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OXIDATION AND OTHER PRODUCTS FROM THE REACTION OF THIONES AND PHOSPHINE SULPHIDES WITH METAL SALTS AND HALOGENS

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A. INTRODUCTION

Metals and their complexes have found extensive use in organic chemistry to assist in a variety of organic syntheses [1]. One class of reaction is the interaction of compounds containing the thiophosphoryl ($\equiv$PS) or thiocarbonyl ($>$CS) moieties with reducible metal ions and pseudo-metals (i.e. halogens). In many cases oxidation of the organic substrate leads to interesting and novel sulphur containing compounds. It is only in the past decade that the structures of many of the products have been fully elucidated, particularly with the aid of full X-ray structural analyses.

Both the thiophosphoryl and thiocarbonyl moieties can be regarded as having a formally divalent sulphur atom bound to either a phosphorus or carbon atom. Although a 3*p* orbital on the sulphur is available for overlap with a 3*d* orbital on the phosphorus (to give a 3*p*—3*d* π bond) or with a 2*p* orbital on the carbon (resulting in a 3*p*—2*p* π interaction) the importance of the π component has been the subject of some discussion. Structural and spectroscopic evidence points to both the thiophosphoryl [2] and thiocarbonyl [3] bonds having some double bond character (Ib) and (IIb) respectively, but the exact nature of a particular bond will depend on the substituents attached to the phosphorus or carbon atoms. The valence bond representations (Ia) and (IIa)

$$\geqslant P^+{-}\underset{\cdot\cdot}{\ddot{S}}{:}^- \qquad \geqslant P{=}\underset{\cdot\cdot}{\ddot{S}} \qquad \gt C^+{-}\underset{\cdot\cdot}{\ddot{S}}{:}^- \qquad \gt C{=}\underset{\cdot\cdot}{\ddot{S}}$$

(Ia) (Ib) (IIa) (IIb)

emphasise the strongly polar nature of the bonds and the nucleophilic character of the sulphur atom.

Such compounds or their oxidation products have found application in a variety of situations. Especially important are the tetraalkylthiuram disulphides [4] and the related dithiocarbamates which are used as antioxidants in rubber products, as accelerators for the cross linking of rubber and in agriculture as fungicides. Tetraethylthiuram disulphide (Antabuse) [5] is employed in the treatment of alcoholism. Thioureas [6] have found use as antiseptics, as pesticides and in photography, and the importance of dithizone [7] as an analytical reagent for the determination of metal ions is well known. The major interest in dithiolylium salts [8] has been in the dye industry and a number of patents describe uses of tertiary phosphine sulphides [9] as extractants for metal ions, as herbicides and as antioxidants. The presence of these compounds, or related ones, in our everyday environment, merits a discussion of an important aspect of their chemistry.

This article will review the oxidation of a selection of these compounds by metal ions and halogens and in addition will consider the significance of such features as the nature of the oxidising agent, the reaction conditions and the substituent bound to the CS carbon or the PS phosphorus, in determining the course of the reaction. Where relevant, comparisons will be made with the oxygen and selenium analogues. The ability of tetraalkylthiuram disulphides to be either reduced at the disulphide linkage or oxidised at the thione sulphur, will also be discussed.

B. MONOTHIONES AND PHOSPHINE SULPHIDES

(i) Tertiary phosphine sulphides

Alkyl and aryl tertiary phosphine sulphides (III) form 1 : 1 adducts (IV) with iodine in chloroform solution [10—12], (for examples see Table 1).

$$R_3P{=}S + I_2 \rightleftharpoons R_3P{=}S \rightarrow I_2$$

(III) (IV)

(e.g. R = Me, n-Bu, Ph, cyclohexyl or naphthyl)

TABLE 1

Representative thermodynamic data for 1 : 1 iodine complexes

Donor	Solvent	Temp. (°C)	K(dm^3 mol^{-1})	$-\Delta H°$ (kJ mol^{-1})	Ref.
$Ph_3P{=}O$	CCl_4	25	33	18.8	14
$Ph_3P{=}S$	CCl_4	25	160	30.5	14
$Ph_3P{=}Se$	CCl_4	25	2800	38.5	14
$Me_3P{=}S$	$CHCl_3$	25	604		11
$(n\text{-}Bu)_3P{=}S$	$CHCl_3$	25	59		11
$(H_2N)_2C{=}S$	$CHCl_3$	25	4400	40.2	15
$(Me_2N)_2C{=}O$	CCl_4	25	6.5	18.4	16
$(Me_2N)_2C{=}S$	CH_2Cl_2	20	49000	37.7	17
	$CHCl_3$	25	13560	39.7	18
	n-Heptane	20	13000	41.4	17
	CCl_4	25	8000	43.9	19
$Me(H_2N)C{=}S$	CCl_4	20	11500		20
$Me(Me_2N)C{=}S$	CCl_4	20	1990	40.8	21
Thiocamphor	Cyclohexane	25	95	46.0	15
$Me_2C{=}O$	Cyclohexane	25	0.8		15
$[Me_2N(C{=}S)S]_2$	CCl_4	20	152	30.0	21

In the case of the phenyl- and naphthylphosphine sulphides, crystalline complexes have been isolated [10,12]. That sulphur—iodine coordination had occurred was indicated by the observed shifts in the IR ν(PS) absorption bands and confirmed by an X-ray structural study [13] on the blue-black crystalline triphenylphosphine sulphide adduct (V)

$$Ph_3P{=}S \rightarrow I_2{\cdots}I_2{\cdots}I_2 \leftarrow S{=}PPh_3$$

(V)

which contains two phosphine sulphide—iodine complexes linked as a dimer by a third iodine molecule. As compared with the values found for the free molecules, both the P—S bond (at 2.02 Å) and the I—I bond (at 2.86 Å) (for the sulphur coordinated iodine molecule) show significant increases in length, indicating that the thiophosphoryl group becomes more polar (Ia) as electrons are donated from the sulphur into the lowest unoccupied antibonding molecular orbital of the iodine. Equilibrium constant values [11,12,14] show the analogous phosphine selenide iodine complexes (VIa) to be more stable but complexes of the oxide (VIb) to be less stable (see Table 1).

$$R_3P{=}X \rightarrow I_2$$

(VIa) $X = Se$ (VIb) $X = O$

This stability order has been explained [12] in terms of the increased availability of the electron pair of the chalcogen for donation with decreasing ionization energy (the ionization energies decrease along the series O > S > Se) or in terms of back donation of p_π iodine electrons into the $3d$ orbitals of sulphur or the $4d$ orbitals of selenium. This p_π—d_π back donation is impossible for the phosphine oxides (VIb) because of the lack of a suitable d_π orbital on the oxygen atom. However, in view of the fact that the I—S bond distance in (V) at 2.69 Å, is not shorter than that expected for an I—S single bond (2.37 Å from covalent radii) and the π acceptor properties of tertiary phosphine sulphides appear to be minimal [22] back donation is probably not significant. Reaction of tertiary arsine sulphides (VII) in chloroform solution with iodine does not stop with adduct formation but leads to trialkyliodoarsonium triiodides (VIII) [10] indicating the As=S bond is more readily ruptured than the P=S bond.

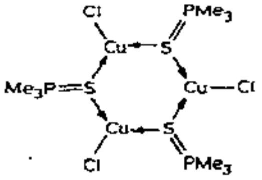
$$R_3As{=}S \xrightarrow[CHCl_3]{I_2} [R_3AsI]^+I_3^-$$

(VII) (VIII)

(R = Me, Et, Ph or cyclohexyl)

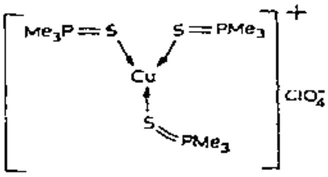
The fate of the sulphur is not known with certainty.

Ethanol solutions of tertiary phosphine sulphides reduce copper(II) to copper(I) [23—27], gold(III) to gold(I) [28—29] and iron(III) to iron(II) [30], but whether the reducing agent is the solvent or the phosphine sulphide has not been proven. In acetone solution phosphine sulphides interact with the appropriate copper(II) salts to initially produce orange coloured copper(II) species, containing the coordinated phosphine sulphides [24], but on standing colourless copper(I) complexes $[Cu(R_3PS)Cl]_n$ and $[Cu(R_3PS)_3]X$ ($X^- = ClO_4^-$ or BF_4^-) are obtained [23—27]. In the case of trimethylphosphine sulphide three dimensional X-ray structures show the complexes (IX) and (X) to contain three-coordinate copper(I) [31].



