Communications to the Editor

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PHOSPHITE TO PHOSPHATE TRANSFORMATION ELECTROCHEMICALLY CATALYZED BY DISULFIDES

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Electrochemical oxidation of diethyl disulfide in acetonitrile in the presence of trialkyl phosphites and a small amount of water resulted in the transformation of the phosphites to the corresponding phosphates under mild conditions, with recovery of the disulfide.

KEYWORDS——indirect electrochemical oxidation; dialkyl disulfide; trialkyl phosphite; trialkyl phosphate; cyclic voltammetry; controlled potential electrolysis

Indirect electrochemical reactions have received much attention in recent years and a fair number of organic electron-transfer agents, effective for the reduction 1) and the oxidation 2) of organic substrates, have been reported. In our study of electrochemical oxidation of organophosphorus compounds, we have found a new catalytic oxidation in which dialkyl disulfides mediate the transformation of trialkyl phosphites to the corresponding phosphates. In contrast to most of the organic electron-transfer agents, which themselves show reversible character on voltammetry,1a,2a) the disulfides are oxidized irreversibly under the experimental conditions (see Fig. 1).3)

Cyclic voltammetry of EtSSEt in acetonitrile in the presence of $(EtO)_3P$ showed a prepeak (Fig. 1), which grew with the amount of the phosphite and gradually reached a limiting value (Fig. 2). Similar prepeaks were observed with other disulfides (Table I).

Table I. Peak Potentials of Prepeaks Observed in the Cyclic Voltammetry of RSSR in the Presence of $(EtO)_3P$ a)

RSSR R	Peak potential b) (V *vs*. S.C.E.)	RSSR R	Peak potential b) (V *vs*. S.C.E.)
Me	1.11 (1.25)	Ph	1.24 (1.43)
Et	1.09 (1.19)	$PhCH_2$	1.20 (1.38)
n-Bu	1.10 (1.18)	p-CH_3Ph	1.20 (1.35)
tert-Bu	1.13 (1.19)		

a) In acetonitrile containing 0.1 M $NaClO_4$ at a glassy carbon electrode at 25°C; concentration of RSSR and $(EtO)_3P$, 5 mM, respectively; voltage sweep rate, 0.05 Vs^{-1}.
b) Values in the parentheses represent the peak potentials in the absence of the phosphite.

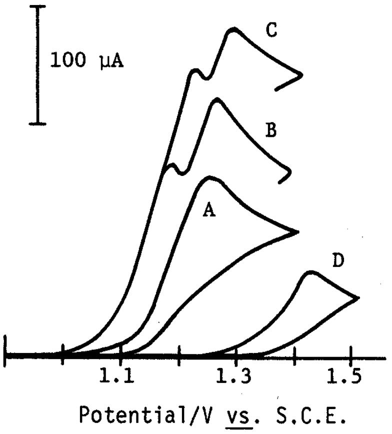

Fig. 1. Cyclic Voltammograms of (A) EtSSEt (10 mM), (B) A + (EtO)$_3$P (10 mM), (C) A + (EtO)$_3$P (16 mM), and (D) (EtO)$_3$P (10 mM)

In MeCN containing 0.1 M NaClO$_4$ at 25°C; glassy carbon electrode (area, 0.071 cm^2); voltage sweep rate, 0.05 V s^{-1}.

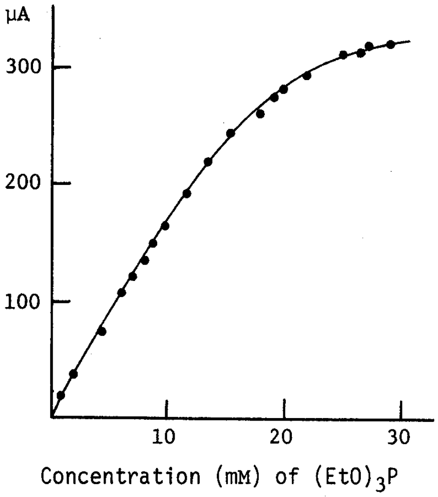

Fig. 2. Effect of Concentration of (EtO)$_3$P on the Peak Height of the Prepeak

The ordinate represents the peak current. Concentration of EtSSEt, 10 mM.

Table II. Results of Controlled Potential Electrolysis of EtSSEt in the Presence of (R'O)$_3$P a)

Run No.	(R'O)$_3$P (Amount/mmol)	Amount (mmol) of EtSSEt	H$_2$O	F/mol b)	Yield (%) c) of (R'O)$_3$PO
1	(EtO)$_3$P (1.0)	1.0	0	2.0	52
2	(1.0)	1.0	3.2	2.0	87 d)
3	(1.0)	1.0	Excess e)	2.0	4
4	(1.0)	0.5	3.2	3.4	56 (112) f)
5	(3.0)	1.0	4.8	6.0	81 (243) f,g)
6	(MeO)$_3$P (1.0)	1.0	3.2	2.0	47
7	(n-BuO)$_3$P (1.0)	1.0	3.2	2.0	61

a) The electrolysis was carried out in acetonitrile containing 0.1 M NaClO$_4$, in a one compartment cell, at anode potential of 1.1 V vs. S.C.E., and at ambient temperature: a graphite plate anode and a platinum foil cathode were used throughout.

b) Consumed electricity based on EtSSEt.

c) Based on (R'O)$_3$P: determined by GLC.

d) 87% of EtSSEt was recovered. e) 3% (V/V).

f) Based on EtSSEt. g) 63% of EtSSEt was recovered.

Typical results of controlled potential electrolysis of EtSSEt in the presence of trialkyl phosphites are listed in Table II. The phosphites alone are not oxidized at the anode potential applied (1.1 V vs. S.C.E., cf. Fig. 1). Recovery of the disulfide in the electrolysis solution (87 and 63% in runs 2 and 5, respectively) and the yields of $(EtO)_3PO$ in the electrolysis with the disulfide to $(EtO)_3P$ molar ratio less than unity (runs 4 and 5) demonstrate that the catalytic oxidation of the phosphite actually takes place. The low yield of the phosphate in the electrolysis with excess water (run 3) is probably due to hydrolysis of the phosphite.[4)]

It is well known that the reaction of $(R'O)_3P$ with RSSR gives $(R'O)_2P(O)SR$ by a radical process[5)] and $(R'O)_3PS$ by an ionic process at elevated temperatures and in the presence of radical inhibitors.[6)] Thus, the electrochemical oxidation constitutes a new process for the reaction between the two calsses of compounds though the products of the reaction may be trivial.

The prepeak observed in the voltammetry may be explained in terms of pre-equilibrium formation of an electroactive adduct betweem the substrates or a nucleophile assisted electron transfer mechanism.[7,8)] However, since it has been shown that a prepeak can also be caused by other mechanisms,[7,9)] no definite conclusion as to the mechanism can be drawn from the present results. Further studies on it and the scope of the reaction are in progress.

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8) In the present case, formation of a complex such as $(R'O)_3P^{\delta+}\cdots S(R)-S^{\delta-}(R)$ can be considered.

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