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Formation and Reactions of Dithiodicarbenium Salts

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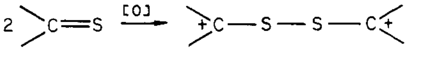
Abstract: The chemical oxidation and electrochemical oxidation of thioureas, thiocarbonates, and thioketones to stable dimeric dications that contain the disulfide linkage are reported. Cyclic voltammetry studies establish the stepwise electron-transfer oxidation of thiocarbonyl compounds to their corresponding monomeric radical cations, followed by addition to a neutral thiocarbonyl compound and one-electron oxidation of the resultant dimer radical cation. These dications, which are conveniently prepared by the oxidation of thiocarbonyl compounds with nitrosonium salts, possess an oxidatively active disulfide linkage coupled to terminal electrophilic centers. Their versatility as chemical oxidants is demonstrated by their reactions with amines, phosphines, silanes, alcohols, oxalate and formate salts, and potassium azodicarboxylate.

The activity of thiocarbonyl compounds toward chemical oxidants, particularly nitrous acid, is well established. Chemical oxidations of thioureas,[2-5] thiocarbonates,[6] and mono- and dithiocarbamates[7-9] produce relatively stable dimeric dications that contain the disulfide linkage (eq 1). The synthetic utility of this oxidative transformation has recently been demonstrated in the conversion of a 2(1*H*)-pyridinethione,[10a] isothiazolinethiones,[10b] and mono- and dithiocarbamates[10c] to their corresponding dimeric disulfides.



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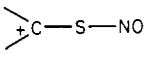
In his early studies of the reaction of nitrous acid with thiourea, Werner observed the initial formation of a colored solution that faded rapidly to produce isolable salts of the *C,C'*-dithiodiformamidinium dication,[11] whose structure has subsequently been established by X-ray crystallography.[12] Recently, Stedman reinvestigated the nitrous acid oxidation of thiourea and alkylthioureas[3] and concluded that the colored species previously observed by Werner is the *S*-nitroso adduct **2** which rapidly decomposes to nitric oxide and the *C,C'*-dithiodiformamidinium dication. Nitrosoamines have also been investigated as direct nitrosating agents of thiourea and alkylthioureas in acidic media, and oxidative dimerization has been similarly established.[2] The recently reported reversible chemical oxidation of 1,3-dithiolan-2-thione by nitrosonium tetrafluoroborate to 2,2'-dithiobis(1,3-dithiolanium) ditetrafluoroborate (**3**) and nitric oxide,[6] which results in the production of 1,3-dithiolan-2-one by nitrosative exchange of sulfur for oxygen (Scheme I), lends support to the intermediate formation of **2**. However, the precise nature of the electron-transfer processes in these reactions has not been established.



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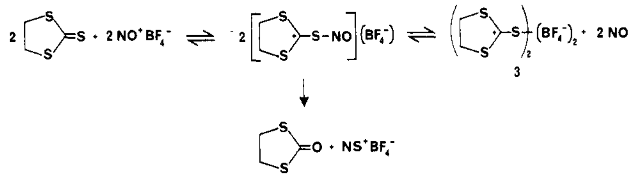
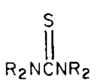
Scheme I



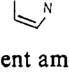
Although significant attention has been directed to the oxidation of thiocarbonyl compounds, reaction processes involving their disulfide products have not been reported. Dicationic disulfide salts such as **3** were anticipated to be novel oxidants and susceptible to nucleophilic reactions at either sulfur or carbon. We now report results that describe the generality of nitrosative oxidation of thiocarbonyl compounds, the mechanism of oxidative dimerization, and the reactions of disulfide dications toward a broad selection of reducing agents and nucleophiles.

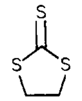
Results and Discussion

Nitrosative Oxidation of Thiocarbonyl Compounds. Treatment of a series of thiocarbonyl compounds that included representative thioureas (**4**), 1,3-dithiolan-2-thione (**5**), and thioketones (**6**) with an equivalent amount of $NO^+BF_4^-$ in anhydrous acetonitrile resulted in the immediate formation of nitric oxide and the corresponding dimeric disulfide dication **1**.[13] However, in each reaction nitrous oxide was formed in addition to nitric oxide, and the carbonyl compound corresponding to **4**, **5**, or **6** was produced as a minor constituent of the reaction mixture in amounts ranging from less than 5% to approximately 15%, based on the reactant thiocarbonyl compound. Reactions with thioureas generally resulted in the production of less than 5% of the urea, and only minor



4a, R = Me
b, R = Et
c, R_2N =





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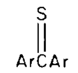

6a, Ar = C_6H_5
b, Ar = p-$CH_3OC_6H_4$

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[1] (a) Calvin College. (b) Hope College.

[2] (a) Williams, D. L. H. *J. Chem. Soc., Perkin Trans. 2* **1977**, 128. (b) Hallett, G.; Williams, D. L. H. *Ibid.* **1980**, 624.

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[11] Werner, E. A. *J. Chem. Soc.* **1912**, 2166, 2180.

[12] Foss, O.; Johnsen, J.; Tvedten, O. *Acta Chem. Scand.* **1958**, *12*, 1782.

[13] Compound **4c**, whose imidazole group inhibits oxidation both by association of the basic imidazole nitrogen with the nitrosonium ion and by destabilization of the dicationic oxidation product, was the only exception. Reaction of **4c** with $NO^+BF_4^-$ was slow, and the product formed by this oxidation was unstable.