(IX)

The structure of (IX) [32] contains a six-membered Cu_3S_3 ring with an approximate chair conformation. Each Me_3PS ligand bridges two copper atoms sym-

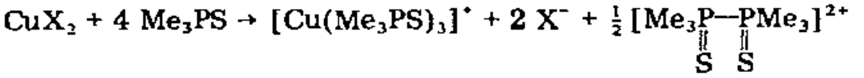


(X)

metrically, the average Cu—S distance being 2.265 Å. The coordination environment around copper is a distorted trigonal plane; in addition the structure contains terminally-bound chloride ligands with the average Cu—Cl distance being 2.216 Å. Angles at copper are in the ranges 103—111.7° (S—Cu—S) and 123.8—125.2° (S—Cu—Cl).

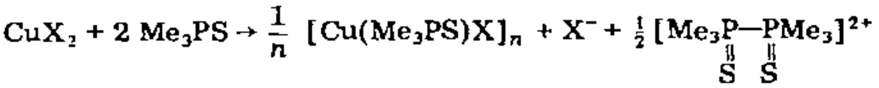
The structure of (X) contains a planar CuS_3 unit which approximates trigonal symmetry. The Cu—S distances average at 2.256 Å and the S—Cu—S angles are in the range 117.8—122.8°.

Meek and co-workers [32] have suggested that the reducing agent for those reactions involving CuX_2 was Me_3PS, as indicated in eqns. (1) and (2).



$$\mathrm{CuX_2 + 4\,Me_3PS \rightarrow [Cu(Me_3PS)_3]^+ + 2\,X^- + \tfrac{1}{2}\,[Me_3\underset{\overset{\|}{S}}{P}-\underset{\overset{\|}{S}}{P}Me_3]^{2+}} \qquad (1)$$

$(X = BF_4, ClO_4, NO_3)$ (XI)



$$\mathrm{CuX_2 + 2\,Me_3PS \rightarrow \frac{1}{n}\,[Cu(Me_3PS)X]_n + X^- + \tfrac{1}{2}\,[Me_3\underset{\overset{\|}{S}}{P}-\underset{\overset{\|}{S}}{P}Me_3]^{2+}} \qquad (2)$$

(X = Cl, Br, I, SCN) (XI)

The oxidised product (XI), which would seem better formulated as $[Me_3P—S—S—PMe_3]^{2+}$, has not to our knowledge been identified, either because it was not searched for or difficulty was encountered in its isolation. However, the reaction of tris(dimethylamino)phosphine sulphide (XII) with $Cu(MeCN)_4(ClO_4)_2$ [33] does result in the formation of a Cu(I) complex (XIII) while the ligand is oxidised to the dipositive cation as in (XIV)

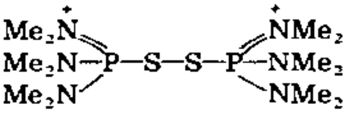
$$\underset{\text{(XII)}}{\mathrm{(Me_2N)_3P{=}S}} \xrightarrow{\mathrm{[Cu(MeCN)_4](ClO_4)_2}} \underset{\text{(XIII)}}{\mathrm{[\{(Me_2N)_3PS\}_4Cu]^+ClO_4^-}}$$

$$+ \underset{\text{(XIV)}}{\mathrm{[(Me_2N)_3P—S—S—P(NMe_2)_3]^{2+}(ClO_4^-)_2}}$$

The reaction of (XII) with copper(II) chloride yielded (XV) as the only isolated product

$$\underset{\text{(XV)}}{\mathrm{[(Me_2N)_3P—S—S—P(NMe_2)_3]^{2+}[Cu_2Cl_6]^{2-}}}$$

In both cases the above reactions were carried out using the ligand (XII) itself as solvent. The replacement of aryl or alkyl substituents in R_3PS compounds by the dimethylamino group would be expected to make the phosphine sulphide more basic by favouring the resonance structure (Ia) [33,34]. This helps to stabilize the dication because the positive charge is delocalized onto the nitrogen atoms, (XVI) being one possible canonical form



(XVI)

Such a dication could result from the oxidation of (XII) to the free-radical ion $[(\mathrm{Me_2N})_3\mathrm{P{=}\dot{\underset{..}{S}}}]^+$ followed by rapid coupling. The same cation was also isolated as the tribromide salt (XVII) after bromine oxidation of (XII) in acetonitrile

$$\underset{\text{(XII)}}{(\mathrm{Me_2N})_3\mathrm{P{=}S}} \xrightarrow[\mathrm{MeCN}]{\mathrm{Br_2}} \underset{\text{(XVII)}}{[(\mathrm{Me_2N})_3\mathrm{P{-}S{-}S{-}P(NMe_2)_3}]^{2+}(\mathrm{Br_3^-})_2}$$

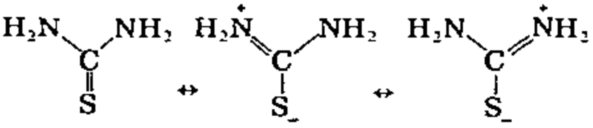
Qualitatively, in ethanol, it has been observed that $\mathrm{Me_3PS}$ and $\mathrm{Ph_3AsS}$ spontaneously and rapidly reduced copper(II) to copper(I), to form compounds of the type $[\mathrm{CuL_3}]^+$, whereas slow reduction occurred with $(\mathrm{Et})_3\mathrm{PS}$ and triisopropylphosphine sulphide while no reduction seemed to take place with the least basic $\mathrm{Ph_3PS}$ [35]. In the latter three cases the solution was treated with gaseous $\mathrm{SO_2}$ to reduce the Cu(II) before the ligand was added. Kinetic studies of the reduction and the electron transfer mechanism for these reactions have not been attempted and it is hoped this will be remedied in the future. Similarly diphosphine disulphides (to be discussed later) deserve the same attention.

(ii) Thioureas

Interaction of thiourea (XVIII) with iodine results in a variety of products depending on the reaction conditions. Spectrophotometric studies indicate that iodine and thiourea (XVIII) (or N-substituted alkyl thioureas) form 1 : 1 molecular adducts of the type (XIX) in a variety of solvents (e.g. chloroform, carbon tetrachloride, dichloromethane, benzene [15,18,19,36]) (see Table 1).

$$\underset{\text{(XVIII)}}{(\mathrm{H_2N})_2\mathrm{C{=}S}} + \mathrm{I_2} \rightleftharpoons \underset{\text{(XIX)}}{(\mathrm{H_2N})_2\mathrm{C{=}S} \rightarrow \mathrm{I_2}}$$

Although (XIX) has been isolated as red-brown crystals they are unstable [38], thus so far preventing an X-ray structure determination. Thermodynamic and spectroscopic data show the strength of the sulphur—iodine interaction to be greatest in the most polar solvents. For instance, for the tetramethylthiourea complex (see Table 1) the K value is greatest in the most polar solvent [17]. Raman spectra of the thiourea—iodine complex (XIX) have been recorded in benzene and acetonitrile. The $\nu(\mathrm{I{-}I})$ stretching frequency and force constant are lowest in acetonitrile, thus pointing to a greater weakening of the I—I bond [37]. Thiourea itself is an almost planar molecule [39] in which the lone pair on the nitrogen atoms can be envisaged as overlapping with the *p* orbital of the carbon atom [40] giving the resonance structures (XVIIIb) and (XVIIIc). The more polar solvents will favour the charge separated structures (XVIIIb) and (XVIIIc) and hence the formation of the donor—acceptor complex (XIX). Equilibrium constant values [15,17,18,19,36,37] for the adducts of the type (XIX) are greater than for the tertiary phosphine sulphide-iodine complexes (IV) [10—12]. When compared with the analogous thioureas, ureas form weaker 1 : 1 adducts (XX) with iodine in inert solvents, [15—17] (see Table 1). As for phosphine chalcogenides, such differences in behaviour can be related to the ionization energies of the donor atoms or to their acceptor properties



(XVIIIa) (XVIIIb) (XVIIIc)

$(R_2N)_2C{=}O \rightarrow I_2$

(e.g. R = H or Me)

(XX)

Thiourea (XVIII) and iodine mixed in a 2 : 1 molar ratio in benzene or chloroform give a yellow crystalline complex which, from an X-ray structural study [38], was shown to be bis(thiourea)iodine(I) iodide (XXI), an unusual example of a formal I^+ complex thus showing that the charge transfer from the sulphur to the iodine was sufficient to cause ionization. The I—S distance at 2.620 Å is among the shortest I—S distances known.

