Contribution from the Department of Chemistry,
The University, Southampton, United Kingdom

Molten Lithium-Potassium and Sodium-Potassium Nitrate Eutectics: the Stabilisation of Manganate(VI) and Manganate(V)

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

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In lithium-potassium nitrate eutectic, manganate(V) was stabilised as a blue suspension in solutions of hydroxide, oxide and peroxide which were above a minimum concentration ($\sim$0.1 m), with solutions below this concentration a black manganate(IV) was precipitated. Somewhat different results were obtained in sodium-potassium nitrate where green soluble manganate(VI) was stabilised in hydroxide solutions and blue soluble manganate(V) in oxide or peroxide solution provided the concentration was $>$0.1 m. With concentrations below 0.1 m oxide or peroxide, mixtures of the two oxidation states were produced, the proportion being dependent on the oxide: manganese ratio. The visible-ultraviolet absorptions of the two species are given. All experiments were conducted at 260°C.

Introduction

The behaviour of single solutes in molten nitrate solutions has now been sufficiently studied that a modest understanding of the chemistry of at least some of the principal oxidation states of the more common elements can be claimed. However, the natural development of this work to the study of reactions between two or more solutes, with which the great bulk of any solution chemistry must obviously be concerned, is at a much earlier and less satisfactory stage. The present studies extend this field a little in elucidating the conditions for the stabilisation of two less common oxidation states of manganese.

In 1963 Bennett and Holmes[1] described the stabilisation of manganate(VI) by sodium peroxide, and manganate(V) by sodium hydroxide in sodium-potassium nitrate eutectic at 260°C. But since they had also reported manganate(VI) as an intermediate, stable for several minutes, in the decomposition of permanganate and this contrasted with the immediate disproportionation of manganate(VI) reported for a lithium-potassium nitrate melt,[2] it seemed worthwhile to investigate any stabilisation which might occur in the latter melt. This in turn led on to a re-investigation of stabilisation in the former mek since the statement of Bennett and Holmes seemed possibly at variance with a later report[3] that addition of permanganate to a solution of sodium oxide in sodium-potassium nitrate resulted in reduction to manganese dioxide.

Another feature of interest in these parallel investigations was to provide evidence for the extent to which the alteration of the alkali metal cation of the melt could change the degree of stabilisation. The commonly held assumption being that such alteration would have relatively little effect, though the lithium containing melt would be expected to be rather more acidic.

Experimental

Materials. Lithium-potassium nitrate was prepared as previously reported.[4] Analar potassium permanganate was dried at 100° for 2 hours. Potassium manganate(VI) was prepared by the method of Scholder.[5] The dark green crystals, after drying at 120°, were analysed. (Found: Mn, 27.4. Calcd for K_2MnO_4, Mn 27.8%). Analar sodium peroxide, sodium hydroxide and potassium hydroxide were used as received. Sodium monoxide was prepared by the decomposition of the peroxide under vacuum at 620°,[5] analysis for peroxide and total basicity indicated 5.3 per cent sodium peroxide and 93.5% sodium monoxide.

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 Transitol controller, all reactions being carried out at 260°.

Analysis. Visible and ultraviolet spectra of aqueous solutions were obtained on a Unicam S.P. 500. 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°. The frozen

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[1] R. M. Bennett and O. J. Holmes, *Canad. J. Chem.*, *41*, 108 (1963).
[2] D. H. Kerridge and S. A. Tariq, *Inorg. Chim. Acta*, *2*, 371 (1968).
[3] H. S. Swofford and P. J. McCormick, *Anal. Chem.*, *37*, 970 (1965).
[4] B. J. Brough and D. H. Kerridge, *Inorg. Chem.*, *4*, 1353 (1965).
[5] R. Scholder and H. Waterstradt, *Z. Anorg. Chem.*, *277*, 172 (1954).
[6] G. W. Horsley, A.E.R.E. Report M/R 1441 (1954).

melts containing manganate(VI) and manganate(V) were dissolved in water when disproportionation took place. The soluble permanganate formed was estimated absorptiometrically and the insoluble manganese dioxide filtered off, washed, oxidised to permanganate with periodate and estimated absorptiometrically. The proportions of the manganese concentrations (2:1 or 1:2 respectively) gave a clear indication of the original oxidation state.

