Contribution from the Department of Chemistry
the University Southampton, S09 5NH, United Kingdom

Molten Lithium-Potassium Nitrate Eutectic: Stabilisation of Permanganate

B. J. Brough, D. A. Habboush, and D. H. Kerridge

Received July 27, 1971

The effect of dissolved potassium periodate, bromate, chlorate, perchlorate and iodate on the decomposition of potassium permanganate dissolved in lithium-potassium nitrate eutectic melt was studied at temperatures of 210° and 260°. The first three solutes were found to stabilise permanganate for extended periods of time (with 0.1M $KBrO_3$ *and approx.* $3 \times 10^{-4}M$ $KMnO_4$ *at 210°, the stabilisation extended for more than two months), which allowed the spectrum of the permanganate ion in nitrate melt solution to be measured. The stabilisation effect was attributed to the preferential reaction of the halates or perhalate with nitrite, produced by thermal decomposition of the nitrate melt, which would otherwide have reduced the permanganate. This hypothesis was correlated with the thermal decomposition curves of all the halates and perhalates in nitrate melt solution.*

Introduction

Whilst the chemistry of molten nitrates is slowly becoming more understood, present knowledge is very largely confined to the reactions of single solutes dissolved in the molten salt. It follows that the study of the interactions of two or more solutes paricularly when these involve oxidation-reduction processe is an area due for considerable expansion.

The present work has developed this theme and taken further some earlier work[1] on the decomposition of potassium manganate(VII), hereafter called permanganate, in pure nitrate melts, by examining the effects of potassium halates and perhalates as the second solute, and in particular the almost indefinite stabilisation which can be achived by the presence of suitable concentrations of certain of these solutes.

Experimental

Materials. Lithium-potassium nitrate was prepared as previously reported.[2] Analar potasium permanganate was dried at 100° for 2 hours. Analar potassium chlorate, bromate, iodate and periodate and reagent grade potassium perchlorate were all dried at 120° for 2 hours. Analar potassium chlorate, bromate, iodate and periodate and reagent grade potassium perchlorate were all dried at 120° for 6 hours.

Procedure. Reactions were carried out in pyrex tubes with B.24 joints, closed with silica-gel drying tubes, which fitted snugly into a resistance furnace connected to an Ether Transitrol controller. Facilities for bubbling dry nitrogen through the melts were provided.

Analysis. Visible and ultra-violet spectra of aqueous solutions were obtained on a Unicam S.P.800, diffuse reflectance spectra of solidified melts were obtained on the same instrument using a single beam reflectance attachment S.P.890. Spectra of the melt solutions were obtained on a Unicam S.P. 700 adapted for use at temperatures up to 700°. Silica cells of 1 cm and 1 mm pathlengths were used according to the permanganate concentrations. Thermogravimetric analysis was carried out on a Stanton TR-1 thermobalance with a heating rate of 2° per minute. Weight losse are reported as a percentage by weight of the initial solute.

Permanganate was estimated absorptiometrically in aqueous solutions, while bromate and periodate were estimated iodometrically. In the case of mixtures of periodate, iodate and permanganate, all three oxidising agents were first estimated together by the iodometric method, then periodate was reduced (with excess permanganate) to iodate, permanganate removed with nitrite and excess nitrite with urea. The total iodate was then estimated iodometrically.

Results

In contrast with the rapid decomposition of potassium permanganate previously observed in pure lithium-potassium melts,[1] when dissolved in melt solutions of potassium periodate, bromate and chlorate permanganate was found to remain stable for extended periods of time. The variation with time of the absorption due to the 18,550 cm^{-1} permanganate peak in melt solutions of all the available halates and perhalates is shown in Fig. 1. This graph illustrates the lack of effect when potassium iodate and perchlorate were the second solutes as opposed to the considerable stabilisation achieved by chlorate, bromate and periodate and in particular the remarkable fact that a 0.1M $KBrO_3$ solution was able to stabilise permanganate of concentration approximately $3 \times 10^{-4}M$

---

[1] D.H. Kerridge and S.A. Tariq, *Inorg. Chim. Acta*, *2*, 371 (1968).
[2] B.J. Brough and D.H. Kerridge, *Inorg. Chem.*, *4*, 1353 (1965).

at 210° for several months, as opposed to decomposition over a few minutes when dissolved in a pure melt.