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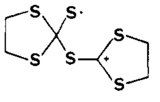
amounts of nitrous oxide were formed. Thioketones **6a** and **6b** and trithiocarbonate **5** exhibited similar behavior in nitrous oxide and carbonyl production.

Mechanistic analysis of the formation of nitrous oxide and carbonyl products has previously been described for the nitrosative oxidation of **5**[6] and is consistent with the mechanism outlined in Scheme I, where the thionitrosonium ion leads to the production of nitrous oxide. That thioureas produce only minor amounts of these products suggests that nitrosative exchange of sulfur for oxygen is not a significant process for these thiocarbonyl compounds. However, reversible oxidation is apparently characteristic of both **5** and **6**.

Electrochemical Oxidation of Thiocarbonyl Compounds. The electrochemistry of trithiocarbonates has been previously described as part of an effort to produce tetrathiofulvalenes and related tetrathioethylenes.[14] Anodic oxidation of **5** was reported to produce a dimer radical cation in the initial oxidation process. By analogy with the observed electrodimerization of trithiocarbenium ions,[14-16] the structure of the dimer radical cation formed from **5** was suggested to be **7** which slowly decomposed to **8** or could undergo one-electron reduction.[14] However, the electrochemical results could not distinguish between **7** and a disulfide radical cation.[14] Since, as a consequence of results obtained from nitrosative oxidation of thiocarbonyl compounds, structural interpretations could now be focused on the disulfide radical cation, we have examined the electrochemistry of the general class of thiocarbonyl compounds and their corresponding dicationic oxidation products by cyclic voltammetry.



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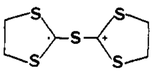

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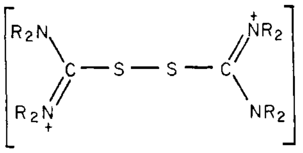
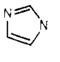
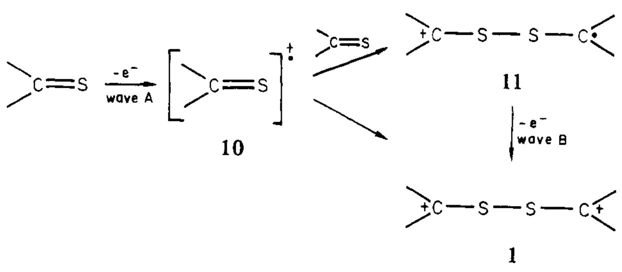
Tetraethylthiourea (**4b**) is readily oxidized at the surface of platinum in anhydrous acetonitrile solution containing tetra-*n*-butylammonium perchlorate (TBAP) as the supporting electrolyte. A cyclic voltammogram of **4b** (Figure 1a) exhibits two oxidative waves (A and B) and one cathodic wave (C) due to the reduction of an oxidation product. Waves A and B centered at 0.54 and 0.83 V (E_{Pt} vs. $Ag^+|Ag$), respectively, are irreversible up to scan rates of 20 V/s. Plots of peak current (i_p) vs. the square root of the scan rate ($v^{1/2}$) are linear for both of these waves, consistent with both of these oxidative processes being diffusion controlled.[17] The slope of the line for wave B is greater than that for wave A, which suggests that the species oxidized at B is derived from the oxidation of **4b** at A.

Figure 1b describes the cyclic voltammogram of **9b** prepared by nitrosative oxidation of **4b**. A single reduction wave is obtained at −0.5 V, which is irreversible up to scan rates of 20 V/s. The reduction wave has a peak area approximately twice that for an equimolar solution of *p*-benzoquinone, a substance that undergoes a reversible one-electron reduction. Interestingly, two oxidative waves are obtained on the reverse scan with peak potentials matching those for waves A and B from **4b**. Since the reduction process for **9b** at −0.5 V coincides with the peak potential of wave C obtained from **4b**, it is reasonable to conclude that the chemical oxidation of **4b** to **9b** is reversible.



9a, R = Me
b, R = Et
c, R = 

Scheme II



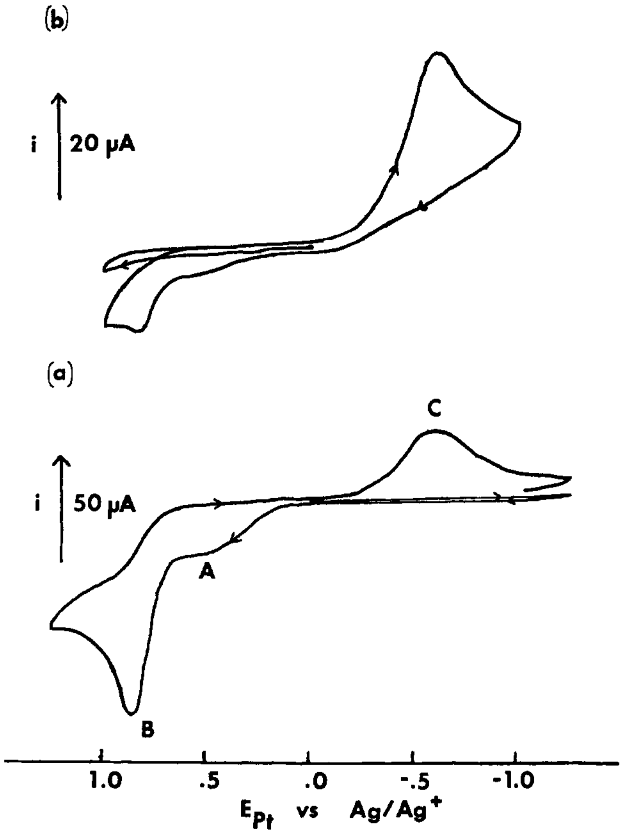


Figure 1. (a) Cyclic voltammogram of 2.5 mM **4b** in acetonitrile containing 0.1 M TBAP at a scan rate of 0.2 V s^{-1}. (b) Cyclic voltammogram of 1.0 mM **9b** in acetonitrile containing 0.1 M TBAP at a scan rate of 0.2 V s^{-1}.