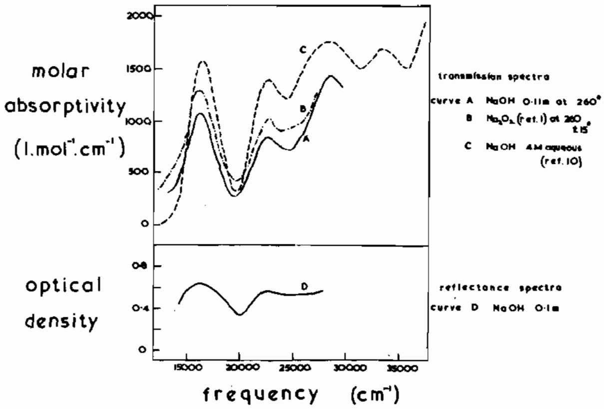

Figure 1. Spectra of manganate(VI) in sodium-potassium nitrate.

Results

Reactions in lithium-potassium nitrate eutectic. The reaction of manganate(VI) in a pure melt is rapid, disproportionation occurring within a few seconds to give a purple permanganate solution and black manganate(IV) precipitate (shown to be K_2MnO_3).[2] In contrast, when manganate(VI) was added to a melt at 260° containing sodium hydroxide, a reaction occurred initially forming a bluish-purple melt which then transformed to a sky-blue suspension. Filtration through a fine glass sinter, or asbestos, retained all the manganese and gave a colourless melt.

Potassium permanganate, which initially dissolved as a purple solution, also reacted within a few seconds in a melt containing hydroxide to give a blue suspensions wich showed no further change over 90 minutes. When frozen these suspensions gave a diffuse reflectance spectrum characteristic of manganate(V) (curve D, Figure 2) and when dissolved in water disproportionated to permanganate and manganese dioxide in the proportions of 1:2.

Similar results were obtained when permanganate was added to melt solutions containing dissolved sodium monoxide, sodium peroxide or potassium hydroxide. Minimum concentrations of base were found to be required for stabilisation of manganate(V) otherwise decomposition to a brown-black precipitate of manganate(IV) was found to occur. These minimum concentrations were found to be a little above 0.10 m for sodium hydroxide and sodium monoxide but more than 0.20 m for potassium hydroxide.

The stability of manganese(IV) compounds towards these basic melt solutions was examined and it was found that the manganate(IV) formed by complete decomposition of permanganate in a pure lithium-potassium melt was not reoxidised in a nitrate melt containing hydroxide, similarly neither manganate(IV) nor manganese dioxide suspensions could be oxidised by sodium peroxide solutions.

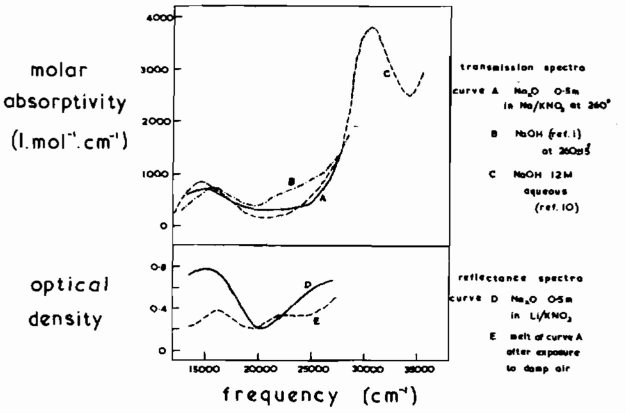

Figure 2. Spectra of manganate(V).

