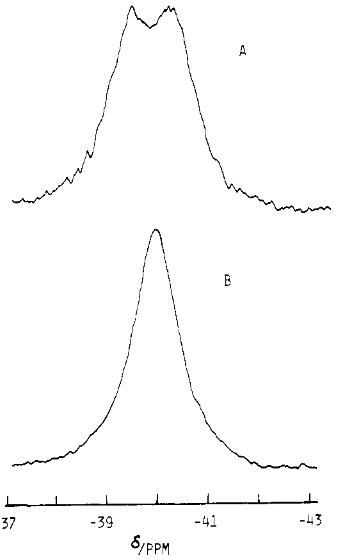

Figure 1. Boron-11 NMR spectrum of $[Fe(NOX)_3(BH)_2]$ vs. $BF_3 \cdot O(C_2H_5)_2$: (A) coupled; (B) proton decoupled.

slowly decomposes, producing a pale yellow solution as has been previously reported for similar clathrochelates without hydridic protons.[4] Nonetheless, a suspension of $[Fe(NOX)_3(BH)_2]$ in concentrated HCl that had been stirred for 16 h at 25 °C still yielded a product that contained an intact B–H bond (ν_{B-H} = 2485 cm^{-1}). This degree of acid stability is similar to that found in the $B_{12}H_{12}^{2-}$ anion and related compounds.[10]

Since the infrared and nuclear magnetic resonance studies show the parameters of the clathrochelate's B–H bond to be comparable to those of other more reactive B–H bonds, it is assumed that the unreactive nature of this bond lies in the steric constraints imposed by the rigid encapsulating ligand. Acid hydrolysis of BH_4^- has been shown to proceed through a five-coordinate BH_5 intermediate prior to loss of H_2, producing trigonal BH_3, which rapidly reacts to produce $B(OH)_4^-$, presumably proceeding through $H_2B(OH)_2^-$ and $HB(OH)_3^-$ intermediates.[11] Analogously, it is unlikely that the rigid clathrochelate ligand would readily distort to form pentacoordinate or even more so tricoordinate boron intermediates. In a sense the complex can be viewed as containing a "trapped" monohydroborato intermediate resulting from the "hydrolysis" of the starting borohydride.

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Electrochemical Oxidation of Zinc Bis(*O*,*O*-dialkyl phosphorodithioates-*S*,*S'*). Mediation by 1,1'-Bis(methoxycarbonyl)ferrocene

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Electrochemical oxidation of zinc bis(*O*,*O*-diethyl phosphorodithioate-*S*,*S'*) (**1a**) and zinc bis[*O*,*O*-bis(1-methylethyl) phosphorodithioate-*S*,*S'*] (**1b**) in CH_3CN at a glassy-carbon electrode (GCE) using cyclic voltammetry gave irreversible waves with peak potentials of +1.5 V (SCE). Constant-potential oxidation of **1a** at +1.4 V produced the disulfide *O*,*O*,*O*,*O*-tetraethyl thioperoxydiphosphate (**4a**) in nearly quantitative yield via a two-electron process. In contrast, constant-potential oxidation of **1b** at +1.4 V gave only low yields of its corresponding disulfide **4b** (ca. 30%) since **4b** was further oxidized at this potential. The oxidation of **1a** and **1b** at a GCE occurs with a large overpotential. This was demonstrated by oxidizing these compounds in the presence of 1,1'-bis(methoxycarbonyl)ferrocene, which undergoes a one-electron, reversible oxidation at a potential of +0.88 V. A large enhancement of current at this potential was observed when either **1a** or **1b** was added to a solution of this ferrocene mediator. In the presence of the mediator, **1b** could be oxidized at +0.90 V to its disulfide **4b** in high yields (85–90%).

