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Molten potassium pyrosulphate: reactions of six metal nitrates

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Abstract

The reactions of $Cr(NO_3)_3 \cdot 9H_2O$, $Fe(NO_3)_3 \cdot 9H_2O$, $Co(NO_3)_2 \cdot 6H_2O$, $Ni(NO_3)_2 \cdot 6H_2O$, $Cu(NO_3)_2 \cdot 3H_2O$ and $Zn(NO_3)_2 \cdot 6H_2O$ with molten $K_2S_2O_7$ were investigated. The reaction products were analysed by different techniques. The gaseous products consisted of a mixture of water vapour, nitrogen dioxide and oxygen, and the potassium pyrosulphate was converted into potassium sulphate. The metal nitrates dehydrate initially and/or decompose to produce either lower hydrates or oxo-nitrates which reacted subsequently with $K_2S_2O_7$ to be converted into the corresponding metal sulphates. However, the $Cr_2(SO_4)_3$ produced in the $Cr(NO_3)_3 \cdot 9H_2O$ reaction was found to react further with K_2SO_4 to form $K_3Cr(SO_4)_3$.

The techniques of thermogravimetry, differential thermal analysis and acidimetry were used to suggest reaction pathways and to determine the stoichiometries of the reactions.

INTRODUCTION

The results of the reactions of molten $K_2S_2O_7$ with alkali metal hydroxides, hydrogen carbonates and carbonates [1], oxides, peroxides, nitrites and nitrates [2], halides [3], sulphur oxo anions [4], oxalates [5], sulphides [6], transition metals [7], lanthanum metal and its compounds [8], carbonates of alkaline earths and manganese, basic carbonates of magnesium, zinc, copper, cobalt and nickel [9] indicate that molten $K_2S_2O_7$ acts as an acceptor of oxide ion as well as an oxidising agent. To explore the reactivity of the melt further, the reactions of the nitrates of some transition metals and of zinc were investigated using differential thermal analysis, and thermogravimetric and acidimetric methods. This paper now presents the results of these studies.

EXPERIMENTAL

Materials

$K_2S_2O_7$ was prepared and analysed as reported previously [5].

It was extremely difficult to dehydrate the transition metal nitrates. All attempts to dehydrate the nitrates resulted in their decomposition. For this reason, $Cr(NO_3)_3 \cdot 9H_2O$ (E. Merck, 98%), $Fe(NO_3)_3 \cdot 9H_2O$ (Ajax Univar, 98%), $Co(NO_3)_2 \cdot 6H_2O$ and $Cu(NO_3)_2 \cdot 3H_2O$ (Hopkins and Williams, 97.5% and 98% respectively), $Ni(NO_3)_2 \cdot 6H_2O$ (BDH AnalaR, 98%) and $Zn(NO_3)_2 \cdot 6H_2O$ (BDH, LR) were used as received.

The procedure, analysis and instrumentation have been described elsewhere [5].

RESULTS AND DISCUSSION

Using mass spectrometry and IR spectroscopy, the gaseous products of the reactions of the nitrates with molten $K_2S_2O_7$ were found to consist of a mixture of H_2O, NO_2 and O_2. Raman spectra of the solidified reaction products contained a band at 981 ± 5 cm^{-1} indicating the presence of sulphate in excess of pyrosulphate [10].

The solidified melts dissolved in water to give solutions which were found by UV–visible spectroscopy to contain metal cations in the same oxidation states as in the original reactants. However, in the reaction of $Cr(NO_3)_3 \cdot 9H_2O$, the solidified melt when stirred with water, produced a pale green precipitate and a clear solution. The solution showed the absence of chromium(III) while the precipitate was found to contain potassium, chromium(III) and sulphate by flame test, diffused reflectance and IR spectroscopy, respectively. The X-ray diffraction pattern of the precipitate gave *d* values of 7.40 (m), 4.10 (w), 3.24 (s), 2.97 (w), 2.75 (m), 2.32 (w) and 2.10 (m) compared with the values of 7.40 (30), 4.20 (8), 3.25 (100), 2.99 (10), 2.76 (30), 2.32 (6) and 2.10 (15) listed for $K_3Cr(SO_4)_3$ in the ASTM index. The formation of this compound has also been reported in the Cr_2O_3–$K_2S_2O_8$ system [11].