$[(H_2N)_2C{=}S \rightarrow I \leftarrow S{=}C(NH_2)_2]^+ I^-$

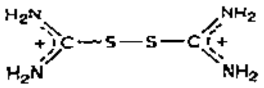
(XXI)

In the more ionising solvent, water, thiourea (XVIII) is oxidised by iodine or bromine to the α,α'-dithiobis(formamidinium) dipositive ion as in (XXII). This reaction could be envisaged to proceed in a manner similar to that proposed for the oxidation of the phosphine sulphide (XII) by bromine, with the initial formation of the radical ion $[(H_2N)_2C{=}\dot{S}]^+$. The disulphide nature of (XXII) was confirmed by an X-ray crystallographic study [41]. The dimensions of the thiourea groups in (XXII) are similar to those in thiourea (XVIII) itself [39] but a slight lengthening of the C—S distance is observed. The positive charge can be envisaged to be spread over the dimethylamino groups

$$(H_2N)_2C{=}S \xrightarrow[H_2O]{X_2} [(H_2N)_2C{-}S{-}S{-}C(NH_2)_2]^{2+}(X^-)_2$$

(XVIII) (X = I or Br) (XXII)

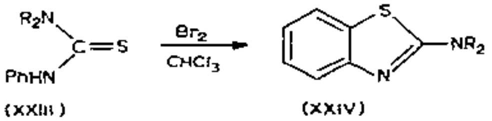
(XXIIa) thus helping to stabilize the cation as suggested for the thiophosphoryl



(XXII a)

analogue in (XVI).

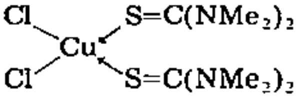
The oxidation of N-aryl substituted thioureas (XXIII) by halogens is complex and leads to various heterocyclic products, most commonly benzothiazoles (XXIV) if inert solvents are used [42].



(XXIII) (XXIV)

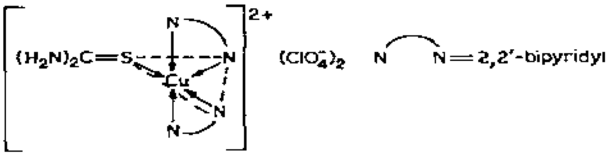
(R = H or alkyl)

Copper(II) is readily reduced to copper(I) by thiourea (XVIII) and its derivatives. The thiourea is oxidised to the α,α'-dithiobis(formamidinium) ion (as in XXII) which has been isolated from the reaction of copper(II) perchlorate and thiourea in acetonitrile [43]. For a variety of substituted thioureas a transitory red colour was observed during this oxidation. ESR and electronic spectral data of these coloured species were indicative of the presence of copper(II)—thiourea complexes which are likely intermediates in the overall oxidation process [43]. These red intermediates are transitory in nature and cannot be isolated. However, with tetramethylthiourea and $CuCl_2 \cdot 2\ H_2O$ (instead of $Cu(ClO_4)_2 \cdot 6\ H_2O$) in aqueous solution ruby red crystals of the copper(II) complex (XXV) have been isolated, and shown by a single crystal X-ray analysis to have a flattened tetrahedral structure [44].



(XXV)

The average bond lengths are: Cu—Cl 2.237 Å, Cu—S 2.314 Å and S—C 1.73 Å (a little longer than 1.68 Å found in the free ligand) and relevant angles are: Cl—Cu—Cl 145.1°, S—Cu—S 140.1° and Cu—S—C 108.8° (average). The crystals are air sensitive and reduce on standing, however, having the hard base co-ligands Cl, and presumably favourable thermodynamic factors allow their stabilization and isolation. On the other hand the interaction of thioureas and $Cu(ClO_4)_2 \cdot 6\ H_2O$ may produce transitory species of the type $[CuL_4]^{2+}$ (L being the appropriate thiourea), which could have an even less distorted tetrahedral structure than seen in (XXV) and furthermore would be expected to be reduced to Cu(I) complexes even more easily than in (XXV). More stable copper(II)—thiourea complexes can be obtained by using ancillary ligands with the ability to accept electrons from the metal via π backbonding [45]; as, for example, in bis(2,2'-bipyridyl)thioureacopper(II) perchlorate (XXVI) which has a trigonal bipyramidal coordination geometry [46].



(XXVI)

The relevant bond lengths are: C—S 1.72 Å (similar to (XXV)) and Cu—S 2.369 Å. Normally the reaction of copper(II) salts with thioureas affords copper(I)—thiourea complexes of which many have been characterized and shown to have a variety of stoichiometries and structures [47,48]. Examples for thiourea (XVIII) itself are $[Cu_2L_6](BF_4)_2$, $[CuL_2Cl]_n$, $[Cu_4L_6](NO_3)_4$, $[Cu_4L_9](NO_3)_4$ and $[Cu_4L_{10}](SiF_6)_2$ (L = thiourea) [47].

The reactions of selenourea (XXVII) with metal salts have been less studied but one interesting reaction is that with silver(I) chloride [49]. Concentrated aqueous solutions of selenourea (XXVII) dissolve silver chloride to give complexes that slowly decompose in solution. After a few days a compound containing no silver was isolated and this was the selenium analogue of the cation found in (XXII), i.e. α,α'-diselenobis(formamidinium) dichloride (XXVIII). The oxidising agent in this case was not known but it may have been selenourea itself, atmospheric oxygen or the Ag⁺ ion.

$$\underset{\text{(XXVII)}}{(H_2N)_2C{=}Se} \xrightarrow[H_2O]{AgCl} \underset{\text{(XXVIII)}}{[(H_2N)_2C{-}Se{-}Se{-}C(NH_2)_2]^{2+}(Cl^-)_2}$$

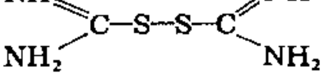
The oxidation of thiourea (XVIII) with $Cu(dmp)_2(ClO_4)_2$ (dmp = 2,9-dimethyl-1,10-phenanthroline) in borate buffered 0.1 M aqueous $NaClO_4$ [50] shows a rate law in which the rate determining step is as shown in eqn. (3a) while in methanol it is as shown in eqn. (3b).

$$[Cu(dmp)(tu)OH]^+ + tu \rightarrow \text{products including } [Cu(dmp)_2]^+ + \text{tu radicals}$$

$$\text{(tu = thiourea)} \qquad (3a)$$

$$[Cu(dmp)_2]^{2+} + tu \rightarrow Cu(dmp)_2^+ + \text{tu radicals} \qquad (3b)$$

An inner sphere electron-transfer mechanism has been suggested. The oxidised product was not satisfactorily identified nor isolated but by analogy with a Ce(IV) reaction [51] the product was considered to be the formamidine disulphide (XXIX) which is the deprotonated form of (XXII). Similarly with Mn-



(XXIX)

(III), in acid solution, Davies [52] has found a rate law $-[d(\mathrm{Mn(III)})]/dt = k_{\mathrm{obs}}[\mathrm{Mn(III)}][\mathrm{tu}]$. An inner sphere electron transfer mechanism has also been suggested for Mn(III) [52] and Fe(III) [53] reactions.

In contrast McAuley and Gomwalk [51] have found that for Ce(IV) in 0.5 M[H^+], the reaction obeys a second order rate law, but there is at best a weak interaction between the reactants, and an outer-sphere process for the electron transfer was proposed. This same electron transfer mechanism has also been suggested for Co(III) [54].

Hoffman and Edwards [55] have commented that thiourea (XVIII) in up to 3M $HClO_4$ does not become protonated as suggested earlier [51,54] and in their study with H_2O_2, thiourea (XVIII) acts as a nucleophile in a displacement on peroxide oxygen, as shown in eqn. (4). This was followed by further reactions (5) and (6).

$$H_2O_2 + \mathrm{tu} \rightarrow \mathrm{HOtu}^+ + OH^- \tag{4}$$

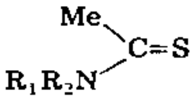
$$\mathrm{HOtu}^+ + H^+ \rightarrow H_2O(\mathrm{tu})^{2+} \tag{5}$$

$$H_2O(\mathrm{tu})^{2+} + \mathrm{tu} \rightarrow \underset{\text{(XXII)}}{[(NH_2)_2CSSC(NH_2)_2]^{2+}} + H_2O \tag{6}$$

Ratajczak and Pajdowski [56] from visible absorption and ESR studies have demonstrated that thiourea (XVIII) and $Cu(NO_3)_2 \cdot 3\,H_2O$ in 0.1 M HNO_3 does not form a complex with Cu(II) upon reduction to Cu(I). As previously mentioned Zatko and Kratochvil [43] found that a series of substituted thioureas gave a transitory red colour with $Cu(ClO_4)_2 \cdot 6\,H_2O$ in acetonitrile at low temperatures, and a similar study with $Cu(NO_3)_2 \cdot 3\,H_2O$ in 0.1 M HNO_3 seems warranted to determine whether the solvent determines the mechanism of electron transfer.