The electrochemical oxidation of **4a** parallels that for **4b**. The cyclic voltammogram of **4a** exhibits two irreversible oxidation waves (up to 20 V/s) at 0.51 and 0.95 V and one reduction wave on the reverse scan at −0.51 V. The oxidation product reduced at −0.51 V is the dimeric dication, as shown by a cyclic voltammogram of **9a** prepared from **4a** with $NO^+BF_4^-$. The electrochemical behavior of **4c** is similar to that for **4a,b**, but the oxidation waves (A, shoulder; B, 1.06 V) and cathodic wave (C, −1.11 V) are significantly displaced from those observed for **4a** and **4b**. The anticipated relative instability of oxidation products from **4c** is reflected in these results and in the relatively low reactivity of **4c** with $NO^+BF_4^-$.

The electrochemical behavior of **4** and **9** suggests the oxidative electron-transfer mechanism that is outlined in Scheme II. Wave A is proposed to result from the oxidation of **4** to its highly reactive radical cation **10**. Dimerization of **10** occurs either directly by the coupling of two radical cations or by addition of **10** to a neutral thiocarbonyl compound followed by one-electron oxidation of the resultant dimeric radical cation **11**. As evidenced by wave B, the latter process (**10** → **11** → **1**) is the dominant pathway for the production of the dicationic product. Direct dimerization of **10** is suggested by experiments in which the anodic scan is reversed

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[14] Moses, P. R.; Chambers, J. Q.; Sutherland, J. O.; Williams, D. R. *J. Electrochem. Soc.* **1975**, *122*, 608.

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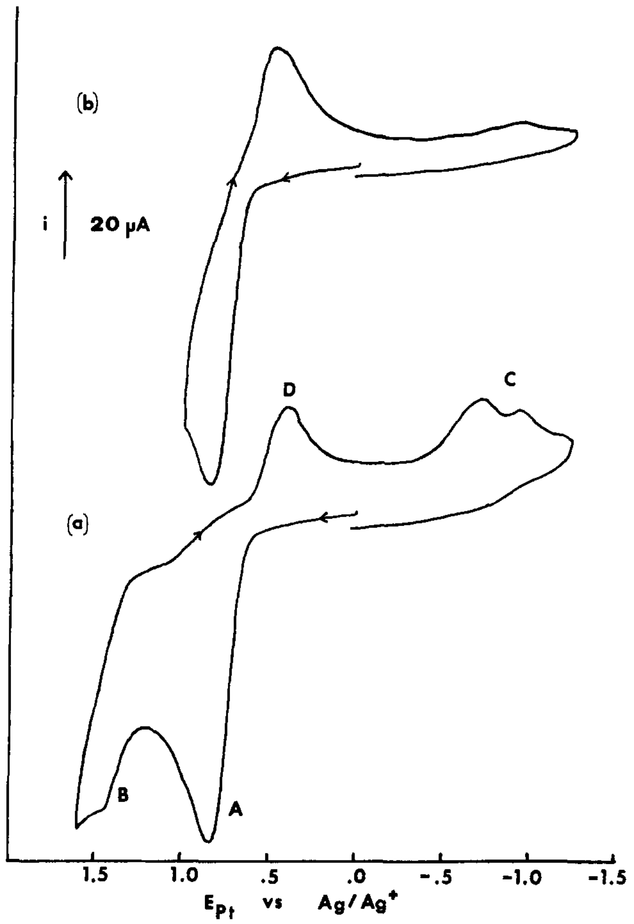


Figure 2. Cyclic voltammograms of 1.0 mM **5** in acetonitrile containing 0.1 M TBAP at a scan rate of 0.5 V s^{-1}.

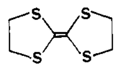
prior to wave B (at 0.55 V for **4b**; re. Figure 1) and wave C is observed, although at a considerably reduced current. An alternative scheme for the production of **1**, disproportionation of **11**, could also be considered, but we have no evidence for this unlikely process.

The mechanistic interpretation given in Scheme II differs from that offered by Chambers and co-workers,[14] who suggested direct oxidation of thiocarbonyl compounds to dimeric radical cations that we now interpret to have structure **11**. Their cyclic voltammogram for **5** exhibited one irreversible anodic wave at 1.08 V (E_{Pt} vs. SCE) and two irreversible cathodic waves on the reverse scan at 0.78 and −0.30 V, respectively, from which they concluded that the wave at 0.78 V resulted from the reduction of the dimeric radical cation. The wave at −0.30 V was assigned to a decomposition product of the dimeric radical cation.

The cyclic voltammograms for **5** that are described in Figure 2 indicate that electron-transfer processes for 1,3-dithiolan-2-thione are considerably more complex than previously envisioned. Figures 2a and 2b describe cyclic voltammograms that differ only in the anodic scan limit. When the anodic scan is extended to +1.6 V (E_{Pt} vs. Ag$^+$|Ag), as shown in Figure 2a, anodic waves A and B at 0.86 and 1.54 V, respectively, are obtained. These waves are irreversible up to scan rates of 20 V/s and result from diffusion-controlled processes. On reversal of the scan, three cathodic waves, two at C (−0.74 and −0.96 V) and one at D (+0.40 V), are obtained. If the scan is held at +1.5 V for 5–10 s and then continued, the current at D is considerably reduced and the waves at C are increased. When the scan is reversed at +1.0 V (Figure 2b), the current at D is markedly enhanced, and the waves at C (of which that at −0.96 V is the larger of the two) are barely detectable. If the scan is held at +0.90 V for 5–10 s and then reversed, the current at both D and C is increased.

