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Molten Lithium Nitrate-Potassium Nitrate Eutectic: the Reactions of Some Compounds of Manganese

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The reactions of four manganese compounds with molten lithium nitrate-potassium nitrate eutectic were studied. Manganese(II) chloride and manganese(II)-sulphate reacted to give manganese dioxide, the reaction being quantitative above 350°. Potassium manganate(VI) disproportionated to give permanganate, a potassium manganate(IV) and free oxide ions. The permanganate formed then reacted more slowly, the final products of manganate(VI) being oxygen and a manganate(IV) containing the lithium cation predominately. Pure potassium permanganate reacted to give oxygen and a manganate(IV) of different stoichiometry but again largely as the lithium salt.

Introduction

Current interest in the chemistry of molten salts makes it increasingly evident that information on the inorganic reactions of transition metal compounds is particularly sparse. As a contribution to this field the stoichiometry of the reactions of several manganese compounds in lithium-potassium nitrate are reported. Comparison with the only detailed study of manganese compounds in nitrate melts,[1] when sodium-potassium eutectic was used, reveals a number of differences.

Experimental Section

Materials. Lithium-potassium nitrate eutectic was prepared as previously reported.[2] Analar $KMnO_4$ was dried at 100° for 2 hours. K_2MnO_4 was prepared by the method of Scholder[3] (Found: Mn, 27.6. Calcd. for K_2MnO_4, Mn, 27.9%). $MnCl_2$ and $MnSO_4$ were rendered anhydrous by heating to constant weight at 200°. Infrared spectroscopy gave no indication of O–H bands and the salts dissolved completely in water. Analyses were as follows (Found: Mn, 43.1; Cl, 56.3. Calcd. for $MnCl_2$ Mn, 43.6; Cl, 56.4%. Found: Mn, 36.9; SO_4, 63.2. Calcd. for $MnSO_4$ Mn, 36.4; SO_4, 63.6%). Potassium pyrosulphate was prepared by heating Analar $K_2S_2O_8$.[4]

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 purified nitrogen were provided.

Analysis. Lithium and potassium were estimated separately using an EEL flame photometer and the total alkali metal gravimetrically as sulphate. Permanganate was estimated absorptiometrically and manganese(IV) and (II) volumetrically, using arsenious oxide and E.D.T.A. respectively. Hydroxide was titrated against standard acid, consistent results only being obtained when the solidified melts were finely ground before addition to water, thus keeping hydrolysis to a minimum. Analyses are reported as the average of 3-5 determinations. Qualitative analysis was carried out on aqueous solutions by conventional methods with the exception that oxide was detected in the melt using phenolphthalein.[4] Visible and ultraviolet spectroscopy of aqueous solutions was carried out on a Unicam S.P. 800 and of melt solutions on a Unicam S.P. 700 spectrometer modified for use up to 700°. Diffuse reflectance spectra were obtained with a Unicam S.P. 500 fitted with a S.P. 540 attachment. Thermogravimetric analysis was carried out as previously described,[5] weight losses being reported as a percentage by weight of the manganese containing starting material. X-ray powder photography used Zr filtered MoKα radiation with a 19 cm powder camera and a Joyce microdensitometer.

Results

Manganese(VII). Potassium permanganate dissolved in lithium-potassium nitrate eutectic to give a purple solution (ν_{max} 18,800 cm^{-1}) which decomposed slowly at 160°, still showing a distinct absorption at 18,800 cm^{-1} after 36 hrs. At higher temperatures decomposition was more rapid, oxygen being evolved and a black precipitate being produced within a few seconds at 260°. Thermogravimetric analysis showed a weight loss of 15.7% between 200-500° and one of 15.4% in an isothermal experiment at 220° (Calcd. for 3/2 0 per $KMnO_4$ 15.2%). Filtration gave a clear melt which contained no oxide, nitrite or

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

(2) B. J. Brough and D. H. Kerridge, *Inorg. Chem.*, *4*, 1353 (1965).

(3) R. Scholder and H. Waterstradt, *Z. anorg. Chem.*, *277*, 172 (1954).

(4) B. J. Brough, D. H. Kerridge, and M. Mosley, *J. Chem. Soc.* (A), 1556 (1966).