(iii) Thioamides

Thioacetamides (XXX) form 1 : 1 complexes with iodine in solvents such



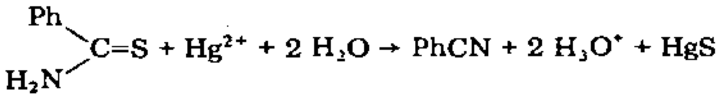
(XXXa) $R_1 = R_2 = H$
(XXXb) $R_1 = H$, $R_2 = Me$
(XXXc) $R_1 = R_2 = Me$

as dichloromethane or carbon tetrachloride [20,21].

Generally the reaction of thioamides with metal salts is complicated by the ready hydrolysis to H_2S and the metal sulphide [57]. However with copper(II) chloride, under neutral conditions, reduction of the metal salt occurs and copper(I) complexes can be isolated, viz. $[CuL_4]Cl$ (L = (XXXa)) and CuLCl

(L = (XXXa) and (XXXc)) [58,60]. Whether the reducing agent is the thioamide itself or not, has not been investigated. However it is perhaps relevant that when the complex $[CuL_4]Cl$ (L = (XXXa)), which has a tetrahedral CuS_4 coordination sphere [59], is subject to ^{60}Co γ-irradiation at liquid nitrogen temperature, it is oxidised to a copper(II) complex [61]. On the basis of its ESR spectrum this has also been assigned to have a tetrahedral structure and if the complex is warmed to room temperature the ESR signals disappear in line with the facile reduction of a copper(II) centre tetrahedrally coordinated by four sulphur donor ligands.

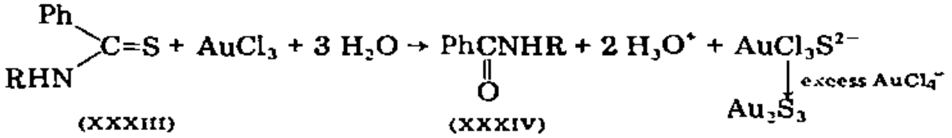
In dilute aqueous perchloric acid under which conditions the rate of the hydrogen-ion catalysed hydrolysis is negligible, thiobenzamide (XXXI) undergoes direct reactions with Hg(II) [57,62], Ag(I) [57] and Cu(II) [57,63] ions to produce the metal sulphide and benzonitrile (XXXII) as shown in eqn. (7)



$$\text{Ph}(\text{H}_2\text{N})C{=}S + Hg^{2+} + 2\,H_2O \rightarrow PhCN + 2\,H_3O^+ + HgS \qquad (7)$$

(XXXI) (XXXII)

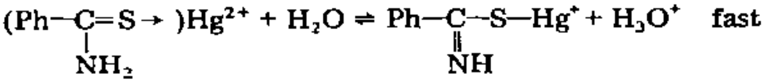
Tl(III) [57,63] and Au(III) [57,63] on the other hand, yield the metal sulphide and O-amide (XXXIV) as shown in eqn. (8).



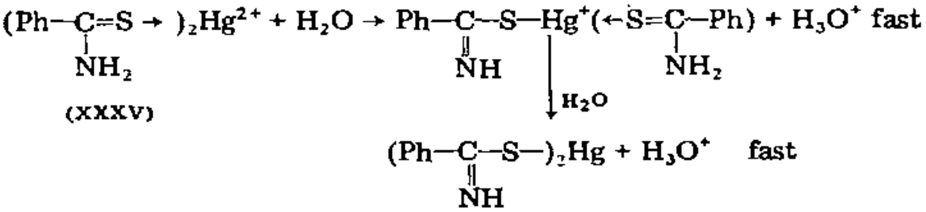
$$\text{Ph}(\text{RHN})C{=}S + AuCl_3 + 3\,H_2O \rightarrow Ph\underset{\underset{O}{\|}}{C}NHR + 2\,H_3O^+ + AuCl_3S^{2-} \xrightarrow{\text{excess } AuCl_4^-} Au_2S_3 \qquad (8)$$

(XXXIII) (XXXIV)

The kinetic details differ with each metal. With mercury, a 2 : 1 S—amide—Hg(II) (XXXV) complex is rapidly formed under all concentration conditions and with a 10-fold excess of Hg^{2+} over thioamide the rate equation at any fixed value of $[H_3O^+]$ takes the form $[-d(2:1 \text{ complex})]/dt = k_{obs}[Hg(II)]$-[2 : 1 complex]. Some of the important steps in the mechanism are outlined eqns. (9—13). Eqn. (13) only leads to decomposition.



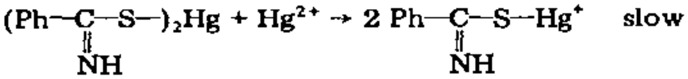
$$(Ph\underset{\underset{NH_2}{|}}{C}{=}S\rightarrow)Hg^{2+} + H_2O \rightleftharpoons Ph\underset{\underset{NH}{\|}}{C}{-}S{-}Hg^+ + H_3O^+ \quad \text{fast} \qquad (9)$$



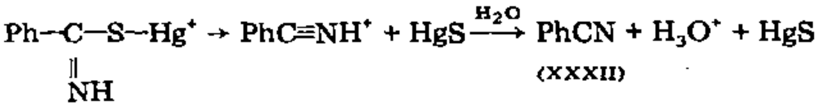
$$(Ph\underset{\underset{NH_2}{|}}{C}{=}S\rightarrow)_2Hg^{2+} + H_2O \rightarrow Ph\underset{\underset{NH}{\|}}{C}{-}S{-}Hg^+(\leftarrow S{=}\underset{\underset{NH_2}{|}}{C}{-}Ph) + H_3O^+ \quad \text{fast} \qquad (10)$$

(XXXV)

$$\xrightarrow{H_2O} (Ph\underset{\underset{NH}{\|}}{C}{-}S{-})_2Hg + H_3O^+ \quad \text{fast} \qquad (11)$$

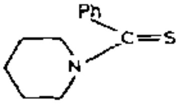


$$(Ph\underset{\underset{NH}{\|}}{C}{-}S{-})_2Hg + Hg^{2+} \rightarrow 2\,Ph\underset{\underset{NH}{\|}}{C}{-}S{-}Hg^+ \quad \text{slow} \qquad (12)$$



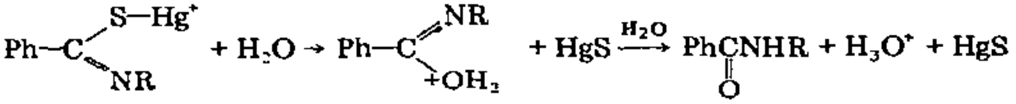
$$\mathrm{Ph{-}\underset{\underset{NH}{\|}}{C}{-}S{-}Hg^+ \rightarrow PhC{\equiv}NH^+ + HgS \xrightarrow{H_2O} \underset{(XXXII)}{PhCN} + H_3O^+ + HgS} \quad \text{fast} \qquad (13)$$

The requirement of N-bound protons for rapid reaction comes from a study of (XXXVI) whose decomposition is negligibly promoted by Hg(II) [57,62].



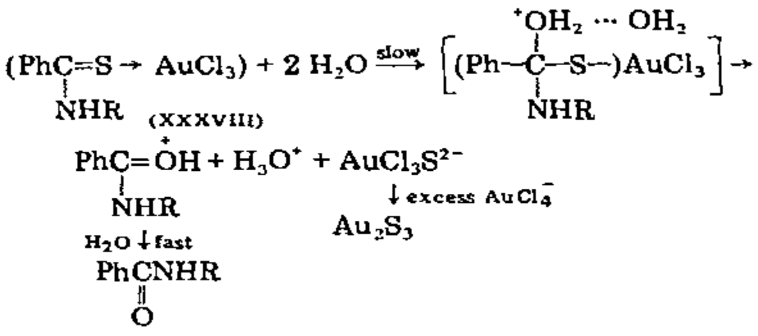
(XXXVI)

Interestingly, N-substituted—S—amides (XXXIII) lead to the O-amides (XXXIV) as product (see eqn. (14)) but display a comparable kinetic scheme to that for the thioamides (XXXI) above [57,62], with (XXXVII) as an intermediate.



$$\mathrm{\underset{(XXXVII)}{Ph{-}C{\overset{\nearrow S-Hg^+}{\underset{\searrow NR}{}}}} + H_2O \rightarrow Ph{-}C{\overset{\nearrow NR}{\underset{\searrow {}^+OH_2}{}}} + HgS \xrightarrow{H_2O} \underset{(XXXIV)}{Ph\underset{\underset{O}{\|}}{C}NHR} + H_3O^+ + HgS} \qquad (14)$$