Zinc bis[*O*,*O*-dialkyl(aryl) phosphorodithioates-*S*,*S'*] (**1**) have been widely used for quite some time as antioxidants and antiwear agents in lubricating oils. Since the early work of Kennerley and Patterson,[1] these compounds or their decomposition products have been known to catalyze the decomposition of hydroperoxides,[2–21] which are intermediates in the oxidation of hydrocarbons. In spite of numerous studies that have been directed at elucidating the

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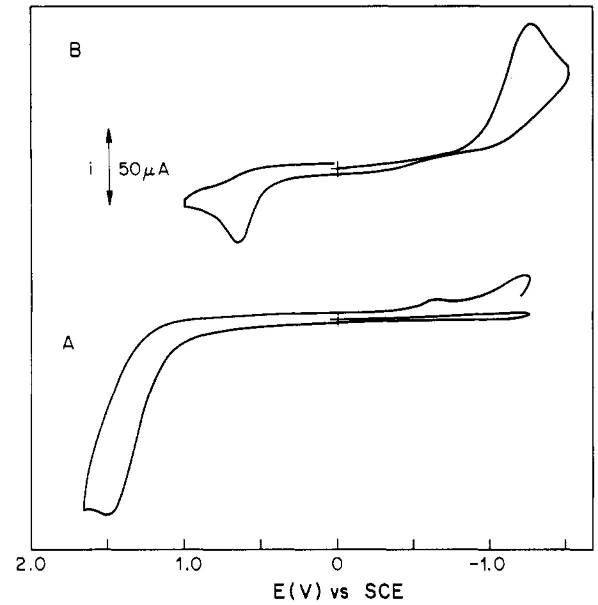

Figure 1. Cyclic voltammograms in CH_3CN (0.10 M $LiClO_4$) at 200 mV s^{-1}: (A) 2.0 mM zinc bis[*O,O*-bis(1-methylethyl) phosphorodithioate-*S,S'*] (**1b**); (B) 2.0 mM *O,O,O,O*-tetrakis(1-methylethyl) thioperoxydiphosphate (**4b**).

mechanism for this process, the precise pathway is not well understood. Earlier workers favored a scheme involving three stages.[3,9,10,18-20] Subsequently, evidence for an electron-transfer or S_H2 process between **1** and the peroxy radical was found.[3,4,16,22,24] More recently, however, it has been suggested that complexes **1** form the acids **2**, which are the species that actually catalyze the decomposition of hydroperoxides.[25-27]

$[(RO)_2PS_2]_2Zn$ $(RO)_2PS_2H$
1a, R = CH_3CH_2 **2**
1b, R = $(CH_3)_2CH$

Previous studies[13,15,17,19-21,23,24,28] have shown that zinc bis-[*O,O*-dialkyl(aryl) phosphorodithioates-*S,S'*] (**1**) are oxidized by hydroperoxides to hexakis[*O,O*-dialkyl(aryl) phosphorodithioato-*S,S'*]μ_4-oxotetrazinc complexes (**3**) and *O,O,O,O*-tetraalkyl(aryl) thioperoxydiphosphates (**4**) as shown in eq 1. Sexton

$$\mathbf{1} + R'OOH \rightarrow \underset{\mathbf{3}}{[(RO)_2PS_2]_6Zn_4O} + \underset{\mathbf{4}}{[(RO)_2PS_2]_2} + R'OH \qquad (1)$$

and co-workers[27] have shown that the disulfides **4** also promote the decomposition of hydroperoxides, possibly via the acids **2**.

In this work we examined the eletrochemical oxidation of zinc bis(*O,O*-diethyl phosphorodithioate-*S,S'*) (**1a**) and zinc bis[*O,O*-bis(1-methylethyl) phosphorodithioate-*S,S'*] (**1b**) at a glassy-carbon electrode (GCE). Our goal was to identify the products from this oxidation and provide some mechanistic insight into their formation. Furthermore, it was anticipated that this study would provide a basis for using electrochemical techniques in the quantitative analysis of **1** in hydrocarbon samples and thereby serve as an alternative to existing titration methods.[29,30]

Results and Discussion

Cyclic Voltammetry Studies. A cyclic voltammogram (CV) of a 2.0 mM solution of **1b** in CH_3CN containing 0.10 M $LiClO_4$ is shown in Figure 1A at a scan rate (v) of 200 mV s^{-1}. Under these conditions **1b** is irreversibly oxidized at a peak potential (E_p) of +1.50 V (SCE). On the reverse scan two cathodic waves are obtained at -0.64 and -1.24 V.

