2.26		
E_p	1.74 2.63	1.70 2.00	1.53		2.10	2.25

Fig.I Polarograms of Phenyl Sulfides

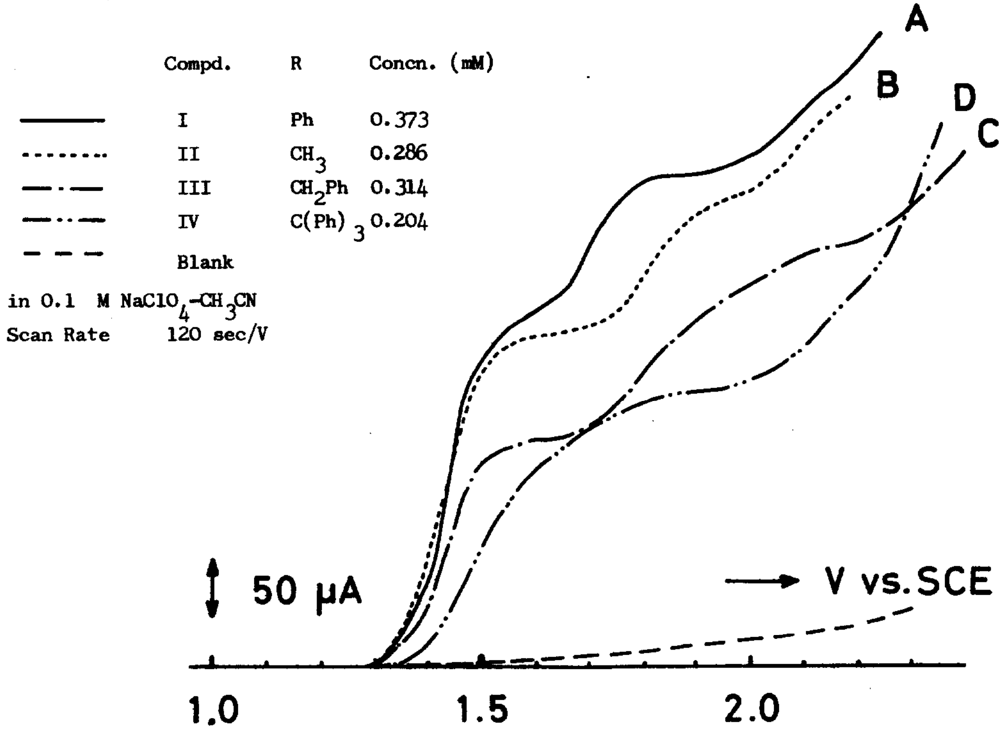


Fig. II

Polarograms of (I)&Related Compounds

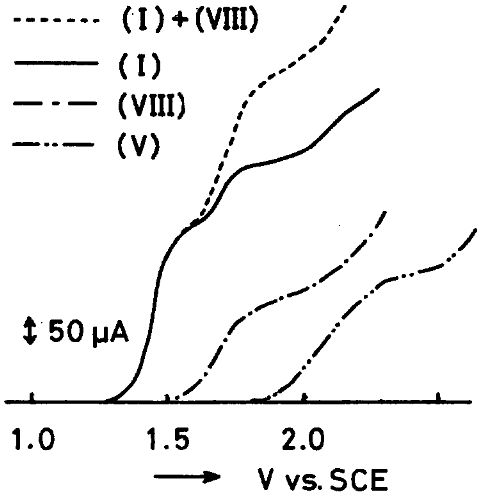
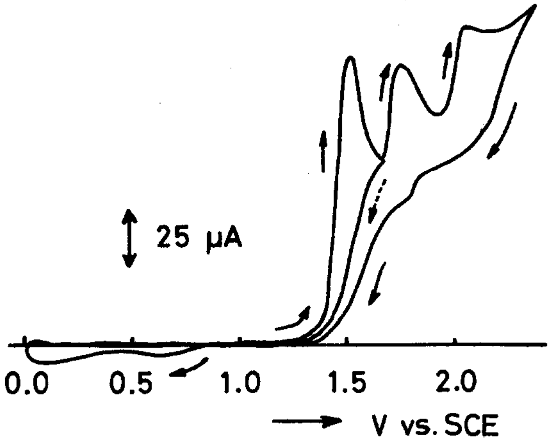
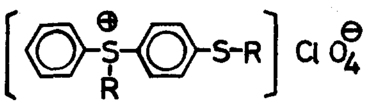


Fig. III

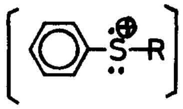
Cyclic Voltammetry of (I)



current relative to hydroquinone as a standard gave the values, 0.94, 1.34, 1.35, and 1.49 for I, II, III, and IV. Both results suggest that the primary oxidation step of the phenyl sulfides involves one electron transfer. However, cyclic voltammetry(9) of I, II, III, and IV showed no marked reduction peaks corresponding to the first oxidation peaks (Fig. III). Thus, the primary electron transfer process would be irreversible and the incipiently formed cation radicals (XIV) would readily undergo successive reactions, namely, sulfoxidation, sulfonium salt formation, S-C bond cleavage, or/and oxidation to the corresponding dication. It is concluded that the anodic oxidation of phenyl sulfides initially takes place at phenylthio group to provide cation radical which readily undergoes chemical or electrochemical reactions depending on the structures of phenyl sulfides.



R: Ph (VIII), CH_3 (IX)



(XIV) R: Ph, CH_3, CH_2Ph, $C(Ph)_3$

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9) Sweep rate was 200 mV/sec.