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

manganese. The black precipitate hydrolysed slowly with water giving an alkaline solution. After being rapidly washed free of nitrate and dried the precipitate reacted with concentrated hydrochloric acid to give chlorine and a solution containing lithium, potassium and manganese(II). X-ray powder photography of the dry precipitate obtained by reaction at 200° gave the d values of 2.419 (w), 2.027 (s), 1.422 (m), 1.354 (vw), 1.236 (vw), 1.154 (vw) Å, relative intensities in brackets. The total alkali metal content of the precipitate was 7.4%, the ratio Li:K=23:2 and manganese content 52.0% (Calcd. for $(Li_{0.92}/K_{0.08})_2Mn_2O_5$, Li+K, 9.1; Mn, 52.6%). Quantitative reaction indicated the black precipitate to be produced with a weight loss of 33.6% (based on weight of $KMnO_4$ reacted) and the mixture of dry chlorides ($LiCl+KCl+MnCl_2$) with an overall gain of 8.4%. (Calcd. for $KMnO_4 \rightarrow \frac{1}{2}(Li_{0.92}/K_{0.08})_2Mn_2O_5$, 33.9% loss; for $KMnO_4 \rightarrow 0.92\,LiCl+0.08\,KCl+MnCl_2$, 8.5% gain).

Manganese(VI). Potassium manganate(VI) reacted immediately at 160°, under an atmosphere of dry air, or nitrogen, to give a purple solution and a brown-black precipitate without any evolution of gas. The purple solution then decomposed, slowly at 160° more rapidly at 250°, giving a colourless melt, evolution of oxygen and precipitation of black particles. The two stages of reaction, *viz.* to purple solution and brown-black precipitate and to colourless solution and black precipitate were therefore examined separately, and referred to as the initial and overall reactions.

After the initial reaction, 5-7 minutes at 160° under nitrogen, the melts were frozen, ground and dissolved in water. Rapid filtration gave a solution which contained permanganate and hydroxide ions but no manganese(II). Acidification of the aqueous solution occasionally gave a purple solution of slightly lower absorbance. If this were attributed to the presence of a reducing ion (*e.g.* nitrite) its concentration was very small (<0.1 mole per mole MnO_4^- produced). The precipitate gave off chlorine when treated with concentrated hydrochloric acid, contained manganese and potassium ions only and hydrolysed slowly in water producing an alkaline solution. X-ray powder photography of the dried precipitate gave the values of 2.419 (vw), 2.027 (s), 1.422 (m) Å. The diffuse reflectance spectrum of powdered solidified melt gave a broad absorption band with much fine structure (maxima at 17700, 18500, and 19200; shoulders at 18800 and 20800 cm^{-1}) typical of the permanganate ion. Quantitative analysis of the manganese(VII), the oxide in the filtrate and the manganese(IV) of the precipitate indicated ratios of reactant K_2MnO_4 to $MnO_4^-:Mn^{IV}:O^{-2}$ of 1 to $0.66\pm0.02:0.36\pm0.02:0.32\pm0.01$. No evidence of oxygen evolution was obtained by visual observation or thermogravimetric analysis.

At 160° the permanganate formed initially slowly decomposed at a rate dependent on the oxygen partial pressure. For example, with a nitrogen flow of 30 ml/min sweeping away the oxygen produced during decomposition, 93% of the permanganate initially formed had decomposed after 7 hr., whereas with the same flow rate of oxygen only 81% decomposed in this time. Decomposition of permanganate was more rapid at higher temperatures and was complete after 2 hr. at 260° under a flow of nitrogen, oxygen and a black precipitate being formed. Isothermal thermogravimetric analysis indicated a weight loss of 7.9% after 1 hr. at 270° (Calcd. for O per K_2MnO_4 8.1%). The reacted melt after filtration at 160° contained no manganese(II) or nitrite ions but had a small quantity of soluble oxide ions, 0.015-0.035 moles/mole of K_2MnO_4, the amount varying irregularly with the time of contact with melt (1-20 hrs). Other reacted melts were solidified and finely ground then extracted with water, the black precipitate being removed and washed as rapidly as possible by centrifuging and filtration. However, the precipitate was so finely divided that despite the utmost speed it was still in contact with water for 2-3 hrs. The aqueous extract contained a variable quantity of hydroxide, equivalent to 0.18-0.35 (average of 5 determinations 0.28) moles per mole K_2MnO_4. The precipitate contained potassium and lithium, and reacted with concentrated hydrochloric acid to produce chlorine. The potassium, lithium and manganese contents varied somewhat, being 1.5-2.0, 6.6-9.7, and 46.5-52.3 wt % of precipitate respectively, as did the remaining constituent which was assumed to be oxygen. However, the ratio of lithium:potassium was practically constant at 24:1, while the ratio of total oxygen (soluble as hydroxide plus insoluble as remainder of precipitate) to manganese was very close to 3:1 (average $3.01\pm.03$), and the ratio of manganese(IV) recovered in precipitate:K_2MnO_4 reacted was 0.97:1. X-ray powder photography gave the values of 2.419 (vw), 2.027 (s), 1.422 (m), 1.354 (vw), 1.236 (vw), 1.156 (vw) Å. A number of attempts were made to hydrolyse the precipitate and remove all alkali metal and oxide ions and thus present a more straightforward analysis. Hydrolysis conditions were varied widely but the insoluble manganese dioxide always became extremely gelatinous and quite impossible to separate from the aqueous extract by filtration or centrifugation.

