Reactions of Some Oxidizing Agents with Potassium Oxalate in Molten $LiNO_3$ – KNO_3 Eutectic

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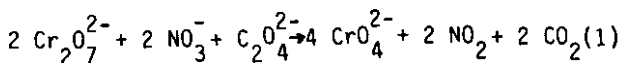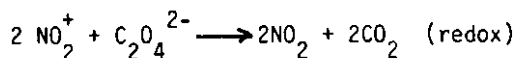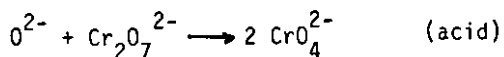*Quaid-i-Azam University,*
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Summary:A few reactions of $K_2S_2O_7$, $KMnO_4$, $Ce(SO_4)_2$ and $FeCl_3$ with $K_2C_2O_4$ in molten alkali metal nitrate eutectic were investigated. The products were characterized by elemental analysis, thermogravimetric and x-ray powder difraction techniques. Potassium pyrosulphate reacted with the melt to form sulphate and nitryl (NO_2^-) ions. Later NO_2^- is reduced by oxalate ion giving NO_2 and CO_2. Potassium permanganate was reduced by oxalate ion to form a mixed valence oxide ion, $Mn_3O_9^{4-}$ and CO_2. Cerium (IV) sulphate and iron (III) chloride were simply reduced to Ce(III) and Fe(II) ions through one electron transfer by oxalate ion. Their oxalates were separated from the melt and characterized.

When excess of oxalic acid was reacted with $K_2Cr_2O_7$ or K_2CrO_4, it produced a well known oxalate complex, $K_3[Cr(C_2O_4)_3]$.

Introduction

Fused salts form useful and interesting media for reactions at elevated temperature [1,2]. In recent years, fused alkali metal nitrates, especially those of lithium and potassium, have been increasingly used as solvents for studying reactions of a number of compounds [3-7]. This has been reviewed by Kerridge [8]. The Lux-Flood concept of acids and bases adequately explains the reactions occuring in molten nitrate eutectic. Recently Duke et al. have investigated kinetics of reactions of dichromate and pyrosulphate ions with nitrate melts and determined their rate constants [9]. These authors have also described an indirect method for measuring concentration of very reactive nitryl (NO_2^-) ion generated by autodissociation of nitrate ion and reaction of resulting oxide with the added salt. The nitrate ion in the eutectic behaves as a good Lux-Flood base while added salts act as acids, thus constituting an acid-base reaction. However other reactions such as metathesis, electron transfer or complexation could also occur in these metals. The reaction of oxalate with dichromate ion studied by Schlegal and Pitak [11] may be included in a combined acid-base and redox reaction as

$$NO_3^- \rightleftharpoons NO_2^+ + O^{2-} \qquad \text{(base)}$$

$$O^{2-} + Cr_2O_7^{2-} \longrightarrow 2\ CrO_4^{2-} \qquad \text{(acid)}$$

$$2\ NO_2^+ + C_2O_4^{2-} \longrightarrow 2NO_2 + 2CO_2 \qquad \text{(redox)}$$

$$2\ Cr_2O_7^{2-} + 2\ NO_3^- + C_2O_4^{2-} \rightarrow 4\ CrO_4^{2-} + 2\ NO_2 + 2\ CO_2\ (1)$$
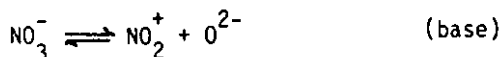
Only a few reactions of this type (e.g. $C_2O_4^{2-}$, Br^- acting as reducing agent) in nitrate melts have been studied [12]. Further investigations of electron transfer or complex formation in liquid nitrate medium are worth study. It is also important to compare these reactions with those observed in aqueous media.

