

SHORT COMMUNICATIONS

THE FORMATION OF MANGANESE(V) IN MOLTEN SODIUM NITRITE

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The formation and reactions of compounds of manganese in oxidation states (II), (IV), (V), (VI), and (VII) in molten alkali nitrates have been reported by several authors.^{1,2} Various oxidation states have been found to be stabilized by the addition of such species as Na₂O₂ and NaOH to the melt.¹ This communication reports briefly on the preparation and identification of manganese(V), as MnO₄³⁻ ion, in molten sodium nitrite.

Experimental

Three separate preparative procedures have been used:

(a) Electrolysis of Molten Sodium Nitrite at 300°C using Manganese Electrodes

A simple Pyrex electrolysis cell was set up, with the catholyte separated from the anolyte by a fine sintered glass filter. As no special precautions were taken to dry the melt, water may be assumed to be present in trace quantities. A potential difference of 4 V between the manganese electrodes was used. The catholyte at first changed colour from the yellow of the molten nitrite to pale green, the intensity of the colour increasing until it was a deep midnight blue. When first quenched, the melt was a bright royal blue colour but on standing in air it slowly absorbed water and turned green; on prolonged standing it became brown-black. In the melt the blue colour proved to be only semi-stable and ultimately decomposed on standing to give a brown-black precipitate.

Agitation of the melt by nitrogen bubbling increased the melt-air contact area and favoured the decomposition of the blue species. Even after prolonged electrolysis no more than c. 2 wt % of manganese could be obtained in the melt, apparently because of the decomposition of the electro-active species produced in the electrolysis process.

(b) Manganese Metal Addition to a Solution of Sodium Peroxide in Molten Sodium Nitrite

Solutions of sodium peroxide in molten nitrite appear to be semi-stable, ultimately decomposing to oxide and nitrate ions.³ This decomposition is accelerated by the presence of dissolved water. Clean manganese metal reacts immediately with peroxide solutions, whether dried or not by previous evacuation in the manner described under (a). A semi-stable blue species is formed which ultimately decomposes to a brown precipitate. The blue species was indefinitely stabilized by evacuation of the system.

(c) Addition of Potassium Permanganate, Potassium Manganate(VI), or Manganese(IV) Oxide to Sodium Peroxide-Sodium Nitrite Solutions

Under anhydrous conditions potassium permanganate decomposes when added to pure NaNO₂ melt at 300°C forming a brown precipitate, oxygen, and a semi-stable blue intermediate. Isothermal thermogravimetric analysis indicated a weight loss of (4.3 ± 0.2) wt % [calc. for

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¹ Bennett, R. M., and Holmes, O. G., *Can. J. Chem.*, 1963, **41**, 108.

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

³ Kerridge, D. H., personal communication, 1971.

0.2O₂ per KMnO₄ 4.1%]. Potassium manganate(VI) decomposed without weight loss when added to pure NaNO₂, with the transient formation of the intermediate blue species. The addition of solid potassium hydroxide to the melt prior to the addition of potassium permanganate was observed to stabilize a transient green intermediate, which rapidly decomposed to the brown oxide. On the other hand addition of sodium peroxide to the molten nitrite either before or after the addition of potassium permanganate produces the deep blue melt characterized in (a). The same result was obtained on adding potassium manganate(VI) or manganese dioxide to a solution of sodium peroxide in molten sodium nitrite. Thermogravimetric analysis showed that the blue species decomposed without weight loss.

Identification

A sample of the quenched melt was ground with dry Nujol, in a dry box, to form a mull and the spectrum was recorded between 10000 and 34000 cm⁻¹ at 90°C in a heated cell on a Unicam SP 700 spectrophotometer. The results were compared with the spectrum of Mn^VO₄³⁻ recorded by Carrington and Symons:⁴ ν_{\max} 30500, 15000 cm⁻¹ (lit.⁴ 30800, 14810 cm⁻¹).

The blue quenched sample was allowed to absorb moisture until it had turned green and its spectrum was again recorded and compared to that of MnO₄²⁻ recorded by the above authors. ν_{\max} 33200, 28200, 23000, 16500 cm⁻¹ (lit.⁴ 33440, 28490, 22940, 16530 cm⁻¹).

These results suggest that the blue compound in the melt is MnO₄³⁻. The identification was confirmed by measuring the magnetic moment of a quenched solution of the electrolysis product in NaNO₂ containing a known weight of manganese. Appropriate corrections were made for the diamagnetism of the salt. The mean magnetic moment was found to be 2.4 ± 0.1 B.M., which is fractionally low for MnO₄³⁻ (d²—two unpaired electrons), but high for one unpaired electron. This appears to be consistent with slight contamination of the MnO₄³⁻ species by MnO₄²⁻ and MnO₂. Attempts to filter out any solid oxide whilst the NaNO₂ was molten were unsuccessful as the blue salt decomposed on the filter, presumably because of the decomposition of the stabilizing O₂²⁻ ion in the sinter.