Table 1 presents the DTA results of the pure $K_2S_2O_7$ and those of the reactions of the metal nitrates with molten $K_2S_2O_7$. The endotherms at 332

TABLE 1

Differential thermal analysis results

Reactant	Melting point (°C) [a]	Peak temperature (°C)	
		Endothermic	Exothermic
$K_2S_2O_7$ (alone)	412	332, 412	–
$Cr(NO_3)_3 \cdot 9H_2O$	60	76, 147, 200, 330, 410	–
$Fe(NO_3)_3 \cdot 9H_2O$	47	52, 127, 202, 332, 408,	–
$Co(NO_3)_2 \cdot 6H_2O$	55	51, 152, 200, 324, 403	–
$Ni(NO_3)_2 \cdot 6H_2O$	56	54, 128, 192, 324, 402	–
$Cu(NO_3)_2 \cdot 3H_2O$	114.5	96, 124, 202, 328, 402	–
$Zn(NO_3)_2 \cdot 6H_2O$	36	74, 152, 200, 324, 426	–

[a] Reference [12] and CRC Handbook, CRC Press, West Palm Beach, Florida, 60th edn., 1980.

and 412 °C for pure $K_2S_2O_7$ have been assigned to the $\alpha \rightarrow \beta$ crystal-structure change of $K_2S_2O_7$ and its melting point, respectively [12]. The DTA curves of the reactions showed no exotherms but contained five endotherms in each reaction. As the literature values for the melting points of the hydrated nitrates are close to the corresponding first endothermic peak values, the first endotherm in each case is taken to represent the melting points of the nitrates. However, the presence of $K_2S_2O_7$ did change the melting points of the nitrates. For example, in the reactions of nitrates of cobalt, nickel and copper, the melting points are lower than those of the respective pure nitrates. This may be due to the solubility of $K_2S_2O_7$ in the melting nitrates. On the other hand, in the reactions of nitrates of chromium, iron and zinc, the melting points are higher than those of the respective pure nitrates. This might be due to the combination of $K_2S_2O_7$ and the nitrates resulting in the formation of mixtures or double salts with melting points higher than the respective metal nitrate. The melting process in all cases was closely followed by a weight loss due to the decomposition of the nitrates resulting in the formation of intermediate species consisting of either lower hydrates or oxo nitrates as shown in Table 2. In each reaction, the second endotherm is therefore assigned to the dehydration or/and decomposition of the intermediate species. The third endotherm can be assigned to melting/decomposition of $KHSO_4$ because its reported value of 207 °C [12] is comparable with the average value of the endothermic peak temperature, about 200 °C. The formation of $KHSO_4$ would have been brought about by hydrolysis of $K_2S_2O_7$ by the water of crystallisation of the nitrates

$$K_2S_2O_7 + H_2O \rightarrow 2KHSO_4 \qquad (1)$$

on further heating, the $KHSO_4$ decomposes

$$2KHSO_4 \rightarrow K_2S_2O_7 + H_2O \qquad (2)$$

The fourth and the fifth endotherms are attributed to the $\alpha \rightarrow \beta$ crystal-structure change of $K_2S_2O_7$ and its melting point, respectively, by comparing our results with the values reported for these processes [12].

Table 2 presents the thermogravimetric and acidimetric results of the reactions of metal nitrates with molten $K_2S_2O_7$. Thermogravimetry yielded the total amount of gaseous products evolved in the reactions. Stoichiometries of the reactions were determined by comparing the experimentally found weight losses with those calculated from the suggested stoichiometries. Acidimetry was carried out to determine the moles of $K_2S_2O_7$ consumed per mole of metal nitrate. The acidimetric results thus complement the thermogravimetric results which together suggest the possible pathways and the overall reaction stoichiometries, see below.