Manganese(II). Manganese(II) chloride dissolved at 160° giving a colourless solution which began to darken after 30 seconds with evolution of nitrogen dioxide and precipitation of manganese dioxide. The colourless solution was stabilised by addition of potassium pyrosulphate when no manganese dioxide was precipitated until all the pyrosulphate had reacted with nitrate ions. The solution showed no measurable absorption over the range 30,000-13,000 cm^{-1}. Unreacted manganese(II) cations were found in melts held at 160°, 200°, and 260° even after 12 hrs. but at 350° complete reaction had occurred in 3 hrs. After complete reaction the melt was found to contain no manganese(II), oxide or nitrite ions, while the washed and dried precipitate contained manganese(IV) but no lithium or potassium ions (Found: Mn, 65.4. Calcd. for MnO_2 Mn, 63.2%) and evolved chlorine with hot concentrated hydrochloric acid. The ratio of original $MnCl_2:MnO_2$ recovered was 1:1.04. X-ray powder photography gave the values of 3.140 (w), 2.730 (s), 2.377 (m), 2.057 (vw), 1.994 (vw), 1.835 (w), 1.657 (s), 1.529 (m), 1.419 (m), 1.379 (vw), 1.350 (vw), 1.293 (w) Å. Isothermal gravimetric analysis at 350° gave a weight loss of 74% (Calcd. for loss of $2NO_2$ per $MnCl_2$ 73%).

Manganese(II) sulphate also dissolved in the melt and reacted in a similar manner. After 3 hrs. at 350° no manganese(II), oxide or nitrite was detectable in the melt. The precipitate reacted with concentrated hydrochloric acid evolving chlorine (Found: Mn, 61.7. Calcd. for MnO_2 Mn, 63.2%), the ratio of original $MnSO_4$:MnO_2 recovered being 1:0.98. X-ray powder photography gave the values 3.049 (w), 2.419 (s), 2.154 (vw), 1.838 (w), 1.604 (vw), 1.534 (m), 1.424 (m), 1.343 (w) Å. Isothermal thermogravimetric analysis at 360° indicated a weight loss of 65% (Calcd. for loss of $2NO_2$ per $MnSO_4$, 61%).

Discussion

The reaction of potassium permanganate with nitrate eutectic can be expressed by the equation

$$2KMnO_4 + 2Li^+ \longrightarrow (Li_{0.92}/K_{0.08})_2Mn_2O_5 + 3/2\ O_2 + 2(Li_{0.08}/K_{0.92})^+ \qquad (1)$$

The formation of manganate(IV) contrasts with the reported decomposition products of potassium permanganate in sodium-potassium nitrate eutectic[1] summarised by the equations

$$4MnO_4^- + 2NO_3^- \longrightarrow 4MnO_4^{2-} + 2NO_2^+ + O_2 \qquad (2)$$

$$2MnO_4^{2-} \longrightarrow 2MnO_2 + 2O^{2-} + O_2 \qquad (3)$$

$$MnO_4^{2-} \rightleftharpoons MnO_2 + O_2^{2-} \qquad (4)$$

$$2MnO_4^{2-} + 2NO_2^+ \longrightarrow 2MnO_2 + 2NO_3^- + O_2 \qquad (5)$$

since with lithium-potassium eutectic no manganese(VI), free oxide ions or nitrogen dioxide (the reaction product of NO_2^+ and nitrate) were detected nor was any evidence obtained that nitrate ions were directly involved in the decomposition.

It is not possible to show that the decomposition in melt is identical with that of the pure salt since the reported stoichiometry of the thermal decomposition of potassium permanganate is complicated by conflicting claims (*e.g.* see select references in Peters *et al.*[6]). However, equation (1) is very like that reported by Roginsky[7] for $KMnO_4$. Since lithium permanganate has been shown to decompose at a temperature markedly lower than that of the potassium salt,[7,8] the formation of manganate(IV) with lithium as the predominate cation is to be expected.

