Chemical and Electrochemical Oxidation of O,O,O-Trisubstituted Phosphorothioates and Triphenylphosphine Sulfide

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Received October 4, 1982

The chemical and electrochemical oxidation of 0,0,0-trialkyl phosphorothioates and triphenylphosphine sulfide are reported. Reaction of the latter compound with nitrosonium tetrafluoroborate produces a dimeric dication that is relatively stable in acetonitrile solution but rapidly decomposes upon attempted isolation. Electrooxidation of triphenylphosphine sulfide similarly gives a dimeric dication via the intermediacy of a dimer cation radical. Reaction of 0,0,0-triethyl phosphorothioate with nitrosonium tetrafluoroborate produces bis(diethylphosphoryl) disulfide and the N-ethylacetonitrilium ion whereas its oxidation at the surface of platinum results in the formation of the N-ethylacetonitrilium ion and products that are not identified.

Tertiary phosphine sulfides² and esters or amides derived from thiophosphoric acid³⁻⁶ are good inhibitors of corrosion of iron and enhance antioxidant and lubricating efficiency of lubricating oils. These and other antioxidants, such as zinc dialkyldithiophosphates which are widely used as additives to lubricating oils,⁷ are believed to function as inhibitors of the oxidation of hydrocarbons by reacting with the intermediate hydroperoxides,^{4,7-11} thereby disrupting the chain reaction.¹² Significantly, phosphates that do not contain sulfur do not act as chain-breaking inhibitors, which suggests that electron transfer from an electron-rich sulfur atom characterizes the antioxidant behavior of these compounds.⁸

We have recently reported¹³ the chemical and electrochemical oxidations of thioureas, thiocarbonates, and thicketones to stable dimeric dications that contain the disulfide linkage (eq 1). Electron-transfer oxidation of

$$2 > c = s \xrightarrow{to_1} > c - s - s - c < (1)$$

thiocarbonyl compounds to their corresponding monomeric cation radicals was established by cyclic voltammetry measurements; subsequent addition of the intermediate radical cation to a neutral compound and one-electron oxidation of the resultant dimer cation radical produced the product dithiodicarbenium salts. The parallel results observed in these chemical and electrochemical transformations suggested a similar pathway for the oxidation of thiophosphorus compounds with resulting inferences for their role as antioxidants. We have now examined the chemical and electrochemical oxidations of 0,0,0-trialkyl phosphorothioates (1) and triphenylphosphine sulfide (2)and report their diverse transformations.

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Results and Discussion

Oxidation with Nitrosonium Salts. Treatment of O,O,O-triethyl phosphorothioate (1a) with NO⁺BF₄⁻ in anhydrous acetonitrile immediately gave rise to a deep orange-red solution that occurred with evolution of nitric oxide. As nitric oxide evolution slowed and eventually ceased, the color of the reaction mixture faded to light yellow. The stoichiometry of this reaction, like that with carbonyl sulfides,¹³ required equimolar amounts of phosphorothionate and nitrosonium salt. A ¹H NMR spectrum of the reaction mixture produced from treatment of 1a with an equivalent amount of $NO^+BF_4^-$ revealed the presence of the N-ethylacetonitrilium ion (3) in 65% yield, and, after an aqueous workup, bis(diethylphosphoryl) disulfide (4) was isolated in 42% yield. Equation 2 is consistent with the reaction stoichiometry for production of nitric oxide and accounts for the formation of 3 and 4.

$$2CH_{3}CN + 2(EtO)_{3}P = S + 2NO^{+}BF_{4}^{-} \rightarrow$$

$$2[CH_{3}CNEt]^{+}[BF_{4}]^{-} + [(EtO)_{2}P(O)S]_{2} + 2NO (2)$$

$$3$$

.____ _____

The slow gas evolution for this oxidation conversion may be a function of the stability of the initially formed Snitrosyl adduct 5 and its subsequent transformation. The transient deep orange-red color observed in this reaction is characteristic of S-nitrosyl compounds^{14,15} and has also been observed in nitrous acid oxidations of thiourea and alkylthioureas.¹⁶ Scheme I outlines a mechanistic pathway