The TG curve of the reaction of $Cr(NO_3)_3 \cdot 9H_2O$ with $K_2S_2O_7$ shows an inflection at 87 °C with a weight loss of about 23% compared with 22.5%

TABLE 2

Thermogravimetric and acidimetric results

Reactant	Temp. range (° C)	Species	Weight loss (%)		Molar ratio $K_2S_2O_7$/ reactant for the overall reaction
			Found	Calc.	
$Cr(NO_3)_3 \cdot 9H_2O$					
	(i) 47–87	$Cr(NO_3)_3 \cdot 4H_2O$	23.0 ± 0.5	22.5	
	(ii) 87–146	$Cr(NO_3)_3 \cdot 2H_2O$	30.3 ± 0.6	31.5	
	(iii) 127–450	$K_3Cr(SO_4)_3$	81.6 ± 5.9	80.9	1.61 ± 0.12
$Fe(NO_3)_3 \cdot 9H_2O$					
	(i) 65–127	$FeO(NO_3) \cdot Fe(NO_3)_3$	47.2 ± 0.6	46.8	
	(ii) 127–456	$Fe_2(SO_4)_3$	76.4 ± 3.8	80.2	1.63 ± 0.10
$Co(NO_3)_2 \cdot 6H_2O$					
	(i) 55–67	$Co(NO_3)_2 \cdot 3H_2O$	19.5 ± 0.6	18.6	
	(ii) 132–350	$CoSO_4$	72.5 ± 3.9	74.2	0.90 ± 0.10
$Ni(NO_3)_2 \cdot 6H_2O$					
	(i) 54–120	$NiO \cdot Ni(NO_3)_2$	26.6 ± 0.8	27.8	
	(ii) 120–470	$NiSO_4$	73.4 ± 2.5	74.3	0.90 ± 0.10
$Cu(NO_3)_2 \cdot 3H_2O$					
	(i) 96–107	$CuO \cdot Cu(NO_3)_2$	23.4 ± 0.7	22.4	
	(ii) 107–398	$CuSO_4$	67.7 ± 1.2	67.0	0.90 ± 0.09
$Zn(NO_3)_2 \cdot 6H_2O$					
	(i) 27–77	$ZnO \cdot Zn(NO_3)_2$	29.5 ± 1.1	30.2	
	(ii) 127–37	$ZnSO_4$	68.5 ± 1.3	72.6	0.93 ± 0.00

calculated for the loss of five moles of water per mole of the nitrate. The second inflection in the TG curve appears at 146 °C with a weight loss of 30.3% as compared with 31.4% calculated for the loss of a further two moles of water per mole of the nitrate. This may be taken to indicate that the nonahydrate was first converted into tetrahydrate, and then into a dihydrate species, before it reacted with $K_2S_2O_7$ to form $K_3Cr(SO_4)_3$ as discussed above, and showed an average total weight loss of 81.6 ± 5.9%. This compares with a theoretical value of 80.9% calculated for the loss of nine moles of H_2O, three moles of NO_2 and 3/4 mole of O_2 per mole of $Cr(NO_3)_3 \cdot 9H_2O$. The reaction pathways including those shown in eqns. (1) and (2) with appropriate factors may be expressed by

$$2Cr(NO_3)_3 \cdot 9H_2O \rightarrow 2Cr(NO_3)_3 \cdot 4H_2O + 10H_2O \qquad (3)$$

$$2Cr(NO_3)_3 \cdot 4H_2O \rightarrow 2Cr(NO_3)_3 \cdot 2H_2O + 4H_2O \qquad (4)$$

$$2Cr(NO_3)_3 \cdot 2H_2O + 3K_2S_2O_7 \rightarrow 2K_3Cr(SO_4)_3 + 4H_2O + 6NO_2 + \tfrac{3}{2}O_2 \qquad (5)$$

and the overall reaction stoichiometry by

$$2Cr(NO_3)_3 \cdot 9H_2O + 3K_2S_2O_7 \rightarrow 2K_3Cr(SO_4)_3 + 18H_2O + 6NO_2 + \tfrac{3}{2}O_2 \qquad (6)$$

Meehan has studied the reaction of Cr_2O_3 with molten $K_2S_2O_7$ and has observed an exothermic peak at 402 °C [13]. The absence of an exotherm in the DTA curve of this reaction indicates that the reaction between the dihydrate and pyrosulphate took place without the formation of Cr_2O_3.