The cyclic voltammogram for the dicationic salt **3** (Figure 3a), which exhibits a broad irreversible wave centered near −0.75 V and an anodic wave on the reverse scan at +0.90 V, allows assignment of the cathodic peak at −0.74 V in the cyclic voltammogram of **5** (Figure 2) to the reduction of this disulfide dimer. The anodic wave A is assigned to the oxidation of **5** to the corresponding monomeric radical cation and the wave at B to oxidation of the corresponding dimer radical cation. The absence of a wave at D in the cyclic voltammogram of **3** is noteworthy since the current function of D has been observed to parallel that of A at increasing sweep rates, whereas the current function for C falls off to zero at sweep rates greater than 0.1 V/s.[14]

The origin of the cathodic waves at +0.40 V (D) and −0.96 V (C′) for the electrochemical oxidation of 1,3-dithiolan-2-thione, whose counterparts are not observed in the cyclic voltamograms of thioureas, is not clear. They do not correspond to the tetrathioethylene **12**,[18] nor are they derived from solvent association,[14] although wave D is not observed on the cyclic voltammogram for **5** in nitromethane. In view of the unique relationship between



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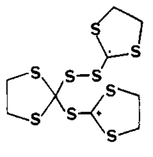
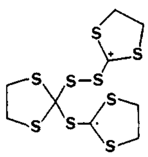
waves A and D that is described by their parallel current functions, however, it is conceivable that wave D is due to the reduction of the dimer radical cation or of an extended trimer radical cation (**13**) or oligomer and that the wave at −0.96 V is due to reduction

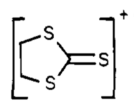


13a



13b

of an extended dication whose structure parallels that of **13** or a corresponding oligomer. An extended dication is consistent with the lower reduction potential wave at C (−0.96 V vs. −0.74 V) and with the observed contributions of these waves at variable scan rates. An extended dication could be formed by electron transfer from **13**, but the dimeric dication **3** could be produced by chemical interaction of the monomeric radical cation with **13** (eq 2) as well as by electron-transfer oxidation of the dimeric



+ **13** ⟶ **3** + 2**5** (2)

radical cation. As evidenced by the fall off to zero of the current function for peak C at high sweep rates, direct dimerization of the monomeric radical cation can be assumed to be negligible.

In agreement with the proposed involvement of radical cation trimers (**13**) or oligomers and the corresponding oxidized trimer or oligomer dication, cyclic voltammetric investigations of solutions containing dication **3** to which variable amounts of 1,3-dithiolan-2-thione were added provided similar voltammograms, of which one is exhibited in Figure 3b. Anodic wave A is not observed even when a twofold excess of **5**, relative to dication **3**, was employed, which indicates the absence of unassociated 1,3-dithiolan-2-thione. Furthermore, wave C′, which was absent in the voltammogram of **3** (Figure 3a) but prominant in Figure 2a, is again observed in voltammograms of solutions obtained by combining **3** with **5**, which is consistent with the proposed oligomerization of **11**. The position of wave D varied with the relative concentration of **5**. Further evidence for the existence of trimer or oligomer dications is suggested in the ^{13}C NMR spectra of **3** in the absence of and in combination with **5** (see Experimental Section).

The cyclic voltammetric behavior of **6b** closely resembles that for **5** and suggests parallel behavior for these two thiocarbonyl compounds. The composite electrochemical results for **4**–**6** are summarized in Table I and provide an interesting contrast in oxidative capabilities for the dimeric dications (C) and in the

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[18] Coffen, D. L.; Chambers, J. Q.; Williams, D. R.; Garrett, P. E.; Canfield, N. D. *J. Am. Chem. Soc.* **1971**, *93*, 2253.