Scheme I

$$(\text{EtO})_3 P = S + \text{NO}^+ \rightarrow [(\text{EtO})_3 P \text{SNO}]^+$$
 (3)
5

$$[(EtO)_3PSNO]^+ + CH_3CN \rightarrow [(EtO)_2P(O)SNO] + 3$$

$$2[(EtO)_2 P(O)SNO] \rightarrow 4 + 2NO$$
 (5)

for nitrosonium ion oxidation of O,O,O-triethyl phosphorothioate that is consistent with intermediate formation of a relatively stable S-nitrosyl adduct (6) and accounts for the formation of disulfide 4 and nitrilium ion 3. The persistence of the deep orange-red color for as long as 15 min after combination of reactants suggests that alkyl transfer (eq 4) occurs prior to disulfide formation (eq 5), and this interpretation is further suggested by results from

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the electrochemical oxidation of 1a (vide infra). Confirmation of this scheme was obtained through observation of nitrilium ion production: after complete addition of 1a to $NO^+BF_4^-$, the yield of 3 remained constant through the last 25% of nitric oxide evolution. Similar results were obtained with O,O,O-triisopropyl phosphorothioate (1b), but the corresponding nitrilium ion was produced in only 50% yield.

Scheme I demands quantitative production of nitrilium ion 3, but only a 65% yield of this product was observed when equivalent amounts of 1a and $NO^+BF_4^-$ were employed. Use of a two-fold molar excess of the nitrosonium salt resulted in a 75% yield of 3 but, in this case, 4 was isolated in only 10% yield. Independent experiments confirmed the instability of 4 toward NO⁺BF₄, but products from its nitrosative decomposition were not isolated. Furthermore, when equimolar amounts of 1a and $NO^+BF_4^-$ were used, O,O,S-triethyl phosphorothioate, 0,0.0-triethyl phosphorothioate, triethyl phosphate, and ethanol were observed as minor components of the reaction mixture (<8% yield of each component) after addition of water, and these products suggest that alkyl transfer to 1a (eq 6) may be competitive with direct alkyl transfer to

$$[(EtO)_{3}PSNO]^{+} + (EtO)_{3}P \Longrightarrow 5$$

$$[(EtO)_{2}PSNO] + [(EtO)_{3}PSEt]^{+} (6)$$

the nitrile solvent (eq 4). Ethylene, which was detected as a minor component of the gaseous products from nitrosative decomposition of 1a, provided further accounting of the complex behavior of phosphorothioate esters toward nitrosonium salts.

Alkyl transfer reactions such as those described by eq 4 and 6 represent fundamental examples of thiono-thiolo isomerization processes which have been well documented in investigations of phosphorothioate esters with nitrogen bases,¹⁷ with alkyl halides,¹⁸ and during thermal isomerization.¹⁹ Results provided from nitrosative decomposition of O.O.O-phosphorothioate esters demonstrate the relative instability of cationic species analogous to 5 and the substantial nucleophilic difference between thiono and thiolo isomers. Phosphorothionates, of which malathion and parathion have been investigated in detail, are readily converted to their oxygen analogues by treatment with the nitrosating agent N_2O_4 in methylene chloride;²⁰ this exchange of thiono sulfur for oxygen is consistent with the formation of a nitrate adduct of a species that is analogous to 5 from which the elements of composition N_2O_3S are extruded. As anticipated from the results that we have reported, trialkyl phosphates are inert toward nitrosonium salts; and even azidophosphates, in contrast to alkyl azides,²¹ do not react with nitrosonium salts. Decomposition of thionitritophosphates such as 6, like disulfide formation from alkyl thionitrites,^{14,15} presumably involves homolytic cleavage between sulfur and the nitrosyl group, but the mechanism of this transformation has not been firmly established.