With Cu(II) and Ag(I) only 1 : 1 thiobenzamide (XXXI) complexes are formed, with the former in small concentration, and their reactivities are not as great as Hg^{2+} [57]. Pb^{2+}, Ni^{2+}, Cd^{2+} and Tl^+ [57] have no detectable effect at 25°C. This is probably because these ions show little tendency to form 1 : 1 complexes and equilibria analogous to (9) lie to the left. With Tl^{3+} and $AuCl_4^-$ [64] the rate of decomposition of thiobenzamides (XXXIII) is independent of $[H_3O^+]$ so prior ionization of an N-bound proton either does not occur or does not facilitate the decomposition of the complexes in these instances. The steps following the formation of a 1 : 1 Au(III) complex (XXXVIII) are given in eqn. (15) and in contrast to the Hg^{2+} and Ag^+ reactions, O-amides (XXXIV) are always produced.



$$\mathrm{\underset{(XXXVIII)}{(Ph\underset{\underset{NHR}{|}}{C}{=}S \rightarrow AuCl_3)} + 2\,H_2O \xrightarrow{slow} \left[(Ph{-}\overset{\overset{{}^+OH_2 \cdots OH_2}{|}}{\underset{\underset{NHR}{|}}{C}}{-}S{-})AuCl_3\right] \rightarrow}$$

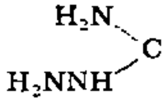
$$\mathrm{Ph\underset{\underset{NHR}{|}}{C}{=}\overset{+}{O}H + H_3O^+ + AuCl_3S^{2-}}$$

$$\mathrm{Ph\underset{\underset{NHR}{|}}{C}{=}\overset{+}{O}H \xrightarrow[H_2O]{fast} \underset{(XXXIV)}{Ph\underset{\underset{O}{\|}}{C}NHR}} \qquad \mathrm{AuCl_3S^{2-} \xrightarrow{excess\ AuCl_4^-} Au_2S_3} \qquad (15)$$

These results allow one to draw some general conclusions about the reactions

[57]. The high covalent affinity of the soft metal for sulphur is an important part of the driving force; the size of the metal ion and the magnitude of its charge are of secondary importance. Neither soft nor hard metal species will normally promote reactions of the oxygen analogues of the sulphur-containing substrates considered, unless the oxygen analogue behaves as a chelate. When the sulphur atom is removed by the metal, the remainder of the substrate either loses protons (as in nitrile formation) or is attacked by an ambient nucleophile (e.g. H_2O). With thiobenzamides, Hg^{2+} and Ag^{+} promote the former reaction while Tl^{3+} and Au^{3+} promote the latter. Some soft metal ions, e.g. Cd^{2+} and Pb^{2+} are surprisingly unreactive [57].

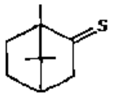
(iv) Thiosemicarbazides

Thiosemicarbazide  $(H_2N)(H_2NNH)C{=}S$ (XXXIX) functions as a chelating agent, binding through the soft sulphur and hard terminal hydrazino N in its reaction with copper(II). As a result high stability is achieved (as shown by the large negative values of ΔH [65] ($\Delta H_1 = -41.0$ and $\Delta H_2 = -74.5$ kJ mol^{-1}) and this, with the X-ray analysis of CuL_2SO_4 [66] and $CuL_2(NO_3)_2$ [67] (L = XXXIX), in which the chelating ligands are bonded in a square planar array about the Cu(II), provide an explanation why these compounds are not so easily reduced in contrast to other systems previously discussed. $CuLX_2$ (X = Cl, Br) probably have distorted octahedral structures with bridging thiosemicarbazide (XXXIX) ligands [68]. No reports of the oxidation of (XXXIX) by metal ions have been noted.

The chemistry of thiosemicarbazides and thiosemicarbazones has been reviewed previously [68].

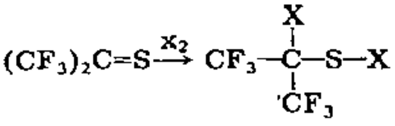
(v) Thioketones

As many reported true thioketones are difficult to prepare in a monomeric form and are unstable in air there is little information on their interaction with halogens. Thiocamphor (XL) does form a 1 : 1 complex with iodine in cyclohexane [15]. However hexafluorothioacetone (XLI) reacts with halogens to



(XL)

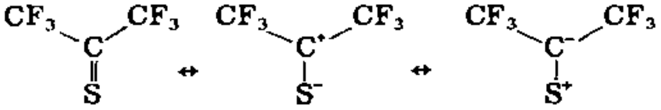
produce sulfenyl halides (XLII) [69]



$$(CF_3)_2C{=}S \xrightarrow{X_2} CF_3{-}C(X)(CF_3){-}S{-}X \qquad (X = Cl\ or\ Br)$$

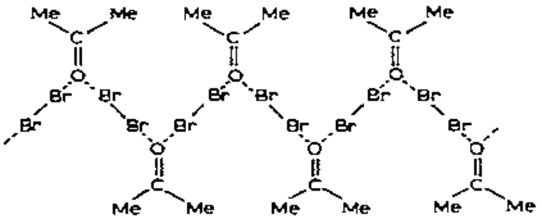
(XLI) (XLII)

The presence of the strongly electron withdrawing trifluoromethyl groups coupled to the polarizable thiocarbonyl groups means the molecule has a high reactivity, both resonance structures (XLIb) and (XLIc) being considered important

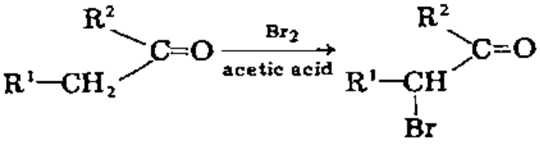


(XLIa) (XLIb) (XLIc)

Ketones form weak charge transfer complexes with iodine in inert solvents such as cyclohexane or freon [15,70] and the 1 : 1 bromine acetone complex (XLIII) has been crystallised and shown to contain bromine bridges [71]. In the presence of acid or base however halogens substitute readily into the alkyl group of the ketone, the reaction being considered to occur via an enol intermediate [72]. Thus ketones of the type (XLIV) are brominated in acetic acid to form (XLV)



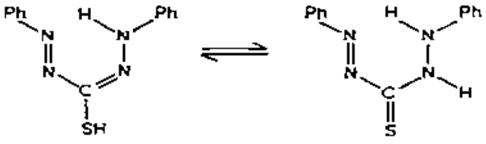
(XLIII)



(XLIV) (XLV)

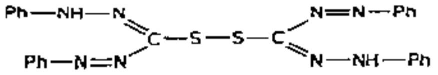
(vi) Dithizone

Interesting oxidations are known with the more complex analytical reagent dithizone (3-mercapto-1,5-diphenylformazan) which exhibits tautomerism in solution, (XLVIa) and (XLVIb). Iodine will oxidise dithizone (XLVI) in car-

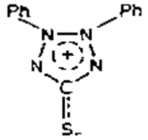


(XLVI a) (XLVI b)

bon tetrachloride in the presence of some water [73] to eliminate HI and afford a postulated disulphide intermediate (XLVII) which disproportionates to give the cyclic sydnone or dehydrodithizone (XLVIII) as well as dithizone (XLVI). Dithizone will also react with oxidising agents such as MnO_2 and

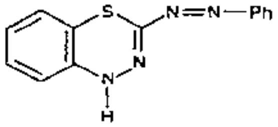


(XLVII)



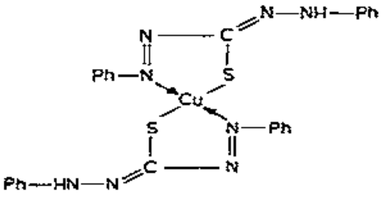
(XLVIII)

$K_3[Fe(CN)_6]$ to produce the same orange coloured sydnone (XLVIII) [74] which can be regarded as arising from dithizone by the loss of two protons and two electrons. The X-ray crystal structure of (XLVIII) [75] shows the tetrazole ring and the sulphur atom to form one plane. The N—N distances are all equal (average 1.316 Å) and intermediate between 1.44 Å (single bond) and 1.24 Å (double bond). Similarly both the C—N distance of 1.360 Å and the C—S distance of 1.687 Å are indicative of partial double bond character. The π electrons are clearly delocalized over the ring system as well as the exocyclic sulphur atom and hence the structure is best represented by (XLVIII). A boiling dioxan solution of dithizone (XLVI) or the sydnone (XLVIII) in acid produces the novel bicyclic oxidation product (XLIX) [74] (note the



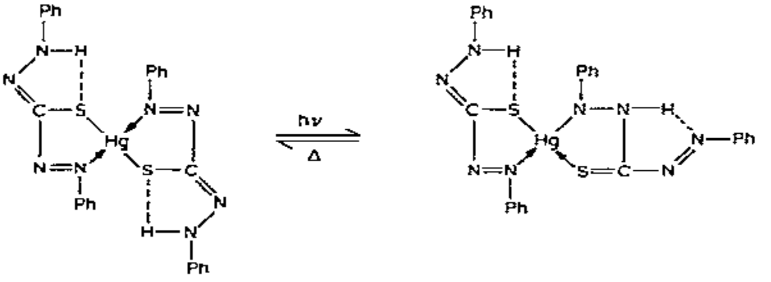
(XLIX)

similarity to (XXIV) where an *ortho* proton of one of the phenyl rings of dithizone (XLVI) as well as the mercapto proton and two electrons have been lost in the oxidation. The actual oxidising agent is not known. Complex formation with dithizone results in proton loss [76] and in the case of copper(II) a stable, neutral copper(II) complex (L) is formed with the ligand acting in a bidentate fashion through nitrogen and sulphur atoms giving a square planar complex [77].