Potassium manganate(VI) clearly reacted in two stages, the first being well represented by the equation

$$3K_2MnO_4 \longrightarrow 2KMnO_4 + K_2MnO_3 + K_2O \qquad (6)$$

The brown-black precipitate is formulated as a manganate(IV) of different stoichiometry, as the powder data indicated it was not identical with either β or γ MnO_2 or the lithium-potassium manganate(IV) formed in the subsequent reaction and by $KMnO_4$. This stoichiometry is supported by the ratio of free oxide ion in the melt and by the slow hydrolysis of the precipitate on washing which is in accord with the properties of manganate(IV).

The stoichiometry of the overall reaction can be understood if the permanganate initially produced decomposed in accordance with equation (1), at a rate dependent on the oxygen partial pressure, and that the manganate ($Mn_2O_5^{2-}$) formed reacted with the oxide ions produced in equation (6) as follows

$$(Li/K)_2Mn_2O_5 + (Li/K)_2O \longrightarrow 2(Li/K)_2MnO_3 \qquad (7)$$

The overall equation thus being

$$K_2MnO_4 + 2Li^+ \longrightarrow (Li_{0.96}/K_{0.04})_2MnO_3 + \tfrac{1}{2}O_2 + (Li_{0.04}/K_{0.96})^+ \qquad (8)$$

The heterogeneous reaction (eqn. (7)) appeared not to proceed quite to completion, the variable amount of soluble oxide found no doubt reflecting the variation in surface properties of the manganate(IV) initially formed. However, a nearly complete exchange of cations of the manganate(IV) produced in equation (6) occurred since the final product contained a similar proportion of lithium to potassium as that found in the manganate(IV) produced by the decomposition of permanganate alone. Subsequent unavoidable hydrolysis of the manganate(IV) on washing complicated the analysis and the resulting mixed manganate(IV), which would probably contain $Mn_2O_5^{2-}$ as well as MnO_3^{2-}, thus gave powder lines very similar to those from permanganate alone.

The reported reaction of manganate(VI) in sodium-potassium nitrate[1] (equations (3)-(5)) is somewhat similar, particularly in a neutral melt (*i.e.* eqn. (5) unimportant) and bearing in mind that any chemical combination of the manganese dioxide and free oxide ion of equation (3) was not investigated by the earlier workers. However, in contrast to the behaviour of permanganate, the presence of melt would seem of prime importance in the decomposition of manganese(VI) since pure potassium manganate(VI) is reported to be thermally stable up to 600°.[6]

The behaviour of manganese(II) ions was less complex, acting as Lux-Flood acids and being oxidised with the formation of manganese dioxide. The x-ray data was generally characteristic of the β form though some additional lines appeared which may be attributable to the formation of some hydrated γ oxide during the aqueous extraction. The analyses, weight losses, *etc.* were in accord with the stoichiometry,

$$Mn^{2+} + 2NO_3^- \longrightarrow MnO_2 + 2NO_2 \qquad (9)$$

though the mechanism by which the nitrate ion reacts is likely to be considerably more complicated and may involve the participation of nitryl ions.

The observation that reaction did not go to completion at temperatures below 300° can be correlated with

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(6) Von H. Peters, K.-H. Radeke, and L. Till, *Z. anorg. Chem.*, *346*, 1 (1966).
(7) S. Z. Roginsky, *Trans. Faraday Soc.*, *34*, 959 (1938).
(8) S. Yu. Elovich, S. Z. Roginsky, and E. I. Shmuk, *Izvest. Akad. Nauk. S.S.S.R., Otdel. Khim. Nauk*, 469 (1950).

the observation that manganese dioxide reacts to a small extent with lithium-potassium nitrate eutectic at 160°.[9] This suggests that the reaction of equation (9) is in fact reversible at these temperatures, though again the mechanism may well be more complex and is probably not merely the reverse of the forward reaction.

Detailed comparison with the reaction in sodium-potassium eutectic is not possible in this case, as it is merely reported that manganese(II) is oxidised to manganese dioxide.[10] The only other published statement being the remark of Gruen that «$MnCl_2$ is oxidised in lithium-potassium nitrate at 184°».[11] However, formation of manganese dioxide is the behaviour expected of manganese(II) in an oxidising medium and is analogous to the oxidation of cobalt(II) to Co_3O_4 in nitrate melt.[12]

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