

SHORT COMMUNICATIONS

THE INFLUENCE OF CATIONS ON THE FORMATION OF HIGH OXIDATION STATE COMPOUNDS OF MANGANESE IN MOLTEN SALTS

By R. B. TEMPLE* and G. W. THICKETT*

[Manuscript received 13 March 1973]

Abstract

The reactions of various oxo compounds of manganese were examined in several melts and peroxide- and/or superoxide-melt solutions. Whilst MnO_4^{3-} appears to be the most stable species in NaNO_2 and Na_2O_2 - NaNO_2 solutions, the green MnO_4^{2-} ion is favoured in KNO_2 melts and also in nitrate melts in which K^+ predominates over Na^+ .

Introduction

In previous communications^{1,2} we described the production of MnO_4^{3-} (blue), FeO_4^{3-} (brown), and CoO_4^{3-} (blue-purple) in molten NaNO_2 , either by electrolysis between suitable electrodes or by the solution of the appropriate oxides in melts containing peroxide ion.

This present communication deals with subsequent investigations with manganese in melts other than NaNO_2 . The importance of the melt cation in determining the nature of the most stable complex ion has been indicated in these experiments.

Experimental

The methods and conditions used in these experiments were the same as those reported in our previous papers.^{1,2}

Manganese

We have previously shown that MnO_4^{3-} was stabilized in molten NaNO_2 at 300°C by O_2^{2-} ion. Manganese(vii) and manganese(vi) compounds were unstable and quickly decomposed to Mn^{V} and eventually $\text{Mn}^{\text{IV}}\text{O}_2$ as the O_2^{2-} slowly decomposed in the melt. Mn^{VII} , however, is known to be semistable in $(\text{K},\text{Li})\text{NO}_3$ melts³ and in $(\text{K},\text{Na})\text{NO}_3$.⁴ In the latter melt the $\text{Mn}^{\text{VII}}\text{O}_4^-$ ion slowly decomposes to $\text{MnO}_2 + \text{O}^{2-}$, with the intermediate formation of the green $\text{Mn}^{\text{VI}}\text{O}_4^{2-}$ ion.

* Physical Chemistry Department, University of Sydney, N.S.W. 2006.

¹ Temple, R. B., and Thickett, G. W., *Aust. J. Chem.*, 1972, **25**, 655.

² Temple, R. B., and Thickett, G. W., *Aust. J. Chem.*, 1972, **26**, 1137.

³ Kerridge, D. H., and Tariq, S. A., *Inorg. chim. Acta*, 1968, **2**, 371.

⁴ Bennett, R. M., and Holmes, G. G., *Can. J. Chem.*, 1963, **41**, 108.

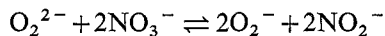
In an attempt to clarify the factors responsible for the stability of the various manganese oxidation states, we have made the following experiments:

(i) Manganese electrodes were used in different melts. In NaNO_2 and NaNO_3 at 350°C , the only cathodic product is the bright blue MnO_4^{3-} ion. In KNO_2 at 450° , however, the melt is initially green, becoming blue-green on standing. In KNO_3 at 350°C the green MnO_4^{2-} ion is the only species produced. Thus sodium ions seem to produce blue MnO_4^{3-} as the most stable intermediate; potassium melts seem to favour the green MnO_4^{2-} .

Lux and Niedermaier⁵ have made similar observations in molten hydroxides, where MnO_4^{3-} is the only stable species in NaOH , while MnO_4^{2-} is also present in KOH . The proportion of MnO_4^{2-} was found to increase in KOH as the temperature was decreased or the partial pressure of oxygen increased. Lux *et al.*⁶ have also shown that exposing fused hydroxides to dry or wet oxygen at 410°C formed peroxides.

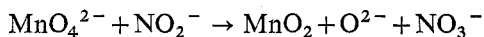
(ii) Clean manganese metal was found to react with various solutions of Na_2O_2 in KNO_2 at 450°C with the formation of green MnO_4^{2-} . Evacuation stabilized the colour, presumably because traces of water destroy the O_2^{2-} ion. The frozen melt is blue-green, which may indicate a mixture of Mn^{VI} and Mn^{V} . Manganese dioxide reacts in the same way in these solutions. If the melt was saturated with Na_2O_2 , the intensity of the blue colour increased and the measured magnetic moment of a frozen melt solution was 2.8 ± 0.1 B.M., which is consistent with the existence of MnO_4^{3-} .