(L)

Using irradiation ($\lambda > 400$ nm) the orange square planar Hg(II) complex of dithizone (LI) photorearranges to give the blue complex (LII) [78]. In (LI) both ligands are of the type (XLVIa) (with removal of the thiol proton) while in (LII) one ligand is of the above type while the second is the same as (XLVIb) (with removal of the terminal N—H proton). A *cis—trans* isomerisation of an azomethine group coupled with a proton shift, as shown in eqn. (16) is the net photochemical reaction. The thermal back reaction involved in the photochromic effect is fast, the rate being sensitive to the nature of the metal atom, to the presence of acids and bases and to the polarity of the solvent [78].



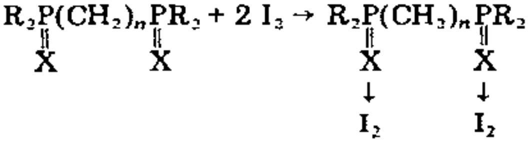
(16)

(LI) (LII)

C. DITHIONES AND DIPHOSPHINE DISULPHIDES

(i) Diphosphine disulphides

The diphosphine disulphides (LIIIa) and (LIIIb) as well as the diselenide (LIIIc) react with iodine in chloroform solution to produce charge transfer adducts of the type (LIV) which were isolated as red-brown solids [79]. The sulphide (LIIIb) also forms a 1 : 1 complex with iodine. Sulphur—iodine coordination is indicated from the observed decrease in the ν(P=S) absorption frequencies in the IR on coordination and the blue shift in the free iodine absorption in the electronic spectrum. The reaction of bromine with (LIIIb) does not stop with adduct formation but leads by substitution at the phosphorus

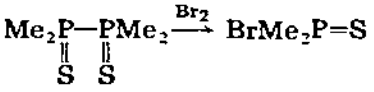


$$R_2\underset{\underset{X}{\|}}{P}(CH_2)_n\underset{\underset{X}{\|}}{P}R_2 + 2\,I_2 \rightarrow R_2\underset{\underset{\underset{I_2}{\downarrow}}{\underset{X}{\|}}}{P}(CH_2)_n\underset{\underset{\underset{I_2}{\downarrow}}{\underset{X}{\|}}}{P}R_2$$

(LIII) (LIV)

	R	X	n
a	Ph	S	2
b	Me	S	0
c	Ph	Se	2

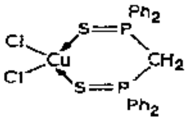
atom to bromodimethylphosphine sulphide [80] (LV) when the P—P bond is cleaved.



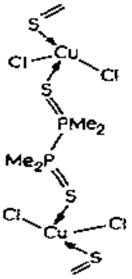
$$\underset{\underset{S}{\|}}{Me_2P}-\underset{\underset{S}{\|}}{PMe_2}\xrightarrow{Br_2}BrMe_2P{=}S$$

(LIIIb) (LV)

On interaction with copper(II) salts in acetone the diphosphine disulphides, (LIIIa) and (LIIIb), and related species, afford unstable orange solutions [24] which on the basis of electronic and ESR spectral evidence appear to contain copper(II) diphosphinedisulphide species. Two complexes, (LVI) and (LVII), have been isolated and have a pseudotetrahedral geometry [24,81]. The single crystal X-ray analysis of (LVII) (which is the minor product in the reaction) has shown the brown compound crystallizes as an infinite polymer in which CuCl$_2$ groups are connected by Me$_4$P$_2$S$_2$ molecules. The coordination geometry at Cu(II) is a flattened tetrahedron with a S—Cu—S angle of 137.3° The mean distances are: Cu—Cl 2.22 Å and Cu—S 2.33 Å. In both cases the



(LVI)

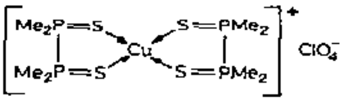


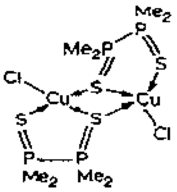
(LVII)

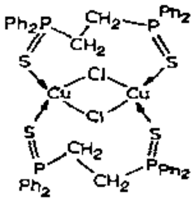
presence of the "hard" chlorines is required to stabilize the copper(II) towards reduction and thus allow the isolation of solid complexes.

On standing more stable copper(I) complexes of the type [CuLX]$_n$ (X$^-$ = Cl$^-$ or Br$^-$) and [CuL$_2$]Y (L = (LIII), Y$^-$ = ClO$_4^-$ or BF$_4^-$) were isolated [23,24,82] but the reducing agent is unknown but suspected to be the phosphine sulphide. Crystal structural studies show these complexes to most commonly contain tetrahedral copper(I), as in (LVIII) [83a], (LIX) [83b] and (LX) [83c], and in one case, three-coordinate copper(I) [24] as in (LXI). (LIX) [83b] is a dinuclear compound in which each Cu(I) is surrounded by a tetrahedral array of the sulphur atoms and one chlorine atom. Each Me$_4$P$_2$S$_2$ chelates one copper, and bridges two via one sulphur atom. The relevant bond lengths are: Cu—S 2.311 Å (terminal) and 2.453, 2.486 Å (bridging) and Cu—Cl 2.244 Å. (LX) [83c] is a dinuclear compound in which each Cu(I) is surrounded by two terminal sulphurs and two bridging chlorines in a distorted tetrahedral array. Each ligand bridges two Cu(I) ions. The relevant bond lengths are: Cu—Cl 2.298 Å, Cu—S 2.311 Å (mean), and P—S 1.975 Å (mean) and the mean

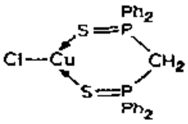
Cu—S—P angle is 108.15°. The geometry about the copper atom in (LXI) is


(LVIII)


(LIX)


(LX)

distorted trigonal planar [24]. Relevant bond lengths are: Cu—S (2.259 and 2.321 Å) and Cu—Cl 2.207 Å and bond angles are S—Cu—S 119.23°, S—Cu—Cl (113.1° and 123.3°) and Cu—S—P (91.5° and 95.6°).

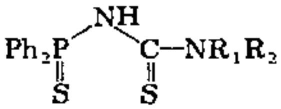

(LXI)

Related to the diphosphine disulphides is the imidotetraphenyldithiodiphosphinate anion (LXII) which at —78°C forms a blue [CuL$_2$] (L = (LXII))


(LXII)

complex which exhibits spectral properties consistent with a tetrahedral environment around the copper(II) ion [84]. The complex is redox unstable and at room temperature is reduced, presumably to a copper(I) complex, in a reaction which is apparently first order in complex concentration with $k \approx 2 \times 10^{-3}$ min^{-1} and a half life of about 300 min demonstrating the low stability of tetrahedral copper(II) coordinated to four sulphur donors.

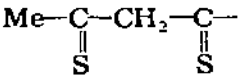
Mixed bidentate phosphine sulphide—thiourea ligands (LXIII) also readily reduce copper(II) chloride to copper(I) species, although the exact nature of these is not clear [85]. However in the case of (LXIIIb) a thermally unstable

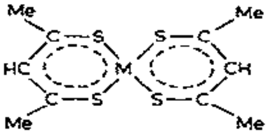

$Ph_2P(=S){-}NH{-}C(=S){-}NR_1R_2$

(LXIIIa) $R_1 = H, R_2 = Ph$
(LXIIIb) $R_1 = R_2 = Me$
(LXIIIc) $R_1 = R_2 = Et$

copper(II) precursor has been detected spectroscopically which appears to contain a CuS$_4$ centre [85].

(ii) Dithioacetylacetone

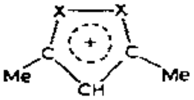
A dithione of interest is dithioacetylacetone  $Me{-}\underset{\displaystyle S}{\underset{\|}{C}}{-}CH_2{-}\underset{\displaystyle S}{\underset{\|}{C}}{-}Me$ (LXIV) which has not been isolated in the free state but can be stabilized on coordination in the monomeric, dithioacetylacetonato square-planar complexes (LXV),



(M = Co, Ni, Pd or Pt)

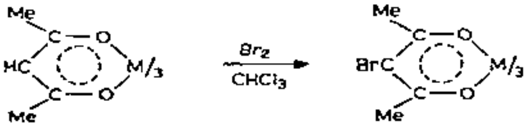
(LXV)

which are obtained from the reaction of acidified alcoholic solutions of acetylacetone with H_2S in the presence of the appropriate metal ion [86]. A similar reaction in the presence of iron(II) or iron(III) ions gave a violet product which has been shown to contain the oxidised form of the ligand, as the 3,5-dimethyl-1,2-dithiolylium cation (LXVIa) [87] with the anion being $[FeCl_4]^{2-}$.