The oxidation process occurring at +1.50 V is diffusion controlled, as demonstrated by plots of i_p (peak current) vs. $v^{-1/2}$, which are linear.[31] E_p does not change with varying concentrations of **1b** (0.5-3.5 mM), which is consistent with a rate-determining step that is first order in **1b**. A plot of E_p vs. log v is linear with a slope of 77 mV/decade (r = 0.992). This rather large slope suggests that charge transfer at the electrode surface is followed by a homogeneous reaction (e.g., an EC process) that is quite fast.[32] The irreversibility of the wave at +1.50 V (Figure 1A) over a wide range of scan rates (v = 0.020-20 V s^{-1}) lends further support to this mechanistic picture.

The cathodic wave at -1.24 V in Figure 1A results from the reduction of *O,O,O,O*-tetrakis(1-methylethyl) thioperoxydiphosphate (**4b**), the oxidation product of **1b**. The CV of the disulfide **4b** in Figure 1B shows that this compound is irreversibly reduced at a -1.25 V potential. On the reverse anodic scan a wave at +0.66 V is obtained. Independent experiments showed that this anodic process is due to the oxidation of $[(CH_3)_2CHO]_2PS_2^-$.

The origin of the wave at -0.64 V in Figure 1A was not probed. One possibility is that it is the reduction of an intermediate formed in the conversion of **1b** to **4b**. Alternatively, it could be the reduction of an oxidation product of **4b**, since CVs of **4b** show that this disulfide begins to oxidize at ca. +1.4 V.

Cyclic voltammograms of compound **1a** are essentially identical with those of **1b** under the same conditions. With v = 200 mV s^{-1}, E_p for **1a** is +1.52 V.

Constant-Potential Oxidation. Constant-potential oxidations of 8-10 mM solutions of **1a** and **1b** were conducted in CH_3CN (0.10 M $LiClO_4$) at a carbon sponge. The choice of a potential for these electrolyses was not trivial. Ideally, the electrolyses for these compounds would be carried out at or slightly beyond their peak potentials (+1.5 V). However, the disulfides **4a** and **4b**, which are the primary products in the electrochemical oxidation of **1a** and **1b**, respectively, oxidize at this potential. Consequently, the constant-potential oxidations of **1a** and **1b** were initially examined at +1.4 V to minimize the formation of secondary oxidation products.

Oxidation of **1a** at +1.4 V gave the disulfide **4a** in an isolated yield of 95%, and 2 faradays/mol of charge was consumed in the electrolysis (corrected for background current). At the end of the electrolysis (40-60 min) the current no longer decreased with time and was only slightly higher than the background current.

In contrast, oxidation of **1b** at +1.4 V for 70 min gave only a 30% yield of **4b** and at least two other compounds that were not identified. A meaningful n value could not be obtained since the current after this period of time was nearly 10 times greater than the current of the CH_3CN electrolyte. These results can be accounted for if **4b** oxidizes at appreciable rates at this potential. Indeed, a CV of **4b** shows that this compound begins to oxidize in the vicinity of +1.4 V. Furthermore, a comparison of the CVs for **4a** and **4b** reveals that the former disulfide is oxidized at a potential nearly 50 mV more positive than that for **4b**, which could account for the fact that **1a** is rather cleanly oxidized to **4a** at the +1.4-V potential with minimal further oxidation.

Mediation by 1,1'-Bis(methoxycarbonyl)ferrocene. The oxidation of **1a** and **1b** at +1.5 V at GC occurs with a large over-