We wish to report a few electron transfer reactions of cerium (IV), iron (III), permanganate and pyrosulphate ions with a common reducing agent, oxalate ion, in molten nitrate eutectic. The nitrate medium does not take part in these reactions (except with pyrosulphate) as NO_2 was not detected at any stage of the reaction. Another interesting reaction is the synthesis of potassium trioxalatochromate(III) by the action of oxalic acid on potassium dichromate or potassium chromate in the high temperature nitrate melt medium. This reaction is a true replica of the one commonly occurring in aqueous solution.

Experimental

Materials

Analytical reagent grade KNO_3, $LiNO_3$, $K_2Cr_2O_7$, $K_2S_2O_7$, $Ce(SO_4)_2$, $FeCl_3$ and all other chemicals supplied by E. Merck were used in these investigations. $K_2Cr_2O_7$ and $K_2S_2O_7$ were

dried at 160°C; $FeCl_3$ was dried under vacuum at 100°C; KNO_3 and $LiNO_3$ were dried at 150° for 24 hours before use.

Calculated amounts of KNO_3 and $LiNO_3$ to give 66:34 mole ratio of the two salts were thoroughly mixed and melted in a beaker in an oven maintained at 160°C. The melt was occasionally stirred and then filtered by high temperature filtration technique under reduced pressure. The melt was cooled to room temperature and stored in a dessicator. Normally, the eutectic, thus prepared contained some moisture which must be removed before use. The eutectic was tranferred to a tube attached to an efficient vacuum line. The tube was heated in a furnace maintained at 160°C. The melt was evacuated slowly over a period of about two hours to ensure the complete removal of moisture.

Procedure

The dry eutectic (5-10g) was introduced into a glass tube with two arms and placed in a furance maintained at 160°. The tube was connected to the vacuum line. The other arm was used for introducing reactant species.

Preliminary tests revealed that $K_2C_2O_4$ immediately dissolved in the melt and showed no sign of its interaction with the melt. Similar behaviour was observed when other salts such as $Ce(SO_4)_2$, $FeCl_3$ or $K_2S_2O_7$ were separately introduced one at a time into the melt. A calculated amount of the reactant compound was introduced into the tube containing potassium oxalate dissolved in the liquid eutectic. The reaction was studied under continuous vacuum conditions and the

evolved gases were pumped into a cold trap for analysis. After the reaction was complete (usually in about 30 minutes), the liquid was poured into a china dish and cooled to room temperature. The solids were reserved for subsequent analysis.

Analysis

Gaseous products were qualitatively analysed for CO_2, N_2O_5, NO_2 by their characteristic tests. The solid reaction mixtures were dissolved in water. In certain cases, the mixtures were only partly soluble in water. The insoluble portion was separated and analyzed. The aqueous solution invariably contained K^+, Li^+, NO_3^- and unreacted $C_2O_4^{2-}$ ions.

Where the reaction mixture was completely soluble in water, the solid was dissolved in water in a volumetric flask and a suitable aliquote portion of the resulting solution was used to precipitate out insoluble salts, for example $BaSO_4$ by adding Ba^{2+} ion.

The brownish black residue obtained by the action of oxalate on permanganate ion was dissolved in aqua regia and analyzed for K^+ and Mn^{2+} ions by atomic absorption method. Lithium was gravimetrically determined by a literature method from the same solution [13]. The colourless residues obtained from the reaction mixtures of $Ce(SO_4)_2$ and $FeCl_3$ were dissolved in dilute sulphuric acid. These solutions were used for estimation of oxalate ion with permanganate and metal ions by atomic absorption method.

The solid residues or precipitated $BaSO_4$ were further characterized by X-ray diffraction and thermogravimetric techniques.

Instrumentations

The thermal decomposition studies were carried out on Stanton Redcroft model TG-750 thermobalance. These analyses were made in ambient atmosphere by taking 10 mg of the sample in a silica crucible (5 x 25 mm) at a heating rate of 20°/min in temperature range 0.–900°C with chart speed 12 cm/hr. A small funnel was inverted on the top of the crucible to prevent splashing during vigorous reactions.