(LXVI a) X = S
(LXVI b) X = Se

The cation (LXVIa) is planar and both the S—S and C—S bonds have some double bond character [87]. In the solid state the compound shows an intense absorption band near 20 000 cm^{-1} which is considered to have its origin in the transfer of charge from the $[FeCl_4]^{2-}$ anion to the $[C_5H_7S_2]^+$ cation (LXVIa) [87]. The close Cl—S contacts suggest a pathway for this charge transfer. This iron complex is a member of a series of compounds $[C_5H_7S_2]^+{}_2[MX_4]^{2-}$ (M = Co and Ni, X = Cl or Br) containing (LXVIa) prepared by oxidising the appropriate chelated complexes (LXV) with a halogen [88]. The analogous diselenolium cation (LXVIb) has been prepared [88], for example, from cobalt(II) carbonate, acetylacetone, and H_2Se in an acidified ethanol solution. Presumably this reaction proceeds via the selenium analogue of the complex (LXV) (M = Co) which is then oxidised in situ by atmospheric oxygen. In contrast,



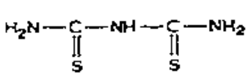
(M = Cr, Co or Rh)

(LXVII) (LXVIII)

the reaction of bromine with the acetylacetonato complexes (LXVII) yields the brominated ligand complexes (LXVIII) [89] rather than an oxidised ligand product.

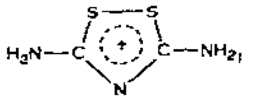
(iii) Dithiobiuret

Dithiobiuret (LXIX) is more easily oxidised than thiourea (XVIII). Iodine reaction in acidic conditions yields the heterocyclic 3,5-diamino-1,2,4-dithiazolium (thiuret) cation (LXX) [90], the counter anion being I^-. This cation can be considered to be formed by oxidation occurring at each of the sulphur atoms of (LXIX) as well as a proton loss from the central nitrogen atom to give an overall charge of +1. The C—S distance of 1.752 Å is longer than in dithiobiuret (LXIX) itself but is still indicative of partial double bond character as are the internal C—N distances of 1.330 Å.



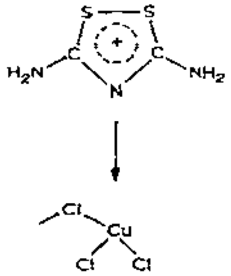
$H_2N-\underset{\underset{S}{\parallel}}{C}-NH-\underset{\underset{S}{\parallel}}{C}-NH_2$

(LXIX)

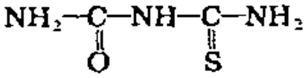


(LXX)

$CuCl_2 \cdot 2\,H_2O$ is reduced by dithiobiuret (LXIX) in a 95% ethanol—ether solution to give, as one of the products, an olive green material whose single crystal structure [91] shows the compound is best represented by the formulation $[Cu^{I}Cl_2]^-[S_2C_2N_3H_4]^+$. The cation is again (LXX), but is attached to copper(I) via the ring nitrogen, being an unusual example of a positively charged ligand complex (LXXI). It is hoped that other products from this reaction will be characterised. Monothiobiuret (LXXII) also reduces copper(II) to copper(I) [92] but the nature of any of the products has not been elucidated.



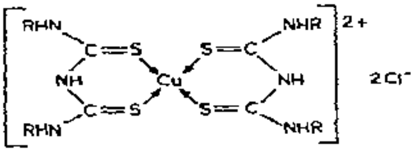
(LXXI)



$NH_2-\underset{\underset{O}{\parallel}}{C}-NH-\underset{\underset{S}{\parallel}}{C}-NH_2$

(LXXII)

In contrast to the previous results, the reactions of substituted dithiobiurets and anhydrous copper(II) chloride in ethanol are reported to give copper(II) complexes (formulated as (LXXIII)). The low magnetic moments (1.11—1.35 B.M.) of these complexes are indicative of metal—metal bonding [93] and would explain their low solubility and hence ready isolation.

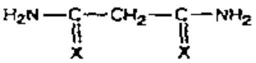


(R = Ph, tolyl or Me)

(LXXIII)

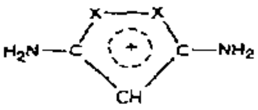
(iv) Dithiomalonamides

Similar oxidations to those described above occur when dithiomalonamide (LXXIV) is oxidised by iodine or iron(III) chloride to yield the 3,5-diamino-



$H_2N-\underset{\underset{X}{\|}}{C}-CH_2-\underset{\underset{X}{\|}}{C}-NH_2$

(LXXIV)



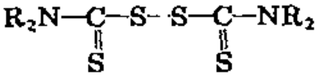
(LXXV)

a X = S
b X = Se

1,2-dithiolylium cation (LXXVa) the counteranions being I⁻ and Cl⁻ respectively [94]. The selenium analogue (LXXIVb) undergoes a similar oxidation to (LXXVb) [95]. Again these reactions may be considered to arise from a two electron oxidation as well as a proton loss.

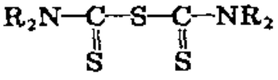
(v) Tetraalkylthiuram disulphides and monosulphides

Another class of dithiones are the tetraalkylthiuram disulphides (LXXVI) and monosulphides (LXXVII). These react with iodine in carbon tetrachloride



$R_2N-\underset{\underset{S}{\|}}{C}-S-S-\underset{\underset{S}{\|}}{C}-NR_2$

(LXXVI)

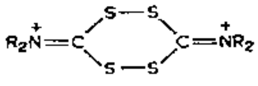


$R_2N-\underset{\underset{S}{\|}}{C}-S-\underset{\underset{S}{\|}}{C}-NR_2$

(LXXVII)

a R = Me
b R = Et

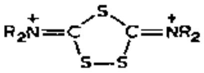
to give initially 1 : 1 complexes as the predominant species [21]. However reaction of (LXXVI) with excess iodine in chloroform or excess $FeCl_3$ in ether, yields ionic compounds in which the cation is likely to be (LXXVIII), the counter anions being I_3^- and $[FeCl_4]^-$ respectively [79,96]. As the positive charge can be held on the nitrogen atoms the dialkylamino substituents will



(LXXVIII a) R = Me
(LXXVIII b) R = Et

help stabilize the cation. The formation of (LXXVIII) may be considered to involve the oxidation of the thione sulphurs followed by ring closure and charge rearrangement (or alternatively oxidation of the appropriate zwitterion). It has also been possible to obtain similar cations where one of the ring sulphur atoms has been replaced by oxygen and also where a methylene group was inserted into one of the disulphide linkages [79].

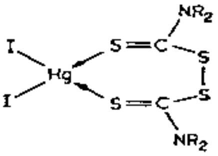
Direct reaction in chloroform of tetramethylthiuram monosulphide (LXXVIIa) with halogens (Cl_2, Br_2 or I_2) also yields solids containing a cyclic cation (LXXIXa) with the anions being Cl^-, Br^- and I_3^- respectively [97]. The



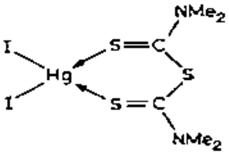
(LXXIX a) R = Me
(LXXIX b) R = Et

X-ray structural determination [98] on the tetraethyl substituted cation (LXXIXb) with $[Hg_2I_6]^{2-}$ as the anion (see below) shows that except for the carbon atoms of the alkyl chain all the atoms lie nearly in one plane. The bond distances would suggest that there is partial π electron delocalisation around the ring.