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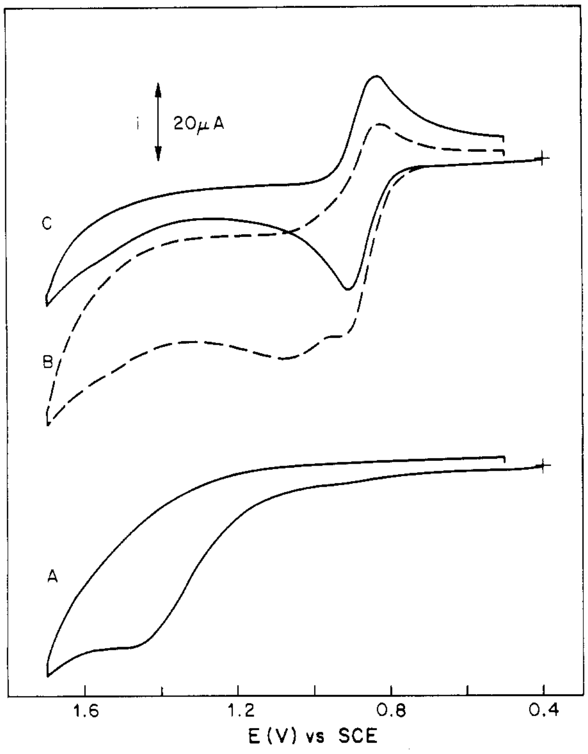

Figure 2. Cyclic voltammograms in CH_3CN (0.10 M $LiClO_4$) at 100 mV s^{-1}: (A) 1.0 mM **1b**; (B) 1.0 mM **1b** and 1.0 mM 1,1′-bis(methoxycarbonyl)ferrocene (**5**); (C) 1.0 mM **5**.

potential. This is demonstrated for **1b** in Figure 2 where CVs of 1.0 mM **1b** (A), 1.0 mM 1,1′-bis(methoxycarbonyl)ferrocene (**5**) (C), and a mixture of 1.0 mM **1b** and 1.0 mM **5** (B) are recorded with v = 100 mV s^{-1}. The ferrocene **5** undergoes a one-electron, reversible oxidation with $E^{\circ\prime}$ = 0.88 V. In the CV of the mixture (Figure 2B) significant enhancement of current occurs at the oxidative wave of **5** at a potential nearly 600 mV less positive than the E_p for **1b**. This shows that **5** acts as a mediator in the oxidation of **1b**. Similar results were obtained for **1a**.

In the presence of the ferrocene mediator, **1b** can be oxidized at potentials where oxidation of **4b** does not occur to an appreciable extent. Thus, oxidation of **1b** (6 mM) at +0.90 V in the presence of **5** (2 mM) for 180 min resulted in a 85–90% yield of **4b**. After correction was made for background current and the charge required to oxidize **5**, an n value of 2.0 was obtained. Equations 2 and 3 describe the mediated oxidation of **1**.

$$\mathbf{5} \xrightleftharpoons{E^{\circ\prime} = +0.88\text{ V}} \mathbf{5}^{+}\cdot + e^{-} \qquad (2)$$

$$2\,\mathbf{5}^{+}\cdot + [(RO)_2PS_2]_2Zn \rightarrow 2\,\mathbf{5} + Zn^{2+} + [(RO)_2PS_2]_2 \qquad (3)$$

In summary, we have shown that **1a** and **1b** are irreversibly oxidized at the GCE at a potential of +1.5 V. This charge-transfer process is irreversible due to a fast homogeneous reaction that follows, ultimately leading to the disulfides **4a** and **4b**, respectively. The details of this EC type process are not known. Whereas constant-potential oxidation of **1a** at +1.4 V gave **4a** in a nearly quantitative yield, **4b** was isolated in only low yields from **1b** due to further oxidation of **4b** at this potential. In the presence of the mediator 1,1′-bis(methoxycarbonyl)ferrocene both **1a** and **1b** were oxidized at +0.90 V to their corresponding disulfides in high yield.

Experimental Section

Electrochemical Measurements. Electrochemical experiments were performed with a Princeton Applied Research (PAR) potentiostat, Model 173, in conjuction with a PAR 175 universal programmer. Voltammograms were recorded on a Houston Model 2000 X-Y recorder at scan rates of 500 mV s^{-1} or less and on a Bascom-Turner Model 4120 Datacenter at scan rates greater than 500 mV s^{-1}. All potential measurements were referred to a saturated calomel electrode (SCE). It was necessary to separate the SCE from the CH_3CN test solution to prevent leakage of aqueous solution into the nonaqueous medium. This was accomplished by using in sequence a coarse glass frit, a 10-cm tube (0.5-cm diameter) containing a DMF (0.50 M $LiClO_4$)/methylcellulose gel followed directly by an aqueous agar (1.0 M NaCl), and a saturated KCl solution in which the SCE was suspended. A one-compartment cell was used in the cyclic voltammetry experiments. The working electrode was a glassy-carbon disk (A = 0.090 cm^{-2}) set in a Teflon tube. Prior to measurements on each solution this electrode was cleaned and polished with 0.30- and 0.050-μm α-alumina (Buehler), wiped with a tissue, and sonicated for 1–2 min. A graphite rod served as a counter electrode.