When lithium hydroxide was used in place of sodium or potassium hydroxides, the permanganate first reacted to form manganate(V) but this then decomposed slowlv forming a brown suspension of manganate(IV) (Table I).

Reactions in sodium-potassium nitrate eutectic. In the pure eutectic, potassium manganate(VI) was found to exist for several minutes as a green solution before decomposing to a black precipitate of manganate(IV). However, if the melt contained sodium hydroxide, the manganate(VI) was found to be stable indefinitely as a green solution. Similarly, if potassium permanganate was added to a melt containing hydroxide a stable green solution of manganate(VI) was obtained. Potassium hydroxide could be used instead of sodium hydroxide but with lithium hydroxide the green solution initially obtained decomposed after 5 minutes to a brown manganate(IV) suspension (Table III).

In melts containing sodium monoxide or peroxide the reaction products were more variable, either manganate(VI) or manganate(V) or both were produced, depending on the concentration of the base and the ratio of base to manganese. The results obtained are listed in Table IV, and show that the minimum concentrations of base required for the formation of manganate(V) were close to 0.10 m for both sodium peroxide and sodium monoxide.

In contrast to the results obtained with lithium-potassium nitrate and reported above, manganese dioxide was found to be oxidised to a blue manganate(V) solution by sodium peroxide solutions with evolution of oxygen (Table V) and when more manganese dioxide was added (reducing the O_2^{2-}:Mn ratio) green manganate(VI) was formed.

Reoxidation of the manganate(V) was observed if the sodium monoxide solutions were left in contact

Table I. Reaction of potassium permanganate in lithium-potassium nitrate (at 260°). Solutions of hydroxides.

Base	Reactant concentration OH^-(m)	Reactant concentration Mn (m×10^3)	Ratio OH^-:Mn	Sampling Time(min)	Proportions of disproportionation products Mn^{VII}:Mn^{IV}	Species (as identified by reflectance spectra)
NaOH	0.07	1.1	64:1	10		MnO_3^{2-} [c]
	0.10	0.5	200:1	5		»
NaOH	0.22	1.25	176:1	10	1:2.3	MnO_4^{3-}
	0.21	4.6	45:1	15	1:1.5	»
	0.21	23.1	9:1	20	1:2.3	»
NaOH [a]	0.96	115	834:1	30	1:2.2	»
	0.97	4.75	204:1	15	1:1.8	»
	0.99	23.5	42:1	10	1:2.0	»
	0.96	18.5 [b]	26:1	15	1:1.6	»
	0.97	96.3	10:1	15	1:1.8	»
KOH	0.20	1.1	182:1	10		MnO_3^{2-} [c]
	0.97	1.1	882:1	10	1:2.4	MnO_4^{3-}
	0.97	4.9	196:1	10	1:2.4	»
$LiOH.H_2O$ [a]	1.16	1.45	800:1	10		MnO_3^{2-} [c]

[a] Incompletely soluble. [b] The reactant was potassium manganate(VI). [c] This species was identified visually.

Table II. Reaction of patassium permanganate in lithium-potassium nitrate eutectic (at 260°) solutions of sodium peroxide or sodium monoxide.

Base	Reactant concentration O_2^{2-} or O^{2-}(m)	Reactant concentration Mn (m×10^3)	Sampling Time(min)	Ratio O_2^{2-} or O^{2-}:Mn	Species (as identified by reflectance spectra)
Na_2O_2	0.10	0.2	15	83:1	MnO_4^{3-}
	0.10	22.7	15	5:1	»
Na_2O_2 [a]	0.47	4.5	10	104:1	»
	0.52	6.6 [b]		79:1	MnO_2 [c]
Na_2O	0.11	1.1	10	100:1	MnO_3^{2-} [c]
	0.11	4.7	15	22:1	»
Na_2O [a]	0.52	99.1	30	5:1	MnO_4^{3-}

[a] Incompletely soluble. [b] The reagent was manganese dioxide. [c] This species was identified visually.