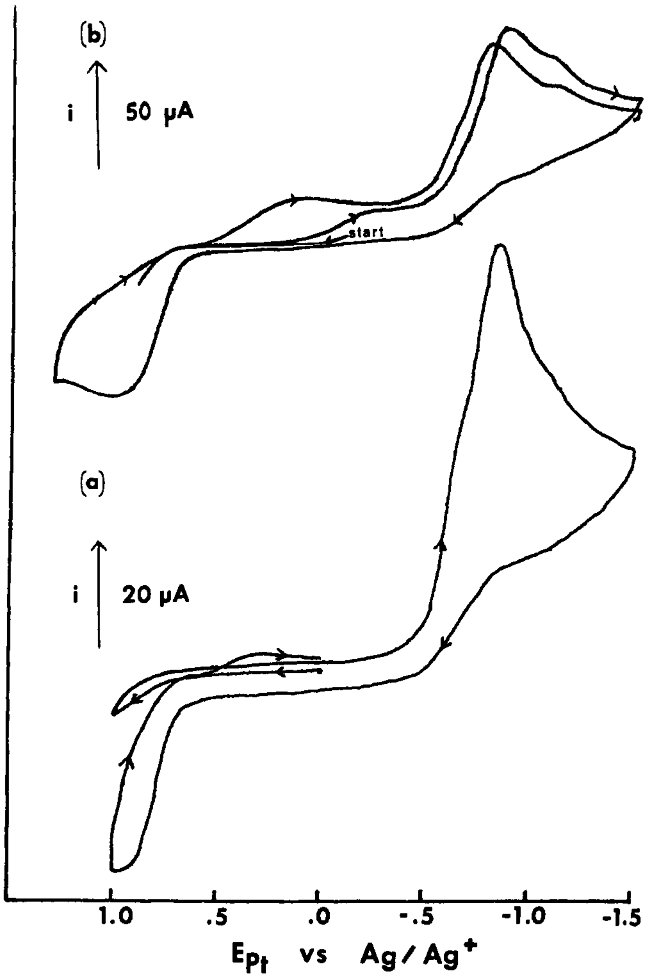


Figure 3. (a) Cyclic voltammogram of 1.0 mM **3** in acetonitrile containing 0.1 M TBAP at a scan rate of 0.2 V s^{-1}. (b) Cyclic voltammogram of a solution prepared by adding 0.50 equiv of **5** to 2.0 mM **3** in acetonitrile containing 0.1 M TBAP. Scan rate: 0.2 V s^{-1}. The observed waves are displaced from those in Figure 2 as a result of an electrode surface modification when the solution is oxidized. Increased displacements are observed at higher ratios of **5** to **3**. However, in the limit as the concentration of **5** approaches zero the displacement from −0.74 V approaches zero.

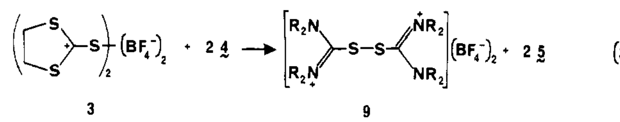
Table I. Peak Potentials for the Electrochemical Oxidations of Thiocarbonyl Compounds[a]

	E_{Pt} vs. Ag|Ag$^+$, V				
compd	A	B	C	C′	D′
4a	0.51	0.95	−0.51		
4b	0.54	0.83	−0.45		
4c	sh	1.06	−1.11		
5	0.86	1.54	−0.74	−0.96	0.40
6b	0.72	1.19	−0.73	−0.94	0.15

[a] Obtained from cyclic voltammograms as outlined in Figures 1-3.

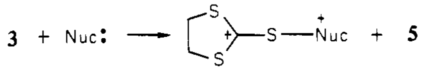
relative stabilities of their corresponding dimeric radical cations (B).

Chemical Transformations of Disulfide Dications. Consistent with the relative reduction potentials of disulfide dications and the oxidation potentials of thiocarbonyl compounds (Table I), reaction of **3** with an equivalent amount of thiourea **4a** or **4b** quantitatively produced the *C,C′*-dithiodiformamidinium dications **9a** or **9b** (eq 3). 1,3-Dithiolan-2-thione (**5**) was quantitatively displaced in this exchange process that presumably involves sequential displacement of **5** from **3** and then from the mixed function dication.


(3)

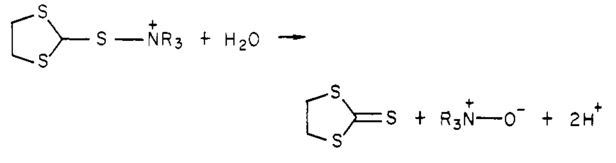
3 9

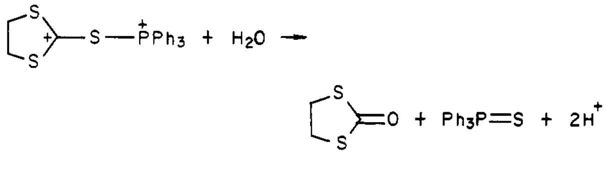
Nucleophilic chemical exchange is a characteristic transformation of **3**. Tertiary amines and triphenylphosphine displace **5** from **3** to form derivative dications (**14**) upon which 1,3-dithiolan-2-thione remains in rapid equilibrium (eq 4). Addition


(4)

14

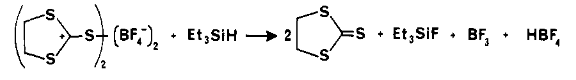
of water to **14** (Nuc: = R_3N:) results in the immediate production of **5** and the N-oxide corresponding to the reactant amine (eq 5), whereas for **14** (Nuc: = Ph_3P:) the addition of water produces triphenylphosphine sulfide and 1,3-dithiolan-2-one (eq 6). Thus,


(5)


(6)

nucleophilic reactions with **14** appear to proceed by attack at nitrogen rather than at carbon (**14**, Nuc: = R_3N:) and at carbon rather than at phosphorus (**14**, Nuc: = Ph_3P:), and these results provide a clear indication of the relative P=S, C=S, and $^+$N—S$^-$ bond strengths. Triphenylphosphite parallels triphenylphosphine in its reaction with **3** and in the subsequent reaction of the derivative dication with water that yields the corresponding thiophosphate.

The activity of **3** toward reducing agents is exemplified in its reactions with triethylsilane and potassium azodicarboxylate. Addition of triethylsilane to **3** results in the immediate and quantitative production of 1,3-dithiolan-2-thione and triethylsilyl fluoride (eq 7), presumably by hydride transfer to the electrophilic


(7)

carbon center[19,20] that occurs with fluoride transfer to silicon.[21,22] Potassium azodicarboxylate, whose reductive capabilities have only recently been recognized,[23] also quantitatively converts **3** to **5** together with the evolution of carbon dioxide and nitrogen in the stoichiometric ratios that are described in eq 8. These novel

$$3 + K^{+-}OOCN{=}NCOO^{-}K^{+} \rightarrow 2\,5 + 2CO_2 + N_2 + 2KBF_4 \quad (8)$$

transformations, which are indicative of the oxidative capability of a species in which an oxidatively active disulfide linkage is coupled to terminal electrophilic centers, suggests the broad versatility of disulfide dications (**1**) as chemical oxidants.