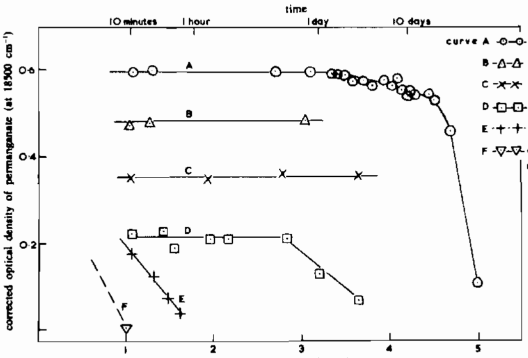

Figure 1. Stabilisation of permanganate by halates and perhalates in Li/KNO$_3$ melt solutions at 210°.

The extent of the stabilisation increased with increasing concentration of solute or with a decreased temperature as is illustrated in Fig. 2 for the solute potassium chlorate. Stabilisation was also found to decrease with an increased concentration of permanganate as may be seen by comparing Figs. 1 and 2 (approximately 3 x 10^{-4}*M* permanganate) with Fig. 3 where the concentration was 2.2 x 10^{-3}*M*. With the more concentrated permanganate solutions the rate of decomposition in the bulk solution was found to be slower than in the spectroscopic cells. Results for the latter are shown in Fig. 3 as smaller open circles and for the bulk solutions as larger circles. With the more dilute solutions this difference was not observed.

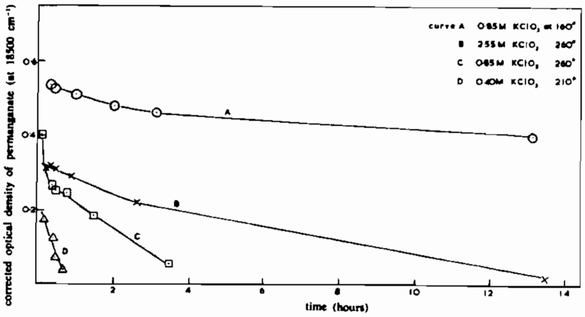

Figure 2. Stabilisation of permanganate by KClO$_3$ in Li/KNO$_3$ melt solutions.

The method used for estimating the absorption of the permanganate, when in the later stages of reaction it was accompanied by a brown suspension of the manganese(IV) product [shown to be $(Li_{0.92}/K_{0.08})_2$-Mn_2O_5 when produced in a pure melt][1] will be described, illustrated by the absorption curves obtained partway through and at the end of a typical decomposition (curves A and B of Fig. 4). The absorption at 18500 cm^{-1} produced by the product after 20 minutes reaction (curve A, Fig. 4) was obtained by means of the interpolation (ab) which was then used as a corrected base line for the permanganate absorption, the latter (cd on Fig. 4) being calculated in the usual way. The validity of this approach was confirmed by determining the actual concentrations of

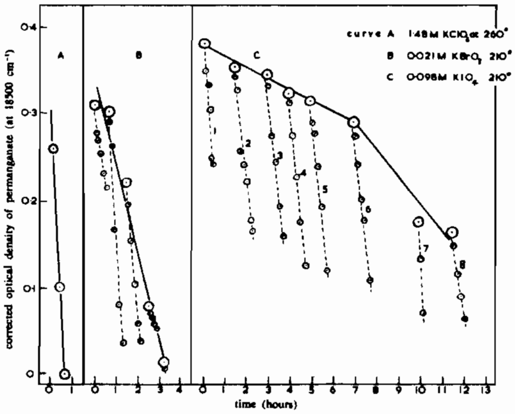

Figure 3. Stabilisation of permanganate by halates and perhalates in Li/KNO$_3$ melt solutions.

