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Parathiocyanogen $[(SCN)_x]$: a Novel Chemical Oxidation Product of Molten Potassium Thiocyanate

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Summary Compounds of iron(III), cobalt(III), copper(II), and tin(IV) react with molten potassium thiocyanate at 200°, to give a new chemical oxidation product, parathiocyanogen.

ALTHOUGH a considerable range of oxidation products of the thiocyanate ion have been identified in potassium thiocyanate melts as a result of the reduction of various transition metal compounds,[1] the pseudo-halogen itself has not previously been detected. This contrasts both with the behaviour of halide melts, where the free halogen is a frequent oxidation product,[2-4] and that of molten potassium cyanide, where cyanogen has been reported as a product of the reduction of manganese(III) and molybdenum(IV).[5] However, parathiocyanogen has been reported recently as the product of the electrolytic oxidation of molten potassium thiocyanate with a platinum anode.[6] The formation of parathiocyanogen as a product of the reduction of several compounds of transition and non-transition metals in molten potassium thiocyanate at 200° under an atmosphere of dry air is now reported.

Iron(III) chloride reacted immediately, giving a yellow melt containing iron(II) (no absorption maximum over the range 22,000—10,000 cm.$^{-1}$ but an intense band at $>22,000$ cm.$^{-1}$), an orange precipitate, and a small quantity of a sharp-smelling gas. The orange solid contained sulphur, nitrogen, and carbon but no iron; the analysis was correct for $(SCN)_x$. The i.r. spectrum showed bands at 2080 and 1600 cm.$^{-1}$, characteristic of parathiocyanogen. The sharp-smelling gas fumed in contact with ammonia and rapidly polymerised to a yellow film of parathiocyanogen. Potassium hexathiocyanatoferrate(III) tetrahydrate reacted in similar fashion with identical products.

Cobalt(III), in the form of either hexamminecobalt(III) chloride or sodium hexanitritocobaltate(III), reacted immediately to give an intense blue solution of cobalt(II) ($\nu_{\text{max.}}$ 17,100 and 15,750 cm.$^{-1}$), an orange precipitate, and a sharp-smelling gas. Copper(II) chloride and copper(II) thiocyanate both reacted immediately to give a pale yellow melt containing copper(I), together with a golden-coloured solid [correct analysis for $(SCN)_x$] $\nu_{\text{max.}}$ 2070 and 1600 cm.$^{-1}$, together with a sharp-smelling gas. In contrast potassium hexachlorostannate(IV) reacted more slowly, dissolving to give a pale yellow solution from which an orange solid was deposited. The precipitate first appeared after 20 min., the reaction apparently being complete after 10 hr., leaving a colourless melt. The precipitate contained no tin and was identical with the other precipitates.

These reactions indicate that the thiocyanate ion is directly oxidised to the pseudohalogen, which rapidly polymerises to parathiocyanogen. The reduction of the metal is not unexpected in the case of tin(IV), in view of the mild reducing character of thiocyanate melts,[1] while copper(II) thiocyanate is known to be unstable. However, the production of cobalt(II) is more unexpected, and the behaviour of iron(III) in the melt must be contrasted with the intensely coloured thiocyanate complex formed in aqueous solution. The observation that the iron(III) reduction product was soluble in the melt [as was iron(II) chloride, which gave identical yellow melts] though accompanied by the precipitate of orange parathiocyanogen, would seem to amplify and explain the bare statement of Harrington and Sundheim[7] that "all of the Fe$^{\text{III}}$ (as the chloride) had been reduced to Fe$^{\text{II}}$, which did not appear to dissolve".

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[1] D. H. Kerridge and M. Mosley, *J. Chem. Soc.* (*A*), 1967, **352**, 1874.
[2] J. D. von Norman and R. A. Osteryoung, *Analyt. Chem.*, 1960, **32**, 348.
[3] I. Sláma, *Coll. Czech. Chem. Comm.*, 1963, **28**, 2810.
[4] M. W. Y. Spink, *Diss. Abs.*, 1966, **26**, 4274.
[5] W. C. Magnuson, E. Griswold, and J. Kleinberg, *Inorg. Chem.*, 1964, **3**, 88.
[6] K. F. Denning and K. E. Johnson, *Electrochim. Acta*, 1967, **12**, 1391.
[7] G. Harrington and B. R. Sundheim, *Ann. New York Acad. Sci.*, 1960, **79**, 950.