Table III. Reaction of potassium permanganate in sodium-potassium nitrate (at 260°) containing various hydroxides.

Base	Reactant concentration OH^-(m)	Reactant concentration Mn (m×10^3)	Ratio OH^-:Mn	Sampling Time(min)	Proportions of disproportionation products Mn^{VII}:Mn^{IV}	Species (as identified by reflectance spectra)
NaOH	0.22	0.35	628:1	15	1:0.43	MnO_4^{2-}
	0.19	0.95 [b]	200:1			»
	0.22	1.15	192:1	10	1:0.45	»
	0.22	4.25	52:1	5		»
	0.23	23.4	10:1	10	1:0.61	»
	0.23	71.8	3:1	15		»
	[d] 0.22	4.25	52:1	600		$MnO_4^{3-}+MnO_4^{2-}$
NaOH	0.98	1.15	844:1	10	1:0.45	MnO_4^{2}
	0.49	4.75	208:1	10	1:0.43	»
	0.99	5.15	192:1	30		»
	[d] 0.99	5.15	192:1	60		MnO_4^{3-}
NoOH [a]	2.52	2.8	900:1	15		MnO_4^{2-}
KOH	0.19	1.1	172:1	10	1:0.45	»
LiOH . H_2O [a]	1.19	1.25	952:1	5		MnO_3^{2-} [c]

[a] Incompletely soluble. [b] The reactant was potassium manganate(VI). [c] This species was identified visually. [d] Reaction mixture under vacuum.

with moist air, when a green layer appeared at the melt-atmosphere interface (a diffuse reflectance spectrum of this frozen melt being shown as curve E of Figure 2). This change from blue to green was gradually reversed when the melt solutions were left in contact with dry air. Conversely melts containing hydroxide and manganese(V) were changed from green to blue by evacuation (*e.g.* a 1 m NaOH melt after pumping to 0.01 torr for 1 hour at 260°), see Table III. The removal of water was confirmed by infrared spectroscopy on a mull of the frozen melt. Manganate(VI) was reformed on addition of more sodium hydroxide.

The solution and diffuse reflectance spectra of manganate(VI) and manganate(V) solutions when stabilised with sodium hydroxide and sodium peroxide or monoxide, respectively are shown in Figures 1 and 2. The extinction coefficients are listed in Table

Table IV. Reaction of potassium permanganate in sodium-potassium nitrate (at 260°) containing sodium peroxide or sodium monoxide.

Base	Reactant concentration O^{2}(m)	Mn (m×10^3)	Ratio O^{2-}:Mn	Sampling Time(min)	Species (as identified by reflectance spectra)
Na_2O_2	0.10	1.1	95:1	15	$MnO_4^{3-}+MnO_4^{2-}$
	0.11	4.6	23:1	15	$MnO_4^{2-}+MnO_4^{3-}$
	0.10	25.2	4:1	10	MnO_4^{2-}
Na_2O_2 [a]	0.51	1.3	392:1	10	MnO_4^{3-}
	0.52	4.6	112:1	10	»
	0.51	5.8 [b]	88:1	240	»
Na_2O	0.11	1.1	100:1	15	»
	0.10	4.5	22:1	5	MnO_4^{2-} ;
Na_2O	0.48	4.3	112:1		MnO_4^{3-}

[a] Incompletely soluble. [b] The reactant is manganese dioxide.

Table V. Extinction coefficients for manganate(VI) and manganate(V) in sodium-potassium nitrate (at 260°) and aqueous solutions (at 20°).