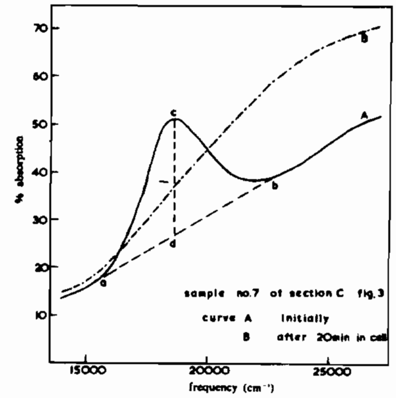

Figure 4. Spectra of permanganate in 0.098M KIO$_4$ melt solution at 260°.

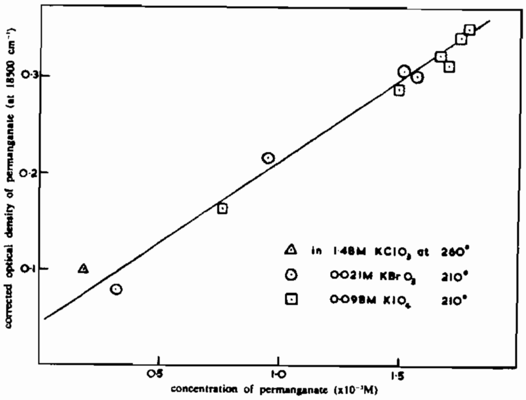

Figure 5. Corrected optical density at 18500 cm^{-1} v. concentration of permanganate in Li/KNO$_3$.

a series of melts by the aqueous colourimetric method when a reasonable straight line for the Lambert-Beer law plot was obtained, as is shown in Fig. 5.

The spectra of the permanganate ion (obtained using the normal solvent-solvent base line) in solutions of both higher and lower concentrations, stabilised by periodate and by bromate respectively, are shown in Fig. 6 together with, for comparison, the aqueous spectrum and the diffuse reflectance spectrum of the solidified periodate stabilised solution.

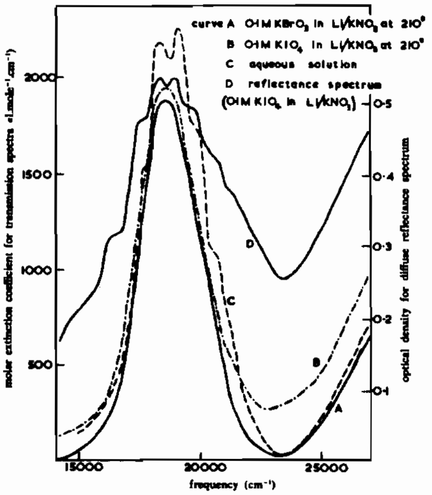

Figure 6. Spectra of permanganate solutions

The concentration of the stabilising solute was found to decrease during the time of stabilisation in the case of potassium bromate and potassium periodate. For example with the latter solute after 11.5 hours (No.8 of Section C of Fig. 3) the concentration of periodate had decreased from the initial value of 0.098*M* to 0.008*M* while analysis showed the solution to be 0.090*M* in iodate.

Potassium chlorate, however, appeared to be stable and no appreciable concentration of chloride was formed during course of the reaction.

The stability of these solutes in a pure nitrate melt not containing any permanganate was relevant to these observations and thermogravimetric curves were determined and are given in Fig. 7. Also shown are curves for solutions containing chlorate and chloride, bromide and bromate, together wih periodate and iodate. Of particular interest is curve I obtained for a melt containing equimolar amounts of periodate and nitrite which showed only a small loss (1.2%) and which should be compared to the 12.1% loss obtained from a solution of periodate not containing added nitrite (curve G). The evolved gases from the latter solute consisted largely of oxygen together with small amounts of nitrogen dioxide and iodine (calc. for loss of ½O_2 per KIO_4 7.0%). The reaction products of the halate solutions in nitrate melts were all initially oxygen and have been described in more detail earlier.[3]

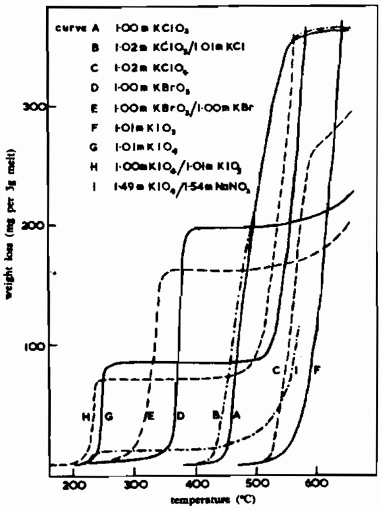

Figure 7. Thermogravimetric analysis of Li/KNO_3 melt solutions.