The stability of dithiodiformamidinium dication salts in aqueous acidic media has been previously established.[2,3,5] In contrast, the less stable 2,2′-dithiobis(1,3-dithiolanium) salt **3** readily reacts with water to form nearly equivalent amounts of 1,3-dithiolan-

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(19) Carey, F. A.; Tremper, H. S. *J. Org. Chem.* **1971**, *36*, 758 and previous papers in this series.

(20) Doyle, M. P.; McOsker, C. C.; West, C. T. *J. Org. Chem.* **1976**, *41*, 1393.

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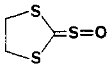
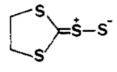
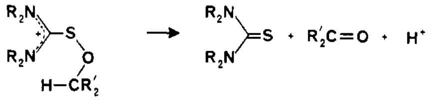
2-thione and 1,3-dithiolan-2-one. These products are suggested to arise from **3** through displacement of **5** by the nucleophilic water, followed by hydrolytic conversion of the resultant intermediate to 1,3-dithiolan-2-one. Disproportionation of the product formed by water displacement of **5** from **3**, analogous to that observed in reactions of formamidinium salts with hydroxide ion,[5] accounted for at most a minor fraction of the reaction process. We had anticipated the formation of the S-oxide **15**, which is normally stable to solvolytic conditions,[24-26] but this compound exhibited only fleeting existence and was evident only as a minor component of the reaction mixture. An alternate route, which would have involved water displacement of the disulfide functional group from carbon in **3** to produce ylide **16**, is excluded by the absence of elemental sulfur as a product from this hydrolytic reaction and by the absence of alkene insertion products from hydrolytic reactions of **3** in the presence of excess olefin.


15


16

Treatment of **3** with benzyl alcohol resulted in the production of benzyl ether, but not benzaldehyde as might have been anticipated from the hydride acceptor capability of **3** (eq 7). Benzyl ether is presumed to arise by a process that extends that for hydrolysis of **3**, but the involvement of other mechanisms such as acid-catalyzed dehydration cannot be discounted. Surprisingly, benzaldehyde is formed, albeit in only 30% yield, by the reaction of benzyl alcohol with **9b** in refluxing acetonitrile. With **3** under similar conditions, no trace of benzaldehyde is observed, even though this dication is the more powerful reactant. The cause of this disparate behavior can be understood to be the result of the involvement of an internal nitrogen base in **17** that serves as a proton acceptor (eq 9). The base site is not present in the analogous alcohol adduct with **3**.

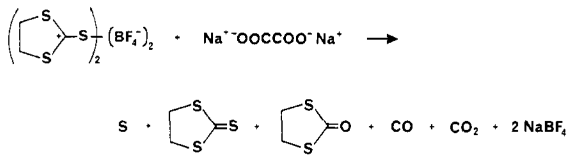


(9)

17

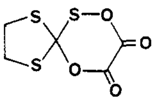
Alcohol oxidations by disulfide dications are related to processes that involve the production of intermediate sulfoxonium salts which are readily converted to carbonyl compounds upon treatment with a weak base.[27,28] By analogy, acetophenone was produced from 1-phenylethanol and **9b**, but only after pyridine was added to the reaction solution. Our efforts are continuing in this area; however, the present results indicate that intermediates such as **17** are involved in these transformations, and they do establish that proton abstraction occurs from carbon bonded to oxygen in the carbonyl formation step.

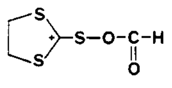
The oxidation of oxalate and formate salts by disulfide dictions provides further evidence for their versatility as oxidants. Treatment of **3** with an equivalent amount of anhydrous sodium oxalate results in the immediate and quantitative evolution of carbon dioxide and carbon monoxide and in the production of 1,3-dithiolan-2-thione, 1,3-dithiolan-2-one, and sulfur (eq 10).



(10)

This reaction process presumably involves nucleophilic displacement of **5** from **3** by oxalate, and **18** represents an attractive intermediate from which all of the principal products could be formed. The reaction of **3** with anhydrous sodium formate resulted in the production of **5** and carbon dioxide, presumably via intermediate **19**. However, attempts to extend these processes to ethylene formation by the reaction of **3** with succinate salts and of carbenium ion production by the reaction of **3** with triphenylacetic acid did not product the desired results.


18


19

Disulfide dications, which are conveniently prepared from thiocarbonyl compounds by treatment with nitrosonium salts, represent a new class of oxidatively active reagents whose versatility is suggested by the results presented in this investigation. The ease of formation of *S*-thionium derivatives such as **14** and their activity in oxidative processes indicates their suitability for a broad spectrum of chemical transformations.

Experimental Section

Instrumentation. Proton magnetic resonance spectra were obtained with Varian Models A-60A and FT-80A spectrometers; ^{13}C NMR spectra were recorded from the Varian FT-80A spectrometer. Chemical shifts are reported in δ units, using tetramethylsilane as the internal standard. Infrared spectra were obtained on a Perkin-Elmer Model 621 grating spectrophotometer. Analytical gas chromatographic analyses were performed on a Varian Aerograph Model 2720 gas chromatograph with thermal conductivity detectors; gas analyses were performed with a 5-ft column of 5 Å molecular sieves. The Finnigan Model 1015 GC/MS spectrometer operated at 70 eV was employed for mass spectral analyses. Melting points were obtained on a Thomas-Hoover apparatus and are uncorrected. Elemental analyses were performed by Galbraith Laboratories, Knoxville, Tenn.