These samples were further analysed by X-ray powder diffraction techniques using ED-XRF Spectrometer model-500 link system. The wavelength of x-rays used was 1.5405 A. The crystal lattice spacings i.e. d values (see Table 1) were evaluated from the diffraction pattern and compared with those of standard or probable compounds.

The metal ions were estimated on a Hitachi Model 170 Atomic Absorption Spectrophotometer. Solution spectra of some of the compounds were recorded on Hitachi model 150 spectrophotometer using a matched set of 1 cm quartz cells.

Results and Discussion

The electron transfer reactions of four compounds, $K_2S_2O_7$, $KMnO_4$, $Ce(SO_4)_2$ and $FeCl_3$ with $K_2C_2O_4$ at 160°C in nitrate melt were investigated. The redox reactions of oxalate ion with permanganate and cerium (IV) in aqueous solution are well known. However such reactions at higher temperature may adopt a completely different and complicated mechanism and form entirely different products. In fact this has happened in the reactions of $KMnO_4$ and $K_2S_2O_7$. On the other hand Ce(IV) and Fe(III) like in aqueous medium, were reduced to Ce

Table-1: X-ray Diffraction Data for Residues Obtained from the Melt

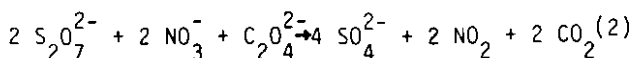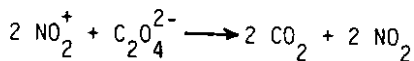| $K_2Li_2Mn_3O_9 \cdot 4H_2O$		$Ce_2(C_2O_4)_3 \cdot 2H_2O$		$FeC_2O_4 \cdot 2.5H_2O$	
2θ	$d(A°)$	2θ	$d(A°)$	2θ	$d(A°)$
		12.75	6.94		
		20.5	4.33		
22.2	4.0			19.5	4.55
				23.5	3.78
				25.7	3.46
28.5	3.12	28.5	3.13	29.5	3.03
		32.75	2.73	34.25	2.62
37.0	2.40	37.2	2.41	37.0	2.43
		38.5	2.34		
42.5	2.12	41.2	2.19	41.0	2.21
		43.5	2.09		
		44.5	2.03	44.0	2.06
		47.2	1.92		
		15.5	1.78	53.0	1.73
		54.5	1.68		
56.5	1.60	55.6	1.65	61.5	1.53
		68.75	1.36		

(III) and Fe(II) ions forming their respective oxalates. When $K_2Cr_2O_7$ or K_2CrO_4 were allowed to react with a 10 fold excess of oxalic acid in the melt, the well known coordination compound $K_3[Cr(C_2O_4)_3]$, was formed.

i) Potassium Pyrosulphate-Potassium oxalate system

Potassium Pyrosulphate instantanously reacted with oxalate ion in the eutectic with evolution of CO_2 and NO_2. The cooled reaction mixture was

completely soluble in water and contained K^+, Li^+, NO_3^-, SO_4^{2-} ions but no $S_2O_7^{2-}$ ion showing its complete conversion to SO_4^{2-} ion. The sulphate ion was precipitated from the solution as $BaSO_4$ by conventional methods.

The powder diffraction pattern of dried precipitate was found comparable to that of an authentic sample of $BaSO_4$. The interplanar spacing for the precipitate were in close comparison with the reported values. The thermogram of the precipitate was similar to that of $BaSO_4$ studied by Paulik and Erdey [14]. These analyses proved the formation of sulphate ion in liquid nitrate. The following acid-base reaction accompanied by oxidation of oxalate ion occurs in the nitrate melt:

$$S_2O_7^{2-} + NO_3^- \longrightarrow NO_2^+ + 2\ SO_4^{2-}$$

$$2\ NO_2^+ + C_2O_4^{2-} \longrightarrow 2\ CO_2 + 2\ NO_2$$

$$2\ S_2O_7^{2-} + 2\ NO_3^- + C_2O_4^{2-} \rightarrow 4\ SO_4^{2-} + 2\ NO_2 + 2\ CO_2 \quad (2)$$