The reactivity of halate and perhalate solutions in fused nitrate towards manganese(IV) oxide (as received and freshly precipitated) was also examined. Periodate and bromate were found to oxidise this to permanganate though only very slowly, but chlorate, iodate and perchlorate were found not to form permanganate at all.

Table I. Decomposition of permanganate in presence of nitrite.

Initial Solution	Nitrite added	Resultant solution
A. 1.1×10^{-2} m.mole $KMnO_4$	0.25 m.mole (0.05*M*)	Purple
(2.2×10^{-3}*M*) Stabilised by 0.51	+0.21 m.mole (0.092*M* in total nitrite)	Reddish- purple
m.mole KIO_4 (0.1*M*)	+0.08 m.mole (0.11*M* in total nitrite)	Brown-suspension of Mn^{IV} (IO_3^- present) (IO_4^- absent)
B. 1.1×10^{-2} m.mole $KMnO_4$ (2.2×10^{-3}*M*) No halate or perhalate	0.09 m.mole (0.018*M*)	Brown suspension of Mn^{IV} in few seconds. Not adherent to walls of tube.

---

(3) D.A. Habboush and D.H. Kerridge, *Inorg. Chim. Acta, 4,* 81 (1970).

The addition of sodium nitrite to stabilised or unstabilised permanganate solutions was found to result in their rapid decomposition. The stoichiometry and observations made during these additions are set out in the Table.

Discussion

It is at once apparent from Figs. 1, 2 and 3 that permanganate, which had only a transient existence in pure lithium-potassium nitrate melts, was very considerably stabilised in melts containing certain halates and perhalates in solution. The order of stabilising effect was periodate ≈ bromate > chlorate ≫ perchlorate ≈ iodate and thus parallels the increase in heat of formation[4] and the thermal stability of the pure salts[5]. The order of stabilisation was also closely similar to the decomposition temperatures of the solutions in nitrate (fig. 7, curves G, D, A, C and F) where the gaseous decomposition product was initaially oxygen. However, it is not considered that the observed stabilisation was due to this evolved gas since oxygen was found to exert only a marginal (13%) reduction in the rate of decomposition of permanganate in nitrate melts at 160°.[1] Nor is the stabilisation effect considered to result from the reoxidation of the manganese(IV), initially formed as the decomposition products, by the halates of perhalate, since not only was no brown suspension seen in the initial stages of the stabilisation but chlorate, though quite an effective stabiliser, was found to be incapable of such reoxidation.

The most likely explanation of the observed stabilisation is that the active reducing species is the nitrite produced by thermal decomposition of the nitrate melt

$$NO_3^- \rightleftharpoons NO_2^- + \tfrac{1}{2}O_2 \qquad (1)$$

and that this reacts with permanganate (cf. section B of Table)

$$2MnO_4^- + 3NO_2^- \rightarrow Mn_2O_5^{2-} + 3NO_3^- \qquad (2)$$

so that together with equation 1, the stoichiometry would be

$$2MnO_4^- \rightarrow Mn_2O_5^{2-} + 3/2O_2 \qquad (3)$$

which is identical with that determined earlier.[1] If, however, a rective halate or perhalate is present it is presumed that this reacts preferentially with the nitrite as it is formed and in the case of the more dilute solutions of permanganate (Figure 1) the permanganate only reacted when the concentration of halate or perhalate had fallen to a suitably low value.

