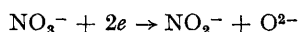


Anodic Chronopotentiometry of Nitrite Ions at Oxidised Platinum Electrodes in Molten Equimolar $\text{NaNO}_3\text{-KNO}_3$

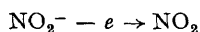
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THE NO_2^+ species may have a finite lifetime in certain nitrate melts but this has not been proved conclusively. It has been postulated as an intermediate in acid-base reactions¹ and electrode reactions² in molten nitrates, although in the latter case it need only have a transient existence. Topol *et al.*³ have shown that acids produce NO_2 rather than NO_2^+ when added to $\text{KNO}_3\text{-NaNO}_3$. Francini and Martini-Francini⁴ have found oxide ions in $\text{LiNO}_3\text{-KNO}_3\text{-NaNO}_3$ melts although this species was not found in $\text{NaNO}_3\text{-KNO}_3$ melts at 250° c by Swofford and McCormick⁵ who showed that NO_2^- was the main impurity. They prepared NO_2^- and O^{2-} by controlled-potential electrolysis using the reaction



The reverse of this reaction has not been studied although the oxidation of NO_2^- in the absence of oxide ions proceeds as follows⁵:—

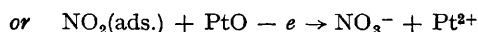
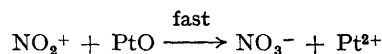


Brough and Kerridge⁶ postulated the formation of NO_2^+ in accounting for some metal reactions in fused nitrate media.

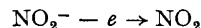
The investigation was performed in the $\text{NaNO}_3\text{-KNO}_3$ (1 mole:1 mole) solvent. A platinum wire sealed in glass was employed as the indicator anode, a large silver helix as the counter cathode, and an Ag/Ag^+ (0.17M in $\text{NaNO}_3\text{-KNO}_3$) couple as the reference electrode. The chronopotentiometric circuit was conventional. The chronopotentiograms obtained with unbiased indicator anodes were very erratic and non-reproducible. Their shapes indicated that part of the applied current was being used to form an oxide film. The anode was therefore biased at a potential positive enough to maintain the oxide film on the surface during the experiments described below.

The concentration of the NO_2^- ions increased significantly as the temperature was raised above 250° c. This process was irreversible. The ions could not always be detected at 250° c except when produced by reducing-impurities. Their concentration was not increased by added Ba^{2+} ions. The electrode was calibrated and the assignment of the chronopotentiometric wave confirmed by adding potassium nitrite. A second chronopotentiometric wave was observed at more

positive potentials as the NO_2^- concentration was increased. The mathematical analysis of the relationship between the first and second transition times will be presented elsewhere. This analysis indicates that the reaction



occurs in parallel with the reaction

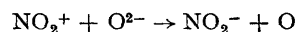


during the second chronopotentiometric wave. The decay curves also support this model. It must be emphasised that NO_2^+ , if present at all, is only proposed as a short-lived intermediate at the anode surface and that it is NO_2 adsorbed on the electrode which is oxidised.

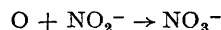
Thus the acid-base dissociation,



is probably followed by the rapid redox step



in $\text{NaNO}_3\text{-KNO}_3$. This would account for the increase in NO_2^- concentration as the temperature is raised. The reverse reaction



which must necessarily involve the dissociation of oxygen molecules, is likely to be very slow as these results suggest. The overall dissociation of the nitrate ion in Na-KNO_3 and other weakly acidic nitrate solvents is thus

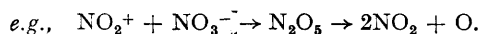


rather than $\text{NO}_3^- \rightarrow \text{NO}_2^+ + \text{O}^{2-}$

(*cf.* Shams El Din and Gerges⁷).

If the redox step above is inhibited (*e.g.*, by the addition of strong acids such as $\text{S}_2\text{O}_7^{2-}$ or by using a solvent containing for example lithium, silver, or alkaline-earth metal ions, NO_2^+ ions will be formed by acid-base reactions. However, they

will be removed by reaction with the solvent NO_3^- ions



(Further investigations of the extent and rate of this reaction in a range of molten salt solvents would certainly help to resolve much of the present controversy concerning the NO_2^+ ion in nitrate melts.)

The residual oxide ion content of the LiNO_3 - NaNO_3 - KNO_3 melt noted by Francini and Martini-Francini⁴ lends support to these conjectures which are also in accord with the well-known thermal decomposition reactions of pure nitrates.

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¹ F. R. Duke, in "Fused Salts", ed. B. R. Sundheim, McGraw-Hill, New York, 1964.

² W. E. Triaca and A. J. Arvia, *Electrochim. Acta*, 1965, **10**, 409; N. Gupta and B. R. Sundheim, *J. Electrochem. Soc.*, 1965, **112**, 836; Yu. K. Delimarskii and G. V. Shilina, *Electrochim. Acta*, 1965, **10**, 973; *Ukrain. khim. Zhur.*, 1964, **30**, 1045; G. V. Shilina, *Ukrain. khim. Zhur.*, 1963, **31**, 693.

³ L. E. Topol, R. A. Osteryoung, and J. H. Christie, *J. Electrochem. Soc.*, 1965, San Francisco Programme, Abstract No. 207.

⁴ M. Francini and S. Martini-Francini, 15th CITCE, London, 1964, Abstract No. 1, 22.

⁵ H. S. Swofford and P. G. McCormick, *Analyt. Chem.*, 1965, **37**, 970.

⁶ B. J. Brough and D. H. Kerridge, *Inorg. Chem.*, 1965, **4**, 1353.

⁷ A. M. Shams El Din and A. A. A. Gerges, *Electrochim. Acta*, 1964, **9**, 613.