Equimolar amounts of triphenylphosphine sulfide (2) and NO⁺BF₄⁻ react slowly in acetonitrile at 25 °C over a period of 30-60 min with quantitative evolution of NO, giving, eventually, a light yellow solution of a substance



Figure 1. Cyclic voltammograms recorded in acetonitrile containing 0.10 M TBAP at 0.20 V s⁻¹. All scans start at 0.0 V and initially scan anodically: (a) Bottom, complete CV of 5.0 mM la; top, partial CV of the same solution with a 20-s hold at 2.0 V prior to the cathodic sweep to enhance concentrations of products. (b) 4.0 mM 3. (c) 4.4 mM 4.

that is relatively stable under N2 but rapidly decomposes when the solvent is removed or when the solution is exposed to air. A ¹H NMR spectrum of the reaction mixture exhibits a multiplet in the aromatic region that is 0.20 ppm downfield from that of 2 with acetonitrile as the solvent. Electroreduction of this reaction mixture produces 2, and, analogous to the behavior of dithiodicarbenium salts,¹³ triphenylphosphine oxide is produced immediately upon treatment of the reaction mixture with water. These results lend strong support for the nitrosative production of the dithiodiphosphinium salt 7 from triphenylphosphine sulfide (eq 7).

$$2Ph_{3}P = S + 2NO^{+}BF_{4}^{-} \rightarrow [Ph_{3}P^{+}SSP^{+}Ph_{3}][BF_{4}^{-}]_{2} + 2NO (7)$$

Electrochemical Oxidation of 1 and 2. Compound 1a is readily oxidized at the surface of platinum in anhydrous acetonitrile containing tetra-n-butylammonium perchlorate (TBAP) as the supporting electrolyte. A cyclic voltammogram of 1a (Figure 1a) exhibits an anodic wave (A) at 1.96 V ($E_{\rm Pt}$ vs. Ag⁺/Ag) which results from a diffusion-controlled process, as shown by a plot of peak current (i_p) vs. the square root of the scan rate $(\nu^{1/2})$ that is linear.²² This oxidative process is irreversible up to scan rates of 1.5 V s⁻¹, showing that the oxidation product, presumably the cation radical of 1a, undergoes rapid reaction upon formation. A rather complex mixture of substances is formed directly or indirectly from the cation radical of 1 as evidenced by the reverse cathodic scan from which at least three waves are observed at B, C, and D (0.05, -0.45, and -1.19 V, respectively). These waves are

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not observed if the initial anodic scan is reversed before wave A is reached.

To ascertain if the electrochemical oxidation of 1a parallels the chemical oxidation of 1a with NO⁺BF₄⁻, we recorded cyclic voltammograms of 3 and 4, and these are shown in Figures 1b,c. Both are reduced irreversibly up to scan rates of 1.5 V s^{-1} at -0.53 and -1.36 V, respectively. A mixture of 3 and 4 gives cathodic waves at approximately the same potentials, but the anodic wave for 4 on the reverse scan is absent. A cyclic voltammogram of the reaction mixture obtained from combining equimolar amounts of (EtO)₃P=S and NO⁺BF₄⁻ in acetonitrile similarly gave two cathodic waves at approximately -0.5 and -1.3 V.

The peak potentials for 3 and 4 do not coincide exactly with the peak potentials of waves C and D (e.g., -0.53 vs. -0.45 and -1.36 vs. -1.19 V). Since peak potentials are sensitive to conditions, a cyclic voltammogram of a mixture of 1a, 3, and 4 was obtained. After scanning to 2.0 V to oxidize 1a, we observed four cathodic waves in the reverse scan, three with peak potentials coinciding with waves B-D and a fourth wave at -1.36 V. Therefore, wave C results from the reduction of 3 and wave D from the reduction of a substance that is not 4. Further support for the assignment of wave C to the reduction of 3 comes from a cyclic voltammogram of 1a in nitromethane which exhibits an anodic wave at 1.9 V in the initial scan but only two cathodic waves in the reverse scan, one at approximately -0.1 V with a large current and one at -1.20 V with a small current. Thus, electrooxidation of 1a in acetonitrile produces its cation radical which rapidly undergoes reaction to give 3, directly or indirectly as one of several products, but not 4.