The TG curve of the reaction of $Fe(NO_3)_3 \cdot 9H_2O$ with $K_2S_2O_7$ shows an inflexion at 127 °C with a weight loss of about 47%. A theoretical value of 40% is calculated for the total dehydration of the nonahydrate while a value of 46.8% is calculated for the formation of $FeO(NO_3) \cdot Fe(NO_3)_3 \cdot 3H_2O$. The presence of an endotherm at 202 °C diagnostic of the melting and decomposition of $KHSO_4$, suggests that three moles of water were not associated with the oxo nitrate species but were used for the hydrolysis of $K_2S_2O_7$ to form $KHSO_4$.

The existence of the above oxo-nitrate species in an anhydrous form is also supported by the presence of an endotherm at 148 °C in the DTA curve of the pyrolysis of $Fe(NO_3)_3 \cdot 9H_2O$ alone and has been assigned to the melting and decomposition of $FeO(NO_3) \cdot Fe(NO_3)_3$ [14]; whereas here, the endothermic peak appeared at 127 °C due to the presence of $K_2S_2O_7$. The existence of the oxo-nitrate species has been also reported by Addison et al. during the decomposition of the $Fe(NO_3)_3 \cdot N_2O_4$ complex [15]. The average total weight loss was found to be $76.4 \pm 3.8\%$ at the end of the reaction. A theoretical value of 80.2% is calculated for the loss of nine moles of H_2O, three moles of NO_2 and 3/4 mole of O_2 per mole of $Fe(NO_3)_3 \cdot 9H_2O$.

On the basis of the results of Table 2 and the above discussion, the pathways of the reaction may be expressed by eqns. (7) and (8) and by eqn. (2) with an appropriate factor

$$2Fe(NO_3)_3 \cdot 9H_2O + 3K_2S_2O_7 \rightarrow FeO(NO_3) \cdot Fe(NO_3)_3 + 6KHSO_4 + 15H_2O + 2NO_2 + \tfrac{1}{2}O_2 \qquad (7)$$

$$FeO(NO_3) \cdot Fe(NO_3)_3 + 3K_2S_2O_7 \rightarrow Fe_2(SO_4)_3 + 3K_2SO_4 + 4NO_2 + O_2 \qquad (8)$$

and the overall stoichiometry by

$$2Fe(NO_3)_3 \cdot 9H_2O + 3K_2S_2O_7 \rightarrow Fe_2(SO_4)_3 + 3K_2SO_4 + 18H_2O + 6NO_2 + \tfrac{3}{2}O_2 \qquad (9)$$

The TG curve of the reaction of $Co(NO_3)_2 \cdot 6H_2O$ and $K_2S_2O_7$ shows a weight loss just after the melting endotherm at 55 °C and a plateau between 67 and 132 °C. The weight loss of 19.5% was recorded before the plateau as compared with a value of 18.6% calculated for the loss of three moles of water. The trihydrate thus formed would have melted and decomposed as shown by the endotherm at 152 ° C in the DTA curve which also contains an endotherm at 200 ° C for the melting and decomposition of $KHSO_4$. This indicates that some moles of water were used for the hydrolysis of $K_2S_2O_7$ to form $KHSO_4$ as expressed in eqn (1). The total weight loss for the reaction till 350 ° C was 72.5 ± 3.9% compared with a theoretical value of 74.2% calculated for the loss of six moles of H_2O, two moles of NO_2 and 1/2 mole of O_2. The pathways of the reaction may be represented by eqns. (10) and (11) in addition to the formation, melting and decomposition of $KHSO_4$ as shown by eqns. (1) and (2) with the appropriate factors

