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Reduction of Chromium Compounds by Molten Potassium Thiocyanate

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MOLTEN potassium thiocyanate has proved of value as a non-aqueous solvent for the investigation of transition-metal complexes,[1] its low melting point (177°C) making it a convenient alternative to a true molten alkali-metal halide (lowest m.p. LiI 446°C). Besides arousing interest because of the co-ordinating power of the pseudo-halide ion, either as thiocyanate or isothiocyanate, the melt has now been found to act as an effective reducing agent for transition-metal oxyanions.

In particular three chromium(VI) compounds have been shown to be reduced at varying speeds to chromium(III). Chromium trioxide is immediately reduced by molten potassium thiocyanate at 200°C, to a green solution, which shows no further decomposition over the course of ten days.* The spectrum of this green solution (over the range 32,000—11,000 cm.$^{-1}$)[2] shows a single peak at 16,300 cm.$^{-1}$ analogous to that shown by $K_3Cr(NCS)_6$ or $CrCl_3$ dissolved in molten KSCN (16,500 cm.$^{-1}$). Analysis of the cooled melt indicated that the oxidation products of the thiocyanate included sulphate and sulphide, but not cyanide or nitrite. Cyanate was only detected when much larger quantities of CrO_3 were used.

Potassium dichromate was more stable and dissolved initially to give a yellow solution, absorption maximum 27,450 cm.$^{-1}$, but decomposed within a few minutes to give a green solution, maximum at 16,200 cm.$^{-1}$; however further reaction took place over the course of seven hours, when a green solid was precipitated leaving a colourless solution containing no chromium. The green precipitate analysed as Cr_2O_3 which if left in contact with the melt slowly darkened, becoming almost black. During this colour change, oxide ions were gradually replaced by sulphide forming Cr_2S_3. The oxidation products of thiocyanate by dichromate were more numerous and included sulphate, sulphide, thiosulphate, cyanate, and a small quantity of cyanide.

Potassium chromate was considerably more stable and dissolved at 200°C to give a yellow solution, maximum 27,500 cm.$^{-1}$ (*cf.* 27,000 cm.$^{-1}$ in nitrate and chloride melts)[3] which slowly decomposed over the course of several hours to give a colourless melt and a green precipitate; the latter was again initially Cr_2O_3 but slowly reacted to form Cr_2S_3. The thiocyanate oxidation products were sulphate, sulphide, cyanate, and cyanide.

It was established that precipitation of chromium(III) only occurred in the presence of cyanate. For example $K_3Cr(NCS)_6$ dissolved in molten KSCN was stable for at least two weeks but on addition of KOCN complete decomposition occurred within seven hours to give a green precipitate

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* All reactions described were carried out at 200°C, and the solutions were exposed to the air throughout.

[1] G. W. Harrington and B. R. Sundheim, *Ann. New York Acad. Sci.*, 1960, **79**, 950.
[2] D. N. Henty and D. H. Kerridge, *J. Sci. Instr.*, in the press.
[3] G. P. Smith and C. R. Boston, *Ann. New York Acad. Sci.*, 1960, **79**, 930.

of Cr_2O_3 slowly reacting to form Cr_2S_3. The chromium(III) solutions with added cyanate were again green, absorption maximum 16,200 cm.$^{-1}$, but with a smaller extinction coefficient than pure Cr^{III} solutions; the adsorption edge had moved towards the ultraviolet and a second smaller maximum, at 22,500 cm.$^{-1}$, appeared. On cooling this melt a green solid was obtained with a diffuse reflectance spectrum of two maxima similar to the solution spectrum, whereas solid $K_3Cr(NCS)_6$, and frozen KSCN solutions of $K_3Cr(NCS)_6$ and $CrCl_3$ were purple with only a single maximum at 16,600 cm.$^{-1}$ These observations suggested that cyanate may be co-ordinated to Cr^{III} through oxygen, even though studies on Mn^{II}, Co^{II}, Ni^{II}, and Zn^{II} cyanate complexes indicated co-ordination by nitrogen.[4] Oxygen co-ordination to Cr^{III} would be in accordance with Pearson's suggestion[5] that Cr^{III} is a "hard acid".

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[4] A. Sabatini and I. Bertini, *Inorg. Chem.*, 1965, **4**, 959.

[5] R. G. Pearson, *J. Amer. Chem. Soc.*, 1963, **85**, 3533.