A priori, several modes of reaction for the cation radical of 1a resulting in the reductions that occur at waves B and D can be considered (Scheme II). Dimerization of 8 to

Scheme II

$$2[(EtO)_{3}P-S]^{+} \rightarrow (EtO)_{3}P^{+}-S-S^{-+}P(OEt)_{3} \qquad (8)$$

$$8 \xrightarrow{1a} (EtO)_3 P^+ - S - Et + (EtO)_2 P(O)S.$$
(9)
9 10

$$8 \xrightarrow{\text{CH}_3\text{CN}} (\text{CH}_3\text{CNEt})^+ + 10 \tag{10}$$

$$8 \xrightarrow{1a} (EtO)_{3}\dot{P} - S - S - {}^{+}P(OEt)_{3} \xrightarrow{CH_{3}CN} 11$$
$$3 + (EtO)_{3}\dot{P} - S - S - P(O)(OEt)_{2}$$
(11)

the dimer dication (eq 8) can immediately be ruled out as a major pathway. The dimer dication would be expected to react rapidly with acetonitrile (eq 4) to give 3 and 4 as products. Alkyl transfer from 8 to 1a is shown in eq 9. Although evidence was cited earlier for the intermediacy of 9 in the formation of several minor products from the reaction of 1a with NO⁺BF₄⁻, the low yields of these products coupled with instability of 9 toward alkyl transfer in dilute solutions of acetonitrile suggest that the concentration of this intermediate would be very low. The radical 10 is anticipated to rapidly dimerize to 4, which is not observed, or to combine with 1a to produce 12. Alternatively, alkyl transfer from 8 to acetonitrile to give 3 and 10 is considered in eq 10. If this path were operative, cyclic voltammograms of 1a in acetonitrile and nitromethane should produce similar peak potentials for 10 and/or its combination product with 1a. Although similar cyclic voltammograms for 1a in acetonitrile and nitro-



Figure 2. (a) Cyclic voltammogram of 3.5 mM 2 in acetonitrile containing 0.10 M TBAP at a scan rate of 0.20 V s^{-1} . (b) Cyclic voltammogram of 3.0 mM 7 in acetonitrile containing 0.10 M TBAP at a scan rate of 0.20 V s^{-1} .

 Table I. Peak Potentials from the Cyclic Voltammograms of Phosphorus Thiones, Thiocarbonyls, and Zinc Di-n-butyldithiophosphate

	E_{Pt} vs. Ag/Ag ⁺ , V		
compound A			
	$\overrightarrow{A \rightarrow} [A]^+ \cdot$	$[A_2]^{2+} \rightarrow \\ [A_2]^+ \cdot \text{ or } 2A$	ref
Ph ₃ PS (EtO) ₃ PS (Me,N),CS	1.52 1.96 0.51	-0.50 -0.51	this work this work 13
\$ 5 5	0.86	-0.74	13
$(p-MeOC_6H_4)_2CS$ $[(n-BuO)_2PS_2]_2Zn$	$\begin{array}{c} 0.72\\ 1.58\end{array}$	-0.73	$\frac{13}{24}$

methane are observed, the dimeric product of 10 is not, and nitromethane is not a comparable nucleophile for alkyl transfer. Reaction of 8 with its precursor 1a would produce a dimer cation radical (eq 11). In the electrooxidation of thiocarbonyls this mode of reaction was found to predominate.13 Trialkoxy(tert-butoxy)phosphoranyl radicals have been observed at -70 °C with ESR spectroscopy.²³ When a sample is warmed, β scission occurs to give the *tert*-butyl radical with an extrapolated rate constant of $5.0 \times 10^5 \,\mathrm{s}^{-1}$ at 30 °C. Since β scission of 11 to give the ethyl radical is expected to be considerably slower, the presence of 11 and/or its alkyl transfer product 12 at the electrode surface in sufficient quantities to produce waves B and/or D cannot be ruled out. If 11 and 12 are the species associated with waves B and D, the composite data from the chemical and electrochemical oxidations of 0,0,0-trialkyl phosphorothioates are basically compatible with the formation of unstable phosphorothionate cations and radical cations, respectively, from which alkyl transfer is the most distinctive process.

