The Production of the Sulphate Anion by Interaction of Thioamides with Copper Compounds in Pyridine Solvent

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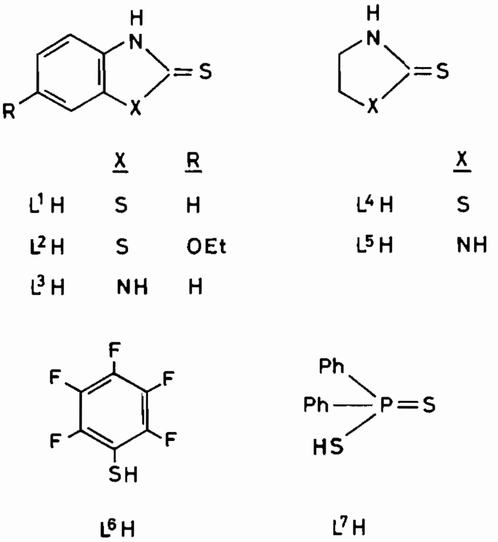
Received July 31, 1984

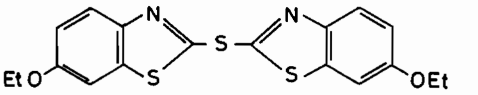
The role of transition metals in promoting oxidation of sulphur containing organic compounds has been well established, the extent of oxidation depending on the particular metal used. Thus copper(II) and iron(III) salts oxidise thiol compounds to disulphides, [1–3] mercury(I), silver(I) and copper(II) can oxidatively cleave disulphides (RSSR) to form sulphinates (RSO_2^-) [4–6], and gold(III) reacts with disulphides to form sulphonates (RSO_3^-) [7].

We report here a copper/pyridine system capable of oxidising thioamides, thiols (Scheme 1), sulphide ion and sulphur to the sulphate ion. In the first two cases concomitant cleavage of the carbon–sulphur bonds occurs, and these are the first instances, as far as we know, of such reactions under mild conditions.



Scheme 1.

When $[Cu(L^1H)_2Cl]$ (0.70 g) is dissolved in pyridine (py) (17 cm^3) a green-yellow solution is obtained. Overnight, dark blue crystals of the complex $[Cu(py)_4SO_4]\cdot 2H_2O$ form – so identified from microanalytical data**, the characteristic infrared absorption spectrum of ionic sulphate [8] and by comparison with an authentic sample [9]. In the case of $[Cu(L^2H)_2Cl]$ crystals of the monosulphide, bis(6-ethoxybenzothiazol-2-yl)sulphide (I) are



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deposited on slow evaporation of the remaining mother liquor. This allows a rationalisation of the sulphur deficiency in the organic moiety, and the proposal of a reaction stoichiometry:

$$[Cu(RSH)_2Cl] + 4py \xrightarrow{[O]} [Cu(py)_4SO_4] + R_2S + 2HCl$$

At this stage, the source of the oxygen is not certain but mechanistic studies of disulphide oxidation to sulphinates have implicated either dioxygen or water [5, 6].

Investigations with a variety of substrates have revealed that the reaction is not restricted to mercaptobenzothiazole systems. The complex, $[Cu(py)_4SO_4]\cdot 2H_2O$, is produced on dissolution in pyridine, of a variety of copper(I) and copper(II) complexes containing ligands of thioamide and thiolate origin, including $[CuL^1]$†, $[Cu(L^3H)Cl]$, $[Cu(L^4H)_3Cl_2]$, $[Cu(L^5H)Cl]$, $[CuL^6]$ and $[Cu(L^7H)Cl]$. In the last case, cleavage of a phosphorus-sulphur bond has occurred. In addition, the provision of a copper complex is not a requirement *a priori* for reaction. Thus sulphate may be similarly generated from the interaction of sources of copper such as CuCl, $[Cu(py)_2Cl_2]$ CuS and CuO with thioamide compounds dissolved in pyridine (see over). Similarly utilising CuCl dissolved in pyridine the source of oxidisable sulphur may be extended beyond thioamide and thiol starting materials to include disulphides and even elemental sulphur.

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**Found: C, 46.7; H, 4.5; N, 10.7. Calc. for $C_{20}H_{24}CuN_4O_6S$: C, 46.9; H, 4.7; N, 10.9%.

†Here and elsewhere, L^1 indicates the deprotonated thiolato form of L^1H.

0020-1693/85/$3.30

$$\left.\begin{array}{l} \mathrm{CuCl + LH} \\ \mathrm{(LH = L^1H, L^3H, L^4H)} \\ \\ \mathrm{CuCl + L^1{-\!\!-\!\!-}L^1} \\ \\ \mathrm{CuCl + S_8} \\ \\ \mathrm{[Cu(py)_2Cl_2] + L^3H} \\ \\ \mathrm{CuS + L^3H} \\ \\ \mathrm{CuO + L^3H} \end{array}\right\} \xrightarrow{\mathrm{py}} \mathrm{[Cu(py)_4SO_4]\cdot 2H_2O}$$

Where CuCl is the Cu source, $[Cu(py)_2Cl_2]$ is a co-product.

Furthermore, pyridine is not the only nitrogen base which promotes formation of sulphate. Quinoline (quin), 3-methylpyridine (3Me-py), and 3-ethylpyridine (3Et-py) similarly give rise to sulphato complexes.

$$\begin{array}{lcl} \mathrm{[Cu(L^1H)_2Cl]} & \xrightarrow{\mathrm{quin}} & \mathrm{[Cu(quin)SO_4]} \\ \mathrm{[CuL^1]} & \xrightarrow{\mathrm{3Me\text{-}py}} & \mathrm{[Cu(3Me\text{-}py)_2SO_4]\cdot 2H_2O} \\ \mathrm{Cu(L^3H)Cl]} & \xrightarrow{\mathrm{3Et\text{-}py}} & \mathrm{[Cu(3Et\text{-}py)_2SO_4]\cdot 2H_2O} \end{array}$$

The evidently cosmopolitan nature of the reaction suggests the presence of common reactive copper species. Currently efforts are being directed toward the elucidation of the reactive entity via ESR spectroscopy. In the case where halogens are absent, *i.e.* for reactions of the type [CuL], CuO, or CuS dissolved in pyridine, a common axial ESR signal with parameters $g_\perp \sim 2.065$, $g_\parallel \sim 2.268$ and $|A_\parallel| \sim 175 \times 10^{-4}$ cm^{-1} is observed. The similarity of this signal with that obtained from freshly prepared $Cu(OH)_2$ in pyridine suggests an intermediate species of the type $[Cu(py)_2(OH)_2]$. Hydroxo ligated copper(II) complexes have also been implicated in the copper promoted cleavage of *o*-benzoquinones and catechols to muconic acid monoalkyl esters [10].

It should be noted that previous authors have misunderstood the nature of their product (actually $[Cu(py)_4SO_4]\cdot 2H_2O$) prepared under similar conditions to our own. El-Shazly *et al.* [11] have earlier misformulated the sulphato complex as '$[\{CuL^1{}_2(L^1H)py\}_2]$'.

Finally the production of sulphate in the above reactions is reminiscent of the processes occuring in chemolithotrophic bacteria such as those of the genus *Thiobacillus* which utilise the oxidation of sulphur, hydrogen sulphide or thiosulphate to sulphate, as an energy source. Details of the bacterial mechanism remain obscure [12], however a transition metal mediated enzymic reaction now may be more strongly implicated from the results presented here.

Acknowledgement

We thank the New Zealand University Grants Committee for support and the award of a Postgraduate Scholarship (to A.G.B.).

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