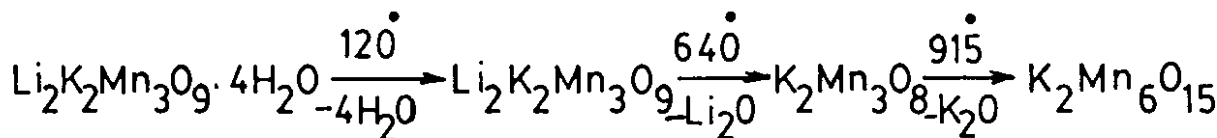This reaction is comparable to that of dichromate with oxalate ion in nit-rate eutectic medium as reported elsewhere [11].

ii) Potassium Permanganate – Potassium oxalate System

The reaction between $KMnO_4$ and $K_2C_2O_4$ produced a brown black product in the melt. The brown black compound was insoluble in water while the aqueous filtrate contained all the other ions except manganese. This indicates the completion of reaction between the two species.

The chemical analysis of the residue after its dissolution in aqua regia proved it a complex material of composition $Li_2K_2 Mn_3O_9 \cdot 4H_2O$ (Found: Li 3.04, K 16.00 and Mn 35.59%. Calcd: Li 2.94, K 16.54 and Mn 34.85%). It seems that the brown residue picked up a few water molecules during leaching with water.

The composition of the brown black material was further confirmed from its thermogravimetric analysis which showed weight loss upto 120°C due to escape of water and two successive losses due to removal of Li_2O and K_2O giving mixed valence manganese oxides. The thermal analysis scheme of the residue reproduced below fits well with observed losses.

$$Li_2K_2Mn_3O_9 \cdot 4H_2O \xrightarrow[-4H_2O]{120°} Li_2K_2Mn_3O_9 \xrightarrow[-Li_2O]{640°} K_2Mn_3O_8 \xrightarrow[-K_2O]{915°} K_2Mn_6O_{15}$$

| weight loss%			
Found:	14.5	7.55	12.55
Calcd.	15.22	7.45	12.70

Scheme -1

The x-ray diffraction pattern of brown black residue is very much different from that reported for MnO_2. A few d-lines of the residue resemble with those of MnO_2 but their intensity is very low. This indicates that the residue is not MnO_2 but a mixed valence oxide probably $Mn_3O_9^{4-}$.

On the basis of these studies, oxidation of oxalate with permanganate ion in nitrate melt leading to a mixed valence managenese oxide and other products may be assumed. This is an entirely a different reaction as compared to the one commonly observed in aqueous solution leading to Mn^{2+}. In this system, nitrate melt is acting as a neutral medium presuambly due to formation of O_2 during the reaction.
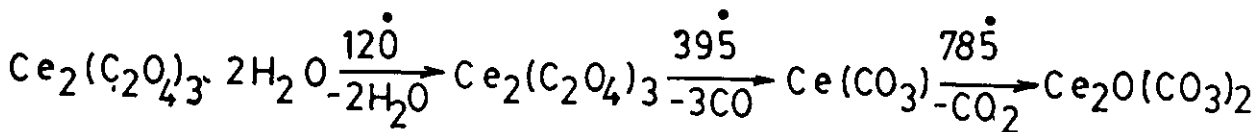
The overall reaction may be represented as

$$6\ MnO_4^- + C_2O_4^{2-} \longrightarrow 2\ Mn_3O_9^{4-} + 2\ CO_2 + 3\ O_2 \quad (3)$$
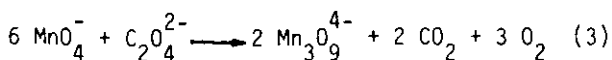
iii) Cerium (IV) Sulphate - Potassium Oxalate System