The electrochemical oxidation of 2 is less complex, and its cyclic voltammogram is illustrated in Figure 2a. An irreversible wave (up to $\nu = 1.5$ V s⁻¹) is observed at 1.52 V, and two cathodic waves are present in the reverse scan at 0.07 and -0.50 V. A cyclic voltammogram for the product from the reaction of NO⁺BF₄⁻ with 2 is displayed in Figure 2b. From a comparison of the two cyclic volt-

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ammograms in Figure 2 it is reasonable to conclude that the electrochemical oxidation and $NO^+BF_4^-$ oxidation of 2 produce the same substance. In addition, reduction of the NO⁺BF₄^{-/2} product gives 2. These observations and the NMR evidence cited earlier strongly suggest that the oxidation of 2 produces the dimeric dication 7. The wave at 0.02 V in Figure 2a is likely due to the reduction of the intermediate dimer cation radical.

As seen in Table I, peak potentials for the electrochemical oxidation of phosphorus thiones are significantly more positive than those of their carbon analogues¹³ but are similar to the peak potential for zinc di-n-butyldithiophosphate.²⁴ Zinc dialkyldithiophosphates are believed to react with peroxy radicals by an S_H2 displacement reaction at the metal center or by electron transfer.⁹ The similarity in oxidation potentials for phosphorus thiones and zinc dialkyldithiophosphates supports the electrontransfer mechanism for these antioxidants. Interestingly, whereas thiocarbonyls are considerably better electron donors than phosphorus thiones, the peak potential for the electrochemical reduction of the dimeric dication derived from 2 is comparable to those derived from the thiocarbonyls, which suggests their suitability in electrontransfer processes.

Experimental Section

Instrumentation. Proton magnetic resonance spectra were obtained with JEOL JNM-PMX60 and Varian FT-80A spectrometers. Unless otherwise indicated, chemical shifts are reported in δ units, with tetramethylsilane as the internal standard. Infrared spectra were obtained on either a Sargent-Welch Pye Unicam 3-200 or a Perkin-Elmer 621 spectrometer. Gas chromatographic analyses were performed on a Varian Model 2720 gas chromatograph with thermal conductivity detectors. Cyclic voltammetry experiments were performed by using an MPI potentiostat and wave generator with a conventional three-electrode cell. The working electrode was a platinum bead, the counterelectrode a platinum wire coil, and the reference electrode a silver wire immersed in an acetonitrile solution of 0.10 M AgNO₃. The reference electrode was separated from the sample by two glass frits and a solution of acetonitrile containing 0.10 M tetra-nbutylammonium perchlorate (TBAP). A Bascom-Turner Model 4120 Datacenter was used to record cyclic voltammograms at high speeds.

Materials. 0,0,0-Triisopropyl phosphorothioate was prepared from its corresponding phosphite ester by heating with elemental sulfur.²⁵ Triphenylphosphine sulfide and 0,0,0-triethyl phosphorothioate were commercially available and purified by recrystallization and distillation, respectively, just prior to use. Bis(diethylphosphoryl) disulfide was prepared by the method of Krawczyk and Skowronska.²⁶ N-Ethylacetonitrilium tetrafluoroborate was prepared by the literature method.²⁷ Nitrosonium tetrafluoroborate was stored in a vacuum desiccator over phosphorus pentoxide prior to use. Acetonitrile was heated at reflux for 6-10 h over calcium hydride, distilled from calcium hydride under nitrogen, and redistilled from phosphorus pentoxide under dry nitrogen. Nitromethane was distilled from calcium hydride under nitrogen prior to use. Tetra-n-butylammonium perchlorate was purified according to the literature method.²⁸

Cyclic Voltammetry Measurements. Solutions were prepared and introduced into the electrochemical cell under nitrogen in a glovebag. The purified acetonitrile was stirred over neutral alumina for 0.25 h in the glovebag prior to use. All cyclic voltammograms were performed in solutions of acetonitrile or nitromethane containing 0.10 M TBAP. Repetitive scans gave reproducible cyclic voltammograms.