This hypothesis is supported by the stoichiometry revealed in the table, in that the nitrite required for reduction of the permanganate to manganese(IV) is equivalent to the periodate rather than to the permanganate, and by the thermal decomposition of halate and perhalates in nitrate melts which can be well explained as a reaction with the equilibrium concentration of nitrite. [No agreement on the precise value of this equilibrium constant (equation 1) has yet been reached by the various investigators[6-10] but it is generally agreed to increase with decrease in size of the alkali metal cation and to increase markedly with temperature. To an approximation the nitrite concentration in lithium-potassium nitrate eutectic can be taken as $10^{-4}M$ at 200°, increasing to $2M$ at 500°]. Certainly the stoichiometry of the reaction of iodate with nitrite in nitrate melt solution has been established as[3]

$$IO_3^- + 3NO_2^- \rightarrow I^- + 3NO_3^- \qquad (4)$$

while the reaction of periodate appears to be

$$IO_4^- + NO_2^- \rightarrow IO_3^- + NO_3^- \qquad (5)$$

in view of the very low weight loss revealed by curve I of Figure 7 as compared to curves G and F.

There is also a satisfactory correspondence between the relative concentrations of chlorate, bromate and periodate required for equivalent stabilisation (Figure 3) and the temperatures of thermal decomposition in nitrate melts (Figure 7 curves A, D and G).

This hypothesis of nitrite formation as the rate controlling step in the reduction of permanganate is also in accord with otherwise curious results indicated on Figure 3 by the smaller open circles. With the latter results the melts were contained in 1 mm silica spectroscopic cells in which the surface to volume ratio was approximately 20, whereas with the results indicated as larger open circles the melt solution had been contained in pyrex tubes with a surface: volume ratio of approximately 2. The nitrate decomposition (equation 1) has been shown to be a heterogenous reaction, with the rate dependant on the nature and area of the solid-liquid interface, so it appears reasonable that the reaction should be of zero order in both containers, with the rate of nitrite production and hence permanganate reduction considerably greater in the 1 mm spectroscopic cells. When the melt solution was contained in 1 cm spectroscopic cells the surface-volume ratio would be reduced by a factor of ten so that the absence of rapid decomposition in Figures 1 and 2 (i.e. any values indicated by small circles) could be expected.

The spectrum of the stabilised permanganate ion (Figure 6) was very similar to that in aqueous solution and was attributed to the same charge transfer transition even though the higher temperature has resulted in the loss of the vibrational fine structure. The characteristic fine structure could be seen however in the diffuse reflectance spectrum of the frozen stabilised melt (curve D). The absorption maximum

---

(4) «Selected values of Chemical Thermodynamic Properties». N.B.S. circular 500, Washington 1952.

(5) C. Duval « Inorganic Thermogravimetric Analysis » Elsevier, Amsterdam, 1963.

(6) E. S. Freeman, *J. Phys. Chem.*, 1954, *60*, 1487; *J. Amer. Chem. Soc.*, *79*, 838 (1957).

(7) R.W. Bartholomew, *J. Phys. Chem.*, 20, 3422 (1966).

(8) G.D. Robbins and J. Braunstein, *J. Electrochem. Soc.*, *116*, 1218 (1969).

(9) A. Lundén, *Electrochim. Acta*, *14*, 1068 (1969).

(10) R.N. Kust and J.D. Burke, *Inorg. Nucl. Chem. Lett.*, *6*, 333 (1970).

(11) B.J. Brough, D.H. Kerridge, and S.A. Tariq, *Inorg. Chim. Acta*, *1*, 267 (1967).

in the fused melt was placed at 18500 cm^{-1}, with an extinction coefficient (from Figure 5) of 1850 l.mole^{-1} cm^{-1}, which is somewhat lower than the value of 2300 l.mole^{-1}cm^{-1} found in aqueous solution, analogous to the lower extinction coefficients found for the chromate, dichromate[11] and triiodide[3] absorptions in fused nitrate solution. The rather larger minimum in the case of the more concentrated permanganate solution, curve B (obtained with 1 mm cells) was attributed to a small amount of decomposition.

Acknowledgments. Grateful thanks are extended to the Science Research Council for grants for the purchase and adaption of the high temperature spectrometer and for a grant to B.J.B., to the Calouste Gulbenkian Foundation, Lisbon for a grant for apparatus and a scholarship to D.A.H. and to Basra University, Iraq for a grant and leave of absence to D.A.H.