The cerium (IV) sulphate dissolved in the melt producing a yellow solution which became colourless upon interaction with oxalate ion. The reaction occured instantanously. The evolved gases contained CO_2 but no NO_2 was detected. The cooled melt was partly soluble in water leaving behind a white residue. The residue was soluble in dilute sulphuric acid and consisted of cerium (III) and oxalate ions. The white residue consisted of $Ce_2(C_2O_4)_3 \cdot 2H_2O$ (Found: Ce 48.12, $C_2O_4^{2-}$ 43.85%, Calcd. Ce 48.30, $C_2O_4^{2-}$ 45.50%). The residue was further characterized by its solution spectrum in UV region and infrared spectrum.

The thermogravimetry of the residue recorded three weight losses at different temperatures. The following scheme is suggested for these losses:

$$Ce_2(C_2O_4)_3 \cdot 2H_2O \xrightarrow[-2H_2O]{120^\circ} Ce_2(C_2O_4)_3 \xrightarrow[-3CO]{395^\circ} Ce(CO_3) \xrightarrow[-CO_2]{785^\circ} Ce_2O(CO_3)_2$$

weight loss %				
Found :	4.47	15.18	9.70
Calcd.	6.20	15.43	9.56

Scheme - II

The $Ce_2(CO_3)_3$ seems to be very stable and losses only one molecule of CO_2 above 785°C, forming a mixed oxide carbonate. This decomposition pattern is similar to the reported in literature [15].

The stoichiometry of this reaction is a simple one electron transfer process as

$$2 \; Ce^{4+} + C_2O_4^{2-} \longrightarrow 2 \; Ce^{3+} + 2CO_2 \quad (4)$$

This is comparable to a similar reaction commonly observed in aqueous solution in presence of an acid. Further reduction of Ce(III) to Ce(II) or Ce(O) does not occur due to unfavourable redox potential of the system.

iv) Ferric Chloride-Oxalic acid System

The reaction between anhydrous $FeCl_3$ and oxalic acid at 160° produced a yellowish green product which was insoluble in distilled water. However, the residue was soluble in dilute sulphuric acid and analysed for FeC_2O_4. $2.5H_2O$ (Found: Fe 29.23, $C_2O_4^{2-}$ 45.6%., Calcd: Fe 29.57 and $C_2O_4^{2-}$ 46.6%).

The chemical composition of the residue was further confirmed by its thermogravimetric and x-ray diffraction techniques and comparing them with standard sample of ferrous oxalate. The residue was stable upto 248° and simple dehydration occured below this temperature.

This reaction may be represented by a simple one electron transfer at 160°C in the melt as

$$2Fe^{3+} + 3C_2O_4^{2-} \longrightarrow 2 \; Fe \; C_2O_4 + 2 \; CO_2 \quad (5)$$
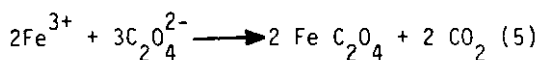
This type of electron transfer reaction in aqueous medium is not common, however, at higher temperature, it occured more or less quantitatively giving ferrous oxalate which decomposes between 248°–550°C.
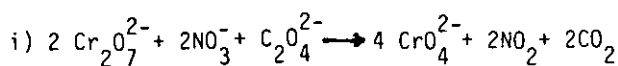
v) Synthesis of Potassium Trioxalato-chromate(III)