Reaction of 0.0.0-Trialkyl Phosphorothioate (1) with Nitrosonium Tetrafluoroborate. General Procedure. Nitrosonium tetrafluoroborate (normally 5.0 mmol) was introduced into an oven-dried, 25-mL, three-necked flask fitted with a reflux condenser, addition funnel, and gas outlet tube. The flask was purged with dry nitrogen, and 3.0 mL of acetonitrile was introduced. With stirring, a solution of 1 (normally 5.0 mmol) in 5.0 mL of acetonitrile was added dropwise over a 15-30 min period, resulting in the immediate formation of an orange-red solution and the evolution of a gas. After the addition was completed, the evolution of gas decreased slowly and the solution faded to light yellow. Total gas evolution was measured on the closed system by water displacement from a calibrated gas buret. Gas chromatographic and infrared analysis of the gas revealed that the principal component was nitric oxide (>95%) with trace amounts of nitrous oxide and ethylene. A ¹H NMR spectrum of the reaction mixture prior to workup showed the presence of the N-ethylacetonitrilium ion or N-isopropylacetonitrilium ion on the basis of a comparison with those reported by Olah.²⁹ Quantitative analyses were performed by the comparison of integrated characteristic absorptions with those of the internal reference, usually chlorobenzene.

The reaction mixture was quenched with water and extracted with ether. The ether extracts were combined and dried over anhydrous magnesium sulfate, and the ether was removed under reduced pressure. The ¹H NMR and IR spectra of the residue were identical with those obtained from a sample of 3 prepared by the literature method.²⁵ The yield of 3 was 42%. The presence of 1a, triethyl phosphate, and O,O,S-triethyl phosphorothionate was determined by GC analysis of the reaction mixture prior to ether extraction and confirmed by NMR analysis after addition of D_2O to the reaction mixture. Ethanol was identified from its characteristic NMR absorptions after quenching the reaction solution with D_2O .

Reaction of Triphenylphosphine Sulfide (2) with Nitrosonium Tetrafluoroborate. By use of the general procedure for the reaction of 1 with nitrosonium tetrafluoroborate (vide supra), a solution of 2 (0.80 mmol) in 10.0 mL of anhydrous acetonitrile was added to nitrosonium tetrafluoroborate (0.80 mmol). Analysis of the gas evolved gave a quantitative yield of nitric oxide.

For the NMR studies a different procedure was used to give a higher concentration of the dimer dication 7. Triphenylphosphine sulfide (1.0 mmol) was partially dissolved in 4.0 mL of anhydrous acetonitrile under nitrogen in a glovebag. A large excess of nitrosonium tetrafluoroborate (2.0 mmol) was added in one portion. After 45 min with occasional stirring, 2 had completely dissolved through reaction with $NO^+BF_4^-$, giving a light yellow solution and undissolved nitrosonium tetrafluoroborate. A ¹H NMR spectrum of this solution exhibited a multiplet 5.5-6.1 ppm downfield from acetonitrile. A ¹H NMR spectrum of 2 in acetonitrile exhibits a distinctly different multiplet 5.3-5.9 ppm downfield from acetonitrile.

Acknowledgment. R.L.B. gratefully acknowledges the support of the National Science Foundation (Grant PRM-8104443). M.P.D. gratefully acknowledges the support of the National Science Foundation (Grants CHE 76-01163 and 8041063) and the National Institute of Environmental Health Sciences (Grant ES 01673) for this work. We thank D. M. Hedstrand for his preliminary results with phosphorothionates.

Registry No. 1a, 126-68-1; 1b, 2464-03-1; 2, 3878-45-3; 3, 462-35-1; 4, 4403-51-4; 7, 84836-46-4; NO⁺·BF₄⁻, 14635-75-7; N-isopropylacetonitrilium tetrafluoroborate, 84836-47-5.

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