General Procedure for Constant-Potential Oxidations. A three-compartment cell was used for the electrolyses. The center compartment, containing a carbon sponge (pretreated by soaking in concentrated HNO_3 for 1–2 min, washing with deionized water, and drying in an oven at 150–200 °C), was separated from the reference electrode and counter electrode compartments by a glass frit (medium) and a DMF (0.50 M $LiClO_4$)/methylcellulose gel. The counter electrode was a carbon sponge (not pretreated), and the reference electrode, a SCE. Both the counter and reference electrode compartments contained CH_3CN (0.10 M $LiClO_4$). Approximately 10 mL of CH_3CN (0.10 M $LiClO_4$) was introduced into the center compartment. After deoxygenation with N_2, the background current was measured. The compound (**1a** or **1b**) or mixture (with **5**) to be oxidized was added (20–35 mg), and the resulting solution was again deoxygenated. After the electrolysis was completed, as evidenced by constant current with time, the contents of the center compartment were transferred to a separatory funnel with ca. 25 mL of CH_2Cl_2. The reaction mixture was extracted with 2 × 20 mL water. The CH_2Cl_2 solution was dried over $MgSO_4$ and stripped of solvent in a rotary evaporator under reduced pressure. The solid residue was chromatographed on silica gel and eluted with CH_2Cl_2. The first substance to be eluted from the column was either **4a** or **4b**.

Chemicals. CH_3CN was heated to reflux over CaH_2 for 6–10 h prior to distillation under N_2. The distillate was redistilled twice from neutral alumina (previously dried under vacuum at 150 °C) under N_2 and then stored under N_2. Lithium perchlorate (Aldrich Chemical Co.) and 1,1′-bis(methoxycarbonyl)ferrocene (Strem Chemicals, Inc.) were used without further purification.

Zinc bis(*O*,*O*-diethyl phosphorodithioate-*S*,*S*′) (1a) was prepared by the literature method.[33] Recrystallization (twice) from hexane gave colorless crystals, mp 72–73 °C (lit.[34] mp 77–79 °C).

Zinc bis[*O*,*O*-bis(1-methylethyl) phosphorodithioate-*S*,*S*′] (1b) was prepared by the literature method.[33] Recrystallization (twice) from hexane gave colorless crystals, mp 145–146 °C (lit.[34] mp 141–142 °C).

***O*,*O*,*O*,*O*-Tetrakis(1-methylethyl) Thioperoxydiphosphate (4b).** To a solution of 0.871 g of **1b** (1.77 mmol) in 15 mL of CH_3CN was added over a 10–15-min period 0.449 g of I_2 (1.77 mmol) in small portions. The reaction mixture gradually turned light yellow as the I_2 was added. The reaction mixture was combined with 35 mL of water, resulting in the precipitation of a light yellow solid. Recrystallization from hexane gave light yellow crystals in 92% yield; mp 91–92 °C (lit.[23] mp 91 °C).

***O*,*O*,*O*,*O*-Tetraethyl thioperoxydiphosphate (4a)** was prepared from **1a** and I_2 as described above for **4b** to give a pale yellow liquid in 94% yield; the IR spectrum coincided with the literature one.[35]

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Registry No. **1a** (cc entry), 16569-75-8; **1a** (salt entry), 7268-60-2; **1b** (cc entry), 28293-11-0; **1b** (salt entry), 2929-95-5; **4a**, 2901-90-8; **4b**, 3031-21-8; 1,1′-bis(methoxycarbonyl)ferrocene, 1273-95-6.

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