Solute	Absorption Maximum	Extinction Coefficient
MnO_4^{2-}	28600 cm^{-1}	1290±170 l $mole^{-1}cm^{-1}$
(0.11m NaOH in Na/KNO_3)	22800	850±60
	16200	1080±80
MnO_4^{2-}	28500	1750 [a]
(4*M* NaOH in aqueous)	22800	1025 [a]
	16300	1290 [a]
MnO_4^{3-}	15100	720±70
(0.5m Na_2O in Na/KNO_3)		
MnO_4^{3-}	15000	900 [a]
(12*M* NaOH in aqueous)		

[a] reference 10.

V together with the comparable values obtained for aqueous solutions. The absorptions at higher energies were not obtained in melt solutions owing to a strong absorption by nitrate (band maximum 33,200 cm^{-1}).

Discussion

The spectral data and the evidence of the ratio of the disproportionation products in aqueous solution clearly indicates that both manganese(VI) and manganate(V) can be effectively stabilised in nitrate melts.

In lithium/potassium nitrate, manganate(V), as an insoluble blue suspension, was rapidly formed from permanganate in melts containing hydroxide, monoxide or peroxide. A similar product was obtained from additions of potassium manganate(VI) but the initial purplish blue colour suggested the disproportionation:

$$2MnO_4^{2-} \rightarrow MnO_4^{-} + MnO_4^{3-} \qquad (1)$$

and thus that manganate(VI) was unlikely to be an appreciable stable intermediate in the reduction of permanganate. This disproportionation (1) was not identical with that observed for manganate(VI) in a pure lithium-potassium nitrate melt, when a manganate(IV) was produced,[2] since this product could not be reoxidised to manganate(V).

The minimum concentrations of sodium hydroxide, sodium monoxide and potassium hydroxide required for stabilisation of manganate(V) were in fact quite similar, because at these temperatures potassium hydroxide has been found to be unstable in lithium-potassium nitrate, dehydrating to form potassium monoxide, whereas sodium hydroxide was stable until 390°.[7] Thus the minimum concentration required for the stabilisation of manganate(V) was ~0.1 m for any of the above three bases and probably also for sodium peroxide.

The ineffective stabilisation observed with lithium hydroxide was attributed to the very sparing solubility of this salt (a similarly low solubility has been reported for the lithium oxide[8]) which was thus presumed to provide a basic solution below the required minimum concentration. The solubility of the other bases are not known at 260°, but at 160° have been reported as follows:[9] Na_2O, 0.15 m; Na_2O_2, 0.008 m; NaOH, 0.44 m; KOH 0.67 m. Those cases where incomplete solubility was observed at 260° are noted in Tables I - IV and are consistent with the above values.

In sodium-potassium nitrate the stabilised oxidation states proved to be more numerous, manganate(VI) being the stable species in sodium or potassium hyddroxide solutions whether added as such or rapidly formed as the reduction product of permagnanate. The incomplete stabilisation observed with lithium hydroxide solutions was again attributed to its low solubility.

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(7) D. A. Habboush and D. H. Kerridge, forthcoming.
(8) D. A. Habboush and D. H. Kerridge, *Inorg. Chim. Acta, 4,* 81 (1970).
(9) B. J. Brough and D. H. Kerridge, *J. Chem. Eng. Data, 11,* 260 (1966).

In sodium monoxide or peroxide solutions manganate(V) was, as in lithium-potassium nitrate, the reduction product of permanganate provided the concentration of base was above the minimum of 0.10m, otherwise the product was a mixture with manganate(VI). This variation of oxidation state with concentration is, of course, analogous to the aqueous system where 12M hydroxide was required to stabilise manganate(V) but 4M hydroxide for manganate(VI).[10] The reduction reactions were probably of the type

$$2MnO_4^- + O^{2-} \rightleftarrows 2MnO_4^{2-} + \tfrac{1}{2}O_2 \qquad (2)$$

and

$$2MnO_4^{2-} + O^{2-} \rightleftarrows 2MnO_4^{3-} + \tfrac{1}{2}O_2 \qquad (3)$$