$$Co(NO_3)_2 \cdot 6H_2O \rightarrow Co(NO_3)_2 \cdot 3H_2O + 3H_2O \tag{10}$$

$$Co(NO_3)_2 \cdot 3H_2O + K_2S_2O_7 \rightarrow CoSO_4 + K_2SO_4 + 3H_2O + 2NO_2 + \tfrac{1}{2}O_2 \tag{11}$$

and the overall stoichiometry by

$$Co(NO_3)_2 \cdot 6H_2O + K_2S_2O_7 \rightarrow CoSO_4 + K_2SO_4 + 6H_2O + 2NO_2 + \tfrac{1}{2}O_2 \tag{12}$$

The TG curve of the reaction of $Ni(NO_3)_2 \cdot 6H_2O$ and $K_2S_2O_7$ shows a weight loss at the start of the melting endotherm of the hexahydrate at 54 ° C. A weight loss of 26.6% was recorded at the inflection point on the TG curve at 120 °C. The DTA curve shows an endotherm at 128 ° C. The presence of the endotherm at 192 ° C due to the melting and decomposition of $KHSO_4$ suggests that during the dehydration and/or decomposition of $Ni(NO_3)_2 \cdot 6H_2O$, some of the moles of water were used for the hydrolysis of $K_2S_2O_7$ to form $KHSO_4$. A weight loss of 27.8% is calculated for the formation of $NiO \cdot Ni(NO_3)_2$ as expressed by eqn. (13). The endotherm at 128 ° C may be due to the melting/decomposition of the oxo-nitrate species. The average total weight loss was found to be 73.4 ± 2.5% at 470 ° C as compared with the theoretical value of 74.3% calculated for the loss of two moles of NO_2, six moles of H_2O and 1/2 molecule of O_2 per mole of $Ni(NO_3)_2 \cdot 6H_2O$. The results of Table 2 and the above discussion support the following steps for the reaction including that of eqn. (2) with appropriate factor

$$2Ni(NO_3)_2 \cdot 6H_2O + 9K_2S_2O_7 \rightarrow NiO \cdot Ni(NO_3)_2 + 18KHSO_4 + 3H_2O + 2NO_2 + \tfrac{1}{2}O_2 \tag{13}$$

$$NiO \cdot Ni(NO_3)_2 + 2K_2S_2O_7 \rightarrow 2NiSO_4 + 2K_2SO_4 + 2NO_2 + \tfrac{1}{2}O_2 \tag{14}$$

and the overall stoichiometry by

$$2Ni(NO_3)_2 \cdot 6H_2O + 2K_2S_2O_7 \rightarrow 2NiSO_4 + 2K_2SO_4 + 4NO_2 + 12H_2O + O_2 \tag{15}$$

In the reaction between $Cu(NO_3)_2 \cdot 3H_2O$ and $K_2S_2O_7$, the TG curve shows an inflection at 107 °C with a weight loss of 23.4% as compared with a calculated value of 22.4% for the formation of either anhydrous $Cu(NO_3)_2$ with loss of three moles of water or for the formation of an oxo-nitrate species, $CuO \cdot Cu(NO_3)_2$, without loss of water. The existence of an endotherm in the DTA curve at 202 °C characteristic of the melting and decomposition of $KHSO_4$ suggests that the water of crystallisation was all used for the hydrolysis of $K_2S_2O_7$ to form $KHSO_4$ and, hence, supports the formation of the oxo-nitrate species. The pathways for the formation of $KHSO_4$ and $CuO \cdot Cu(NO_3)_2$ and its reaction with $K_2S_2O_7$ may be represented by eqns. (16) and (17), respectively, in addition to that shown by eqn. (2) with an appropriate factor

$$2Cu(NO_3)_2 \cdot 3H_2O + 6K_2S_2O_7 \rightarrow CuO \cdot Cu(NO_3)_2 + 12KHSO_4 + 2NO_2 + \tfrac{1}{2}O_2 \qquad (16)$$

$$CuO \cdot Cu(NO_3)_2 + 2K_2S_2O_7 \rightarrow 2CuSO_4 + 2K_2SO_4 + 2NO_2 + \tfrac{1}{2}O_2 \qquad (17)$$