The reaction of $K_2Cr_2O_7$ with $K_2C_2O_4$ forming K_2CrO_4 in nitrate melt has already been studied [9]. However, this reaction was carried out in the presence of excess oxalic acid with a view to syhnthesis the well known $K_3[Cr(C_2O_4)_3]$ in liquid nitrate medium. When $K_2Cr_2O_7$ was reacted with oxalic acid (molar ratio 1:10 at 160°C in nitrate melt, a bluish green product was obtained. The same complex was produced if K_2CrO_4 was used in place of $K_2Cr_2O_7$. The cooled melt was completely soluble in water and produced bluish green solution characteristic of $[Cr(C_2O_4)_3]^{3-}$ ion. The complex was crystallized and purified from the aqueous solution by slowly adding ethanol. It was characterized by elemental analysis, absorption and infrared spectra. (Found: K 23.13, Cr 10.77 $C_2O_4^{2-}$ 53.19%, Calcd for K_3 $[Cr(C_2O_4)_3]3H_2O$. K 24.02, Cr 10.67, $C_2O_4^{2-}$ 54.22%, $_{max}$. 570, 415 nm, lit 586, 416 nm [16].
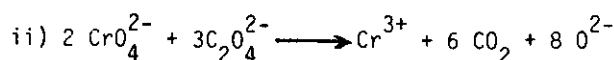
The composition of the complex was further confirmed by thermal and x-ray differaction techniques.

This complexation reaction seems to occur in distinct steps. It has been earlier reported that $K_2Cr_2O_7$ is converted into K_2CrO_4 by potassium oxa-
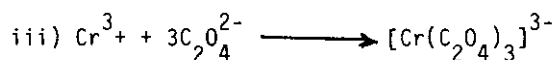
late in nitrate melt. This obviously is the first step in the complex formation. Thus formation of the complex by interaction of K_2CrO_4 with oxalic acid is appropriately studied to establish subsequent steps of the reaction. The reaction of K_2CrO_4 with oxalic acid occurred in two steps i.e. reduction of CrO_4^{2-} into $Cr(III)$ followed by formation of oxalate complex. The overall reaction can be explained in three steps as

i) $2\ Cr_2O_7^{2-} + 2NO_3^- + C_2O_4^{2-} \longrightarrow 4\ CrO_4^{2-} + 2NO_2 + 2CO_2$

(Acid base/redox)

ii) $2\ CrO_4^{2-} + 3C_2O_4^{2-} \longrightarrow Cr^{3+} + 6\ CO_2 + 8\ O^{2-}$

(Redox)

iii) $Cr^{3+} + 3C_2O_4^{2-} \longrightarrow [Cr(C_2O_4)_3]^{3-}$
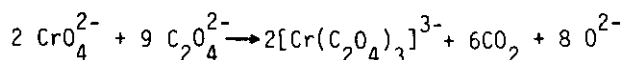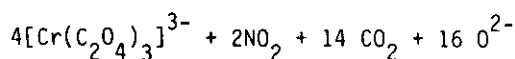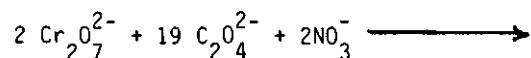
(complexation)

It is worth mentioning that nitrate ion is not involved in the last two steps of the reaction probably due to shift of equilibrium of nitryl and oxide ions to the left caused by oxide ion formed during reduction of CrO_4^{2-} ion. As such the eutectic melt behaved as an inert medium during these reactions. The stoichiometry of these reactions determined by their steps may be given as:

$2\ Cr_2O_7^{2-} + 19\ C_2O_4^{2-} + 2NO_3^- \longrightarrow$

$4[Cr(C_2O_4)_3]^{3-} + 2NO_2 + 14\ CO_2 + 16\ O^{2-}$

$2\ CrO_4^{2-} + 9\ C_2O_4^{2-} \longrightarrow 2[Cr(C_2O_4)_3]^{3-} + 6CO_2 + 8\ O^{2-}$

It is evident from the preceding discussion that oxalate ion behaves as a reducing agent for carrying out a variety of reactions in molten nitrate eutectic. In some of these reactions, nitrate acts as an inert medium taking no part as a chemical species. When appropriate amounts of oxalic acid is used, reduction of potassium chromate or dichromate followed by complexation occurs giving a well known potassium trioxalatochromate(III).

Acknowledgement

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