or

$$2MnO_4^- + O_2^{2-} \rightleftarrows 2MnO_4^{2-} + O_2 \qquad (4)$$

and

$$2MnO_4^{2-} + O_2^{2-} \rightleftarrows 2MnO_4^{3-} + O_2 \qquad (5)$$

The observation that in the lithium-potassium nitrate melt the reductions were completely to manganate(V), *i.e.* reactions 3 and 5 predominating over reactions 2 and 4, or some equivalent reaction reducing manganate(VII) directly to manganate(V), is most probably to be linked with the observed insolubility of manganate(V) in this melt, presumably as the lithium salt. The absence of sufficiently small cations in the sodium-potassium nitrate melt would thus impose a higher manganate(V) solubility and enable equilibria 2-5 to become sensitive to changes in the nature and concentration of the base anions. However, the finding that hydroxide was apparently capable of acting as the reducing species for reactions 2 and 4 but not for reactions 3 and 5 in sodium-potassium nitrate is not easy to rationalise. It does appear to be a specific effect of the hydroxide ion since manganate(VI) was formed once water was admitted to a sodium oxide solution and reduced if a hydroxide solution was dehydrated by evacuation.

Potassium hydroxide was also expected to dehydrate in the sodium-potassium nitrate melt[7] but the green solution reported formed by 0.19*m* hydroxide melt (*i.e.* 0.09*m* in potassium oxide) is comparable to the green solution obtained with a 0.10*m* sodium oxide solution though at a lower oxide: manganese ratio.

The observed stability and solubility of sodium peroxide in sodium-potassium nitrate as opposed to the surface decomposition to monoxide observed in lithium-potassium nitrate[7] was considered to be the likely explanation of the oxidation of manganese dioxide to blue manganate(V) or green manganate(VI) according to concentration and oxide: manganese ratio.

The spectra of the two manganese oxyanions were very like those in aqueous solution, though all the absorptions have reduced extinction coefficients in fused nitrate solution, as has now become a common pattern having been observed for chromate,[11,12] dichromate,[12] permanganate[13] and triiodide.[8]

These spectral curves may be compared with those reported by Bennett and Holmes who claimed that green manganate(VI) solutions could be stabilised in sodium-potassium nitrate at 260 ± 15° with sodium peroxide (Figure 1 curve B) and blue manganate(V) by sodium hydroxide (Figure 2 curve B) both bases being of unspecified concentration. These apparent discrepancies may be resolved by presuming (a) that the peroxide concentration was below the minimum of 0.1*m* and thus manganate(VI) would be the expected stable oxidation state (certainly curve B of Figure 1 is very like curve C, except for a slightly higher absorption), and (b) that the sodium hydroxide, "added to a manganate(VI) solution" was added to a solution which already contained sodium peroxide and thus that the resulting blue solution was a mixture of manganate(VI) and manganate(V). (The reported absorption curve (curve B of Figure 2) is very like curve E of Figure 2 which was interpreted as a mixture of maganate(VI) and manganate(V). The shoulder at 22600 cm^{-1} on curve E and "betwen 20000 - 25000 cm^{-1}" on curve B was correlated with the 22000 cm^{-1} absorption of magnate(VI) rather than with the 18000 cm^{-1} absorption of permanganate as was suggested by Bennett and Holmes).

The precipitation of manganese dioxide reported during the reaction of permanganate with oxide solutions[3] at 250°C was most likely to be due to a low concentration of oxide (0.0005m concentrations had been used earlier by this author) otherwise the higher oxidation states of manganese would have been expected to be formed.

In conclusion, the point can hardly be too strongly made that in the reactions discussed, a change in the alkali metal cation of the melt has had very major effects on the reaction products, on their solubility, on the intermediates and presumably also on the reaction pathways. In particular it should not be too easily assumed in future that extrapolation of results from one nitrate melt to another and possibly also from one temperature to another is necessarily reasonable and meaningful.

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