Cyclic voltammetry experiments were performed with use of a MPI potentiostat and wave generator with a conventional three-electrode cell. The working electrode was a platinum bead, the counterelectrode was a platinum wire coil, and the reference electrode was a silver wire immersed in an acetonitrile solution of 0.10 M AgNO$_3$. The reference electrode was separated from the sample by two glass frits and a solution of acetonitrile containing 0.10 M tetra-*n*-butylammonium perchlorate (TBAP).

Materials. The thiocarbonyl compounds that were commercially available were purified by distillation, recrystallization, or, in the case of **4c**, sublimation prior to their use. Thiobenzophenone was prepared from benzophenone by the standard procedure.[29] Potassium azodicarboxylate was prepared by the hydrolysis of azodicarbonamide in 50% aqueous potassium hydroxide,[30] dried under vacuum with use of phosphorus pentoxide, and stored under dry nitrogen in a vacuum desiccator. Nitrosonium tetrafluoroborate was stored in a vacuum desiccator at 25 torr over phosphorus pentoxide prior to use. Acetonitrile was distilled from calcium hydride and stored over molecular sieves. Tetra-*n*-butylammonium perchlorate was purified according to the literature method.[31]

Reactions of Thiocarbonyl Compounds with Nitrosonium Tetrafluoroborate. General Procedure. Nitrosonium tetrafluoroborate (5.0 mmol) and 2.0 mL of anhydrous acetonitrile were placed in an oven-dried 25-mL three-necked flask fitted with a reflux condenser, addition funnel, and gas outlet tube. After placing the thiocarbonyl compound (5.0 mmol) dissolved in acetonitrile in the additional funnel, the entire reaction system was flushed with an inert gas, usually nitrogen. Dropwise addition of the thiocarbonyl compound to the nitrosonium salt caused immediate evolution of gas and a change in the color of the reaction solution from light yellow to a dark orange-red that is characteristic of the S-nitrosyl adduct.[3a] Interuption of the addition caused gas evolution to cease and the color of the reaction solution to fade to pale yellow. Continuation of the addition caused a return to the orange-red color and a resumption of gas evolution. Total gas evolution was measured on the closed system by water displacement from a calibrated gas buret. Nitric oxide was identified as the principal gaseous constituent collected by water dis-

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placement through infrared and gas chromatographic analyses; nitrous oxide was a minor constituent of the gaseous product (<5% for reactions with **4**, 10–15% with **5** or **6**).

The physical and chemical characteristics of products formed by nitrosative oxidation of **4a** and **4b** were identical with those previously reported.[3a,5,32] Thiourea **4c** reacted more slowly with $NO^+BF_4^-$ than either **4a** or **4b** to produce nitric oxide and a product whose spectrum was interpreted to be that of **9c**: ^1H NMR (CD_3CN) δ 8.33 (t, J = 0.9 Hz, H-2), 7.70 (t, J = 1.7 Hz, H-5), 7.24 (d of d, J = 0.9, 1.7 Hz, H-4). Further characterization of this unstable compound was not performed.

When 1,3-dithiolan-2-thione was added to nitrosonium tetrafluoroborate in the manner described in this procedure, a white solid precipitated from the acetonitrile solution. The limited solubility of this material (~3 g/100 mL of acetonitrile) facilitated its isolation and recrystallization: mp (sealed tube) 105 °C dec. Spectral measurements were consistent with the proposed structure **3**: ^1H NMR (CH_3CN) δ 4.47 (s); IR (Nujol) 1200–800 cm^{-1} ($\nu_{BF_4^-}$); UV (CH_3CN) transparent above 250 nm; ^{13}C NMR (CD_3CN) δ 49.2 (CH_2). Trithiocarbonate **5** exhibits absorptions at δ 231.2 (quaternary C) and 45.1 (CH_2) in CD_3CN. The ^{13}C NMR spectrum of **3** in the presence of **5** did not exhibit absorptions at either δ 49.2 or 45.1, but did describe an absorption at δ 47.1 that we attribute to the extended dication trimer derived from **13**. The quaternary carbon of **3** could not be distinguished from background prior to decomposition of the salt. Elemental analyses obtained for this air- and water-sensitive compound following several recrystallizations agreed with the molecular formula of the disulfide dication salt **3**.

Anal. Calcd for $C_6H_8B_2F_8S_6$: C, 16.15; H, 1.81; F, 34.07; S, 43.12. Found: C, 16.53; H, 1.97; F, 34.09; S, 43.53.

Results from elemental analyses of the product formed by nitrosative oxidation of **5** were dependent on the relative amount of the nitrosonium salt that was employed. When $NO^+BF_4^-$ was in excess of **5** the reported analysis was obtained. When **5** was in excess of $NO^+BF_4^-$, analyses were obtained that approached the composition of the trimeric dication produced from **13**, but attempts to prepare this compound as a stable product were not successful.

The products derived from nitrosative oxidation of **6a** and **6b** were characterized by NMR spectroscopy and from their carbonyl reaction product formed upon treatment with water. Dication from **6a**: ^1H NMR (CH_3CN) δ 7.9–7.3 (m). Dication from **6b**: ^1H NMR (CD_3CN) δ 7.95 (d, J = 9.0 Hz, 2 H), 7.18 (d, J = 9.0 Hz, 2 H), 7.97–7.78 (m, 2 H), 7.37–7.16 (m, 2 H), 4.07 (s, 3 H), 3.85 (s, 3 H).