The similarity between the electrolytic process and the reaction of manganese metal with Na₂O₂ in molten NaNO₂ seems to indicate that the electrolytic reaction produces O₂²⁻ ion as a cathode species, which subsequently attacks the electrode.

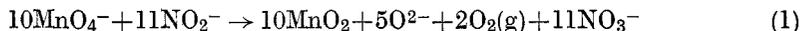
Analysis of the manganese(IV) oxide decomposition product from the electrolytic preparations showed that it had a variable stoichiometry. It appears to be formed by the complex association of O²⁻ and MnO₂ in various molar proportions in the melt. As the quantity of O²⁻ present is quite variable because of the electroreduction of NO₂⁻ and because of the decomposition of O₂²⁻, the stoichiometry of the precipitate is uncertain and difficult to determine. However, using ordinary analytical procedures it has been possible to establish the overall stoichiometry of the reaction between permanganate and molten nitrite, in which the MnO₄³⁻ ion is stabilized as an intermediate when the reaction vessel is evacuated.

When KMnO₄ is added to molten NaNO₂, thermogravimetric analysis indicates an ultimate weight loss of $4.3 \pm 0.2\%$. No nitrogen oxides could be detected and the gas was assumed to be oxygen. In addition, using standard methods of analysis, it has been shown that 0.91 ± 0.08 mol of MnO₄⁻ react with 1 mol of NO₂⁻. The

⁴ Carrington, A., and Symons, M. C. R., *J. chem. Soc.*, 1956, 3373.

stoichiometry of the precipitate formed in this case has been shown to be very close to $2\text{MnO}_2 : \text{O}^{2-}$ corresponding to the manganate(IV) found by Kerridge and Tariq² when MnO_4^- decomposes in molten nitrates. In addition, nitrate ion has been found to be the only oxidation product of NO_2^- , by the method of W. Leithe.⁵

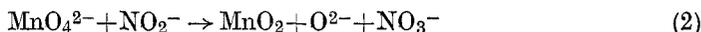
These findings can be represented by the empirical equation



for which the mole ratio $\text{MnO}_4^-/\text{NO}_2^-$ equals 0.91, the mole ratio for $\text{MnO}_2/\text{O}^{2-}$ in the product equals 2, and the weight loss due to oxygen release is 4.1% of KMnO_4 . In addition to these quantitative findings we should note that visual observation shows the bright blue MnO_4^{3-} to be formed as a semi-stable intermediate in the anhydrous melt.

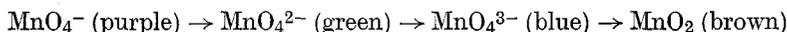
On the other hand, when green potassium manganate(VI) (prepared by the method of Scholder⁶) was added to fresh molten NaNO_2 , no loss in weight was found thermogravimetrically. In this case the overall reacting weights were found to correspond to a molar ratio of $\text{MnO}_4^{2-}/\text{NO}_2^-$ of 0.96 ± 0.10 . Nitrate was again identified as a product by the above method. Titration of the aqueous solution of the frozen melt with standard acid revealed an $\text{O}^{2-}/\text{MnO}_4^{2-}$ ratio of 0.96 ± 0.05 , which is fractionally less than 1.0 because of difficulties in complete hydrolysis of the manganate(IV) precipitate.²

These data correspond to an overall reaction which can be represented as



Visual observation shows that the blue MnO_4^{3-} is again formed as an intermediate.

Our observations therefore suggest very strongly that the decomposition of MnO_4^- in the molten nitrite takes place in steps:



The rather weak green of the MnO_4^{2-} is easily masked by the intense blue of the MnO_4^{3-} and in the absence of high temperature absorbance measurements its existence as an intermediate in the decomposition of MnO_4^- can only be inferred. However, this hypothesis receives support from the fact that when KMnO_4 is added to molten nitrite containing OH^- , a transient green colour is produced.

Bearing in mind the overall analytical results and the intermediate formation and decomposition of MnO_4^{2-} and MnO_4^{3-} it would be possible to write plausible empirical equations for the intermediate steps involving these ions. However, it is very doubtful if anything is gained by doing so, especially as it is obvious that the reaction mechanisms must be complex.

The production of the blue MnO_4^{3-} by adding Na_2O_2 to molten nitrite *before* or *after* adding MnO_4^- , and also by adding *either* MnO_4^{2-} or MnO_2 to a solution of Na_2O_2 in molten nitrite, indicates that MnO_4^{3-} is stabilized by O_2^{2-} . This stabilization is prolonged when the apparatus is evacuated, possibly because of the removal of water vapour which destroys both MnO_4^{3-} and O_2^{2-} .

⁵ Leithe, W., *Mikrochim. Acta*, 1960, 762.

⁶ Scholder, R., and Waterstradt, H., *Z. anorg. Chem.*, 1954, **277**, 172.