Condensation of Metal Atoms into Molten Salts

Paul D. Hooker and Peter L. Timms

Department of Inorganic Chemistry, The University of Bristol, Bristol BS8 1TS, U.K.

Condensation of metal vapours of molten salts *in vacuo* at 100—200 °C, provides a new way of making highly dispersed forms of metals and metal oxides and, in a few cases, metal complexes.

Condensation of metal vapours *in vacuo* with vapour or liquid forms of organic compounds at temperatures of −269 to 0 °C is an established way of making metal compounds or dispersed forms of metals.[1,2] We report here condensation of metal vapours into molten salts at temperatures of 100—200 °C.

Suitable molten salt systems are those with a low vapour pressure ($<10^{-3}$ Pa) and with fairly low viscosity; some we have used are given in Table 1. Samples of the salt system (*ca.* 20 g) were melted by flame heating in an evacuated, rotating 50 cm^3 Pyrex flask to give 10—15 cm^3 of liquid which wet the

Table 1. Some salt melts of low vapour pressure.

Salts (Molar ratio)	M.p./°C	Redox characterisation
KNO_3–$LiNO_3$ (1.27 : 1)	140	Oxidising
KNO_3–$NaNO_2$ (1 : 1)	150	Oxidising
K–Na–LiOAc (0.38 : 0.30 : 0.32 : 1)	170	'Neutral'
KNCS	170	Weakly oxidising

Table 2. Products of the reaction of metal atoms with KNO_3–$NaNO_2$ melts.

Metal	Product[a]
Cr	Cr_2O_3
Mn	MnO_2
Fe	Fe_2O_3
Co	Co_3O_4
Ni	NiO
Cu	Cu_2O
Ag, Au, Pd	Ag, Au, Pd powders

[a] Identified by powder *X*-ray studies, i.r. spectra, and chemical analyses.

glass. Metal was evaporated (0.1—2 g over 1 h) from a resistance heated crucible in the flask while the salt was kept just molten by applying flame heat or air cooling depending on the heat radiation from the crucible. Condensing atoms entered the melt to give slurries or solutions of the products.

Products insoluble in the melt were isolated anaerobically, either by dissolving the solidified salts with water or other solvents and filtering, or by hot filtration of the melt through a glass frit followed by washing of the collected solid at <100 °C to remove entrained salts. Products soluble in the melt were more difficult to isolate; success depended on finding suitable selective solvents for extraction from the solid salts.

Condensation of metal vapours into KNO_3–$NaNO_2$ melts gave mainly dispersed forms of metal oxides or metals as shown in Table 2. The Cr and Fe oxide products, obtained by dissolving the salts in water, were the least crystalline and resembled 'hydrous oxides' obtained by precipitation from solutions of Cr^{III} or Fe^{III} salts. The Cu_2O formed from copper vapour was a yellow powder which oxidised slowly in air to CuO. Electron microscopy showed that the nearly spherical particles of Cu_2O changed to a more obviously crystalline CuO. Silver, gold, and palladium were extracted from the melts as fine powders. Similar oxide products were obtained with KNO_3–$LiNO_3$ melts, except in the case of copper which gave CuO.

With each melt, gas evolution accompanied the oxidation of Cr, Mn, Fe, Co, Ni, and Cu atoms. Chromium caused the greatest gas evolution (*ca.* 1 mol N_2 evolved per mol Cr condensed), limiting the amount of chromium which could be condensed without too high a pressure developing in the reaction flask. Copper caused least gas evolution; with KNO_3–$NaNO_2$, evolution of an equimolar mixture of N_2 and NO was detectable; with KNO_3–$LiNO_3$, some N_2O was also observed. These results are in line with earlier studies which have shown that redox reactions in these melts are highly complex and can lead to a variety of gaseous products in addition to reduction of NO_3^- to NO_2^-.[3—5] Condensation of chromium atoms into KNO_3–$NaNO_2$ and –$LiNO_3$ melts also gave some chromate ions (5% of condensed Cr was converted into CrO_4^{2-}), possibly formed by secondary oxidation of Cr_2O_3 by the melts.[3]

Simultaneous condensation of Co and Pd or Ni and Pd atoms into KNO_3–$NaNO_2$ melts gave products which appeared, from chemical tests, to be Co_3O_4–Pd or NiO–Pd mixtures. However, the products were pyrophoric unlike the powdered palladium formed from condensation of Pd alone, and the exact nature of the products is still being studied.

Condensation of Cu or Pd atoms into the Li–Na–K–acetate eutectic mixture gave dispersed metals. The palladium contained 1% C + H and was pyrophoric like palladium formed by condensation with alkanes at low temperatures.[1] When Pd atoms were condensed into an acetate melt which also contained crotonate ions (melt molar composition Li : Na : K : OAc^- : $MeCH{=}CHCO_2^-$, 0.32 : 0.30 : 0.38 : 0.70 : 0.30), a brown melt solution was produced. The viscosity of the melt increased as Pd was added but no gas was evolved. The cooled melt was completely soluble in water; ^1H n.m.r. studies of a D_2O solution of the melt gave evidence for several species in addition to unchanged acetate and crotonate ions, corresponding to allylic co-ordination to Pd^{II}, butyrate, and crotonate oligomers $[-MeCH{=}CH(CO_2)-]_n^{n-}$. The formation of the oligomers probably caused the increase in viscosity of the melt.

Oxidative complexation of Ni and Pd atoms also occurs when the atoms are condensed into molten KNCS. The Pd atoms dissolved to give a brown melt from which a brown product (of approximate composition $K_2Pd_4C_2N_2S$) was obtained after removal of the KNCS with acetone. The structure of this product is not yet known, but it is decomposed by water to give H_2S and HCN, suggesting it is a cyano sulphido complex, rather than a thiocyanato complex.

In summary we have shown that transition metal atoms react easily with some molten salt systems. We are currently investigating the structure and catalytic properties of the products and developing new melts with greater complexing ability.

We thank the S.E.R.C. for research support and for a studentship (to P. D. H.).

Received, 1st October 1987; Com. 1430

References

1 K. J. Klabunde, 'Chemistry of Free Atoms and Particles,' Academic Press, New York, 1980.
2 P. L. Timms, *Proc. R. Soc., London, Ser. A*, 1984, **396**, 1.
3 B. J. Brough and D. H. Kerridge, *Inorg. Chem.*, 1965, **4**, 1353.
4 D. H. Kerridge and S. A. Tariq, *Inorg. Chim. Acta*, 1969, **3**, 667.
5 D. A. Nissen and D. E. Meeker, *Inorg. Chem.*, 1983, **22**, 716.