We carried out some experiments with KNO_2 in which we avoided adding sodium ions by using KO_2 as the oxidant. Manganese and its dioxide react with KO_2 - KNO_2 melts to form a deep emerald solution which is green on freezing (MnO_4^{2-} present). Magnetic measurements on this frozen melt solution were unfortunately impossible because of the paramagnetism of the O_2^- ion. Since magnetic measurements of a frozen solution of KO_2 in KNO_2 indicate that the sample is strongly paramagnetic, O_2^- appears to be appreciably stable in this medium. On the other hand Na_2O_2 in NaNO_2 is totally diamagnetic. In both cases the oxygen anions slowly decompose with the formation of oxide (or OH^-) and the Pyrex vessel walls are observed to be variably attacked. This apparent stability of O_2^- in NO_2^- is unexpected from the value for the equilibrium constant of the reaction



($K = 6.7 \times 10^{-11}$) given by Zambonin and Jordan.^{7,8} This value of K suggests that O_2^- should only exist in NO^{-2} in very low concentrations.

Other experiments revealed the following: (a) Traces of Na_2O_2 stabilize Mn^{VI} in $(\text{K}, \text{Na})\text{NO}_3$ at 250°C but excess produces the blue MnO_4^{3-} . (b) K_2MnO_4 reacts with Na_2O_2 in NaNO_3 melts with vigorous evolution of oxygen and the formation of the blue MnO_4^{3-} . (c) K_2MnO_4 reacts with NaNO_3 with the evolution of oxygen and formation of manganese dioxide. In NaNO_2 - NaNO_3 melts however, no oxygen is evolved when K_2MnO_4 is added. This seems to indicate a selective reaction of MnO_4^{2-} with NO_2^- , perhaps¹



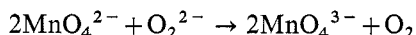
⁵ Lux, H., and Niedermaier, T., *Z. anorg. allg. Chem.*, 1956, **285**, 246.

⁶ Lux, H., Kuhn, R., and Niedermaier, T., *Z. anorg. allg. Chem.*, 1959, **298**, 285.

⁷ Jordan, J., *J. electroanal. Chem.*, 1971, **29**, 127.

⁸ Zambonin, P. G., and Jordan, J., *J. Am. chem. Soc.*, 1969, **91**, 2225.

From these observations and those recorded by Lux for molten hydroxides, we may suspect that the proportion of various manganese oxidation states is controlled by the relative O^{2-} , O_2^{2-} , and H_2O levels in these melts. Melts containing sodium cations are known to contain larger quantities of dissolved water than melts containing potassium cations.⁹ If NO_3^- and NO_2^- melts exist in equilibrium with species such as O_2^{2-} and O_2^- , then we may expect that the relative proportions of these species will depend on moisture levels. The KNO_3 or KNO_2 melts with low concentrations of dissolved water would favour higher oxidation states. Apart from this, O_2^{2-} appears to act as a reductant in its reactions with MnO_4^{2-} since oxygen is evolved:



whereas in its reaction with manganese or manganese dioxide it acts as an oxidant. In aqueous systems hydrogen peroxide is well known for its ability to act in both ways.

TABLE 1

REACTION OF KMnO_4 IN NITRATE MELTS WITH VARIABLE K/Na RATIO

100 mg KMnO_4 in 54.6 g melt at 260°C. Four stages are recognizable: *A*, purple melt (MnO_4^- present); *B*, green-purple melt ($\text{MnO}_4^- + \text{MnO}_4^{2-}$ present); *C*, green melt (MnO_4^{2-} only, and MnO_2); *D*, brown precipitate of MnO_2 (reaction complete)

K/Na mole ratio	Times of appearance (min)			
	<i>A</i>	<i>B</i>	<i>C</i> ^a	<i>D</i>
2.2	0-2	3-9	10-24	25
1.0	0-3	4-11	14-42	44
0.69	0-6	6-20	21-130	135

^a Pale blue colour observed in high sodium melt at end of stage *C*.

The influence of melt cations was further illustrated in a series of experiments in which KMnO_4 was allowed to react in mixed KNO_3 - NaNO_3 melts. The results are shown in Table 1. The stability of Mn^{VI} was found to parallel the proportions of potassium ion present and was further increased on evacuation, as in molten nitrites.

⁹ Frame, J. P., Rhodes, E., and Ubbelohde, A. R., *Trans. Faraday Soc.*, 1961, **57**, 1075.