Cyclic Voltammetry of 4–6. Solutions were prepared and introduced into the electrochemical cell under nitrogen in a glove bag. All cyclic voltammograms were performed in a solution of 0.10 M TBAP in acetonitrile maintained under an inert atmosphere. Sufficient sample was dissolved in the acetonitrile solution to give substrate concentrations of 0.50–3.0 mM. Concentration changes had little effect on the cyclic voltammograms of the compounds studied. Repetitive scans produced reproducible cyclic voltammograms.

Exchange Reactions of 3. Treatment of **3** (usually 2 mmol) in anhydrous acetonitrile (10 mL per mmol of **3**) with either **4a** or **4b** resulted in the immediate and quantitative production of **5**, based on the thiourea, and **9a** or **9b**, respectively. With triphenylphosphine, triethylamine, triisopropylamine, or triphenylphosphite, **3** produced new cationic species together with an equivalent amount of 1,3-dithiolan-2-thione. The production of **5** was monitored by observing its characteristic NMR absorption at δ 4.0 (CH_3CN).

Addition of an equivalent amount of triphenylphosphine to **3** resulted in a cationic species characterized by NMR absorptions at δ 8.1–7.6 (m, 15 H) and 4.35 (s, 4 H). When less than an equivalent amount of triphenylphosphine is employed, the chemical shift of the ethylene absorption is dependent on the molar ratio of Ph_3P to **3**. Addition of water to the mixed dication produced 1,3-dithiolan-2-one[33] and triphenylphosphine sulfide, which were identified by comparison with independently prepared authentic samples.

Treatment of **3** with tertiary amines resulted in the production of ammonium analogues of **14** which, following the addition of water, yielded **5** and corresponding tertiary amine oxides quantitatively. The NMR spectrum of the reaction solution following treatment of **3** with triethylamine exhibited characteristic absorptions at δ 4.32 (s, 4 H), 3.21 (m, 6 H), and 1.27 (t, 9 H). Excess triethylamine resulted in the production of a new absorption at δ 4.07 at the expense of that at δ 4.32. Similar results were obtained with tri-*n*-propylamine.

Reactions of **3** with triphenylphosphite formed a cationic product that did not exhibit the spectral characteristics of a rapid equilibrium between this product and **5** (eq 4), as did triphenylphosphine and the tertiary amines. The NMR absorption attributed to **5** (δ 4.00) was distinct, and new absorptions at δ 7.7–6.8 (m, 15 H) and 4.27 (s, 4 H) were clearly evident. Treatment of this reaction mixture with water produced triphenylthiophosphate and 1,3-dithiolan-2-one quantitatively.

Reaction of 3 with Potassium Azodicarboxylate. Treatment of **3** (2.5 mmol) in 25 mL of anhydrous acetonitrile with an equivalent amount of solid potassium azodicarboxylate at 25 °C, after thoroughly flushing the reaction system with helium, resulted in immediate gas evolution. Gas evolution was monitored as earlier described. Molecular nitrogen and carbon dioxide were the only gaseous products, and their molar ratio (1:2) remained constant throughout the addition. Trithiocarbonate **5** was the only organic product.

Reaction of 3 with Triethylsilane. Treatment of **3** (2.5 mmol) in 25 mL of anhydrous acetonitrile with a molar equivalent of triethylsilane resulted in the immediate conversion of **3** to **5** and in the production of triethylsilyl fluoride.[22]

Reactions with Water and Alcohols. Dication **3** is converted to an equimolar mixture of 1,3-dithiolan-2-one and **5** by treatment with an equivalent amount of water. The existence of **15** in minute amounts was suggested in several reaction solutions by the presence of an NMR absorption at δ 3.3 and an IR absorption at 1005 cm^{-1}, which has been attributed to the oxythiocarbonyl group,[24] but no further effort was taken to isolate this minor product.

Reaction of **3** with an equivalent amount of benzyl alcohol did not produce benzaldehyde even when the acetonitrile reaction solution was heated at reflux for 2 h. Benzyl ether was the only identifiable product. However, **9b** converted benzyl alcohol to benzaldehyde in 30% yield after 2 h at the reflux temperature; no reaction had been evident at 25 °C. Benzyl ether was formed in a competing process along with the carbonyl derivative of the reactant dication. 1-Phenylethanol was unreactive with **9b** even after refluxing the acetonitrile solution for 12 h; however, upon the addition of an equivalent amount of pyridine, acetophenone was produced in 40% yield.

Reactions with Formate and Oxalate Salts. Addition of an equivalent amount of solid sodium formate to an anhydrous acetonitrile solution of **3** at 25 °C resulted in the immediate evolution of carbon dioxide and in the formation of **5**. Gas evolution was monitored as previously described.

After thoroughly flushing the reaction system with helium, addition of an equivalent amount of sodium oxalate to **3** at 25 °C resulted in the immediate evolution of 2.0 equiv of gaseous products. Carbon monoxide and carbon dioxide were identified by spectroscopic methods as the only gaseous products, and the ratio of carbon dioxide to carbon monoxide (1:1) remained constant throughout the addition. Equivalent amounts of 1,3-dithiolan-2-one and **5** were produced. Elemental sulfur, formed as a yellow precipitate, was quantified by its conversion to barium sulfate.

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