The disulphides (LXXVI) and (LXXVII) react with metal halides (e.g. Co(II), Cr(III), Zn(II) and Hg(II)) to give complexes where the ligand remains intact [99] and in the case of the mercury(II) iodides X-ray structural data [100] shows the mercury environment in both (LXXXa) and (LXXXI) to have an unusual pseudo-trigonal pyramidal geometry. The complex (LXXXb) reacts with iodine to undergo an oxidation in which the previously discussed



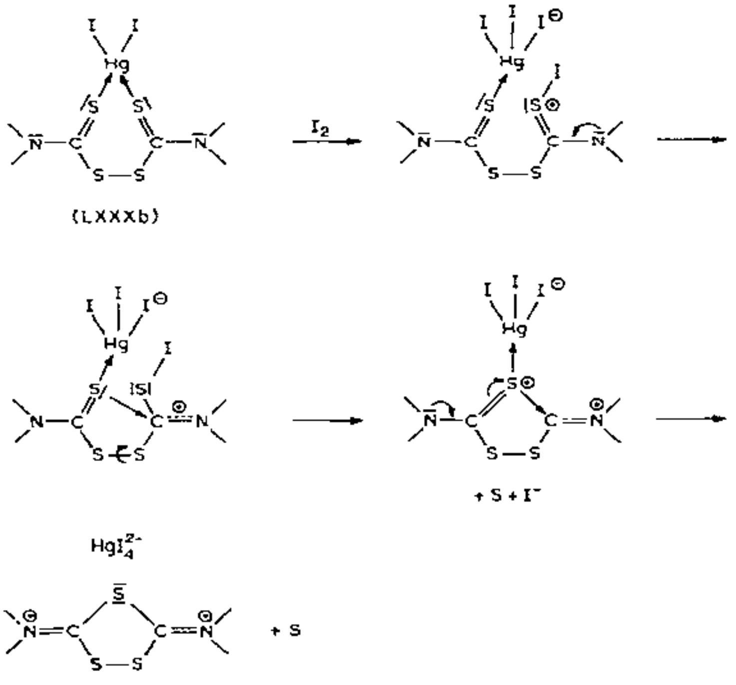
(LXXX a) R = Me
(LXXX b) R = Et



(LXXXI)

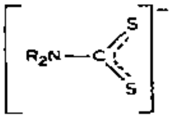
cation (LXXIXb) is produced together with sulphur [101]. A proposed mechanism for the ligand oxidation (eqn. (17)) suggests loss of electrons from the thione sulphurs, ring closure, removal of sulphur, and charge rearrangement [101].

An additional feature of the thiuram disulphides (LXXVI) not seen with other dithiones, is their ability to be reduced. Thus if the disulphides (LXXVI) are added to excess of an oxidisable metal ion in acetone solution the general feature of the reaction is the isolation of dithiocarbamato ligand (LXXXII)



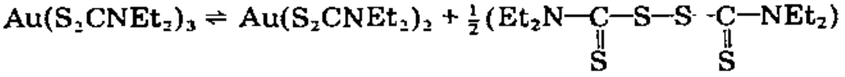
(17)

complexes [79,102]. For example [53] with the appropriate copper(II) salts



(R = Me or Et)
(LXXXII)

the copper(III) derivatives $[CuCl_2(S_2CNR_2)]$ and $[Cu(S_2CNR_2)_2][BF_4]$ (R = Me or Et) have been isolated. The disulphide (LXXVIa) with $Ni(BF_4)_2 \cdot 6\,H_2O$ and $NiCl_2 \cdot 6\,H_2O$ gives the probable nickel(IV) complex $[Ni(S_2CNMe_2)_3]X$ ($X^- = BF_4^-$ or Cl^-) and with $Fe(ClO_4)_2 \cdot 6\,H_2O$ gives the iron(IV) complex $[Fe(S_2CNMe_2)_3]ClO_4$. Related to these reactions is the observation by Vänngard and Åkerstrom [103] that $Au(S_2CNEt_2)_3$ dissociates in benzene according to eqn. (18).



$$Au(S_2CNEt_2)_3 \rightleftharpoons Au(S_2CNEt_2)_2 + \tfrac{1}{2}(Et_2N{-}\underset{\underset{S}{\|}}{C}{-}S{-}S{-}\underset{\underset{S}{\|}}{C}{-}NEt_2) \qquad (18)$$

(LXXVIb)

Reduction of the Au(III) by a $[S_2CNEt_2]^-$ ligand occurs and an unusual Au(II) complex is formed along with tetraethylthiuram disulphide. The Au(II) complex was detected by ESR, but presumably the reverse reaction prevents its isolation. The reduction of the disulphide linkage of (LXXVI) appears to be a facile reaction and the resultant higher oxidation state metal ion is stabilized by the dithiocarbamato ligand (LXXXII). Overall the ability of the thiuram disulphides (LXXVI) to be oxidised at the thione sulphur, or reduced at the disulphide linkage is an interesting feature which could prove useful in the design of new ligand systems.

D. CONCLUSIONS

This article has drawn together examples of redox reactions from a wide area and shown that there is a common pattern of behaviour whether the substrate contains a thiophosphoryl (⋛PS) or thiocarbonyl (>CS) function and the oxidant is a reducible metal ion or a halogen. The formation of cationic products containing a disulphide linkage is a common feature. In the case of dithiones (and possibly diphosphine disulphides) ring closure to give novel cyclic cationic systems, which can be stabilized by π electron delocalization can also occur. An important step in these reactions is the ability of these reagents to oxidise the polarisable sulphur atom. Substituents such as dialkylamino groups bound to the phosphorus or carbon atoms can facilitate these reactions by making the sulphur atom more nucleophilic and stabilising the resulting cationic disulphide product. Substituents that cannot carry a positive charge and do not increase the electron availability on the sulphur atom may, especially in the case of monothiones and phosphine sulphides, give rise only to iodine charge transfer complexes. The nature of the products is also dependent on the dielectric constant of the medium, the more polar solvents favouring redox reactions rather than complex formation.

Some comments can be made about the nature of the metal ions favoured for oxidation of phosphine sulphides and thioureas. Only those that give rise to lower accessible oxidation states (e.g. Cu(II) to Cu(I), Fe(III) to Fe(II), Au(III) to Au(I) and Ce(IV) to Ce(III)) are likely to be favoured, whereas Cd(II), Ni(II) and Co(II) etc. do not fall into this category because even though they form complexes with these ligands, the metal ion is not easily reduced. Metal ions can be classified into hard and soft acids. Cu(II) is considered to be on the borderline of this classification and its interaction with soft polarisable sulphur bases can be envisaged to produce moderately strong Cu—S bonds which become stronger when the metal has become reduced to Cu(I) (a soft acid), perhaps via an inner sphere mechanism. With Ce(IV) (a hard acid) the Ce—S (thiourea) bond would be expected to be weak (if a bond is formed) and hence an outer sphere electron-transfer mechanism appears to operate. Similarly for the hard Mn(III) ion, an outer sphere process is possible.

The effectiveness of Cu(II) as an oxidising agent will be determined by several factors. Firstly it depends on the nature of the solvent. The redox potential of Cu(II) is greater in acetonitrile than in methanol or water, and so redox reactions in the former solvent would be more likely. Secondly the stereochemistry of the intermediate Cu(II) complex is important (where one is proposed). Evidence suggests that thioureas (XVIII) and phosphine sulphides (III) initially react with $CuCl_2 \cdot 2\ H_2O$ or $Cu(ClO_4)_2 \cdot 6\ H_2O$ to form complexes which have distorted tetrahedral structures, so facilitating reduction to tetrahedral Cu(I) complexes via electron-transfer processes. On the other hand, thiosemicarbazide (XXXIX) and substituted dithiobiurets (LXXIII) are S, N and S, S chelating agents respectively, and form complexes containing two moles of the appropriate ligand bound to the Cu(II) in a planar arrangement thus being less likely to be easily reduced. The former complex also achieves an extra stability by having harder N coligands while the latter may have metal—metal bonding. Two of the anions of dithioacetylacetone (LXIV) are bonded in a square planar array about Co(II) and Ni(II) in the complexes (LXV). Oxidation of the ligand in these cases can be achieved with bromine or chlorine. Thirdly, factors such as basicity and bulkiness of the sulphur donor ligands must also exert their usual roles, particularly in the reduction of Cu(II).

The metal ion promoted reactions of thiobenzamides (XXXI) rely on the formation of strong metal—thione sulphur bonds. Where the metal is Hg(II) or Ag(I) (soft metal ions) a proton from the N—H group attached to the thione carbon is ionised (the above metals acting as strong acid catalysts) whereas for Tl(III) and Au(III) (hard metal ions) no prior ionisation was necessary before further reaction, suggesting the metal—sulphur bonds were not as strong as above.

Tetraalkylthiuram disulphides (LXXVI) react with oxidising agents such as $FeCl_3$ and iodine to produce dications of the type (LXVIII) whereas Cr(III) and Hg(II) etc. form complexes with the ligand intact. With $CuCl_2 \cdot 2\ H_2O$, $Fe(ClO_4)_3 \cdot 6\ H_2O$ and $Ni(BF_4)_2 \cdot 6\ H_2O$, reduction of the ligand occurs to give stable dithiocarbamato (LXXXII) complexes of Cu(III), Fe(IV) or Ni(IV) respectively. In these latter cases accessible higher oxidation states must be available or alternatively, as the ligand must be able to be reduced by the metal ion, metals such as Hg(II), Au(III), Cd(II), Cr(III) and Tl(III) would not be suitable

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