The average total weight loss was found to be 67.7 ± 1.2% as compared with a value of 67.0% calculated for the loss of two moles of NO_2, three moles of water and 1/2 mole of O_2 per mole of the nitrate as indicated by eqn. (18) to express the overall reaction

$$2Cu(NO_3)_2 \cdot 3H_2O + 2K_2S_2O_7 \rightarrow 2CuSO_4 + 2K_2SO_4 + 4NO_2 + 6H_2O + O_2 \qquad (18)$$

The TG curve of the reaction of $Zn(NO_3)_2 \cdot 6H_2O$ and $K_2S_2O_7$ shows two weight losses and a plateau between 77 and 127 °C. The first weight loss of 29.5% occurred between 27 and 77 °C, and the second between 127 and 378 °C. The average total weight loss was found to be 68.5 ± 1.3%. The theoretical weight loss of 30.2%, closer to the first weight loss, may represent either the formation of anhydrous zinc(II) nitrate with one mole of water being used for the hydrolysis of $K_2S_2O_7$ and the loss of five moles of water per mole of the nitrate as shown by

$$Zn(NO_3)_2 \cdot 6H_2O + K_2S_2O_7 \rightarrow Zn(NO_3)_2 + 2KHSO_4 + 5H_2O \qquad (19)$$

or the formation of an oxo-nitrate species, $ZnO \cdot Zn(NO_3)_2$ with the loss of two moles of water and one mole of NO_2 and 1/4 mole of O_2 per mole of the nitrate. In the latter case, four moles of water are being used for the hydrolysis of $K_2S_2O_7$ per mole of the nitrate as shown by

$$2Zn(NO_3)_2 \cdot 6H_2O + 8K_2S_2O_7 \rightarrow ZnO \cdot Zn(NO_3)_2 + 16KHSO_4 + 4H_2O + 2NO_2 + \tfrac{1}{2}O_2 \qquad (20)$$

The DTA curve of the reaction shows an endotherm at 200 °C characteristic of the melting and decomposition of $KHSO_4$. The area of the endotherm indicates that a substantial amount of water was retained by $K_2S_2O_7$ and hence supports the reaction pathway shown by eqn. (20). The second intermediate reaction between $ZnO \cdot Zn(NO_3)_2$ and $K_2S_2O_7$ may be represented by

$$ZnO \cdot Zn(NO_3)_2 + 2K_2S_2O_7 \rightarrow 2ZnSO_4 + 2K_2SO_4 + 2NO_2 + \tfrac{1}{2}O_2 \qquad (21)$$

The sum of eqns. (1) and (2) with appropriate factors, eqns. (20) and (21) is represented by eqn. (22) to express the overall reaction stoichiometry

$$Zn(NO_3)_2 \cdot 6H_2O + K_2S_2O_7 \rightarrow 2ZnSO_4 + 2K_2SO_4 + 2NO_2 + 6H_2O + \tfrac{1}{2}O_2 \qquad (22)$$

The absence of SO_2 in the gaseous products and the existence of metal cations in the same oxidation states as the reactants indicated that molten $K_2S_2O_7$ was not able to act as an oxidising medium in these reactions.

The acid–base nature of a reaction can be ascertained by a differential thermal analysis study. Lux–Flood acid–base reactions in molten salts are accompanied by exothermal processes, as are acid–base reactions in aqueous solutions. The appearance of an exothermal peak in the DTA curve of an acid–base reaction is a well known phenomenon which takes place not only in aqueous systems [16] but also in molten salt systems [17,18]. The absence of an exotherm in the DTA curves of all the reactions could be taken to indicate that all the reactions would have occurred during a process involving an endotherm. One such process is the melting and decomposition of $KHSO_4$. The resulting melt would have dissolved metal nitrates and $K_2S_2O_7$ and induced reactions between them. Provided the amount of heat evolved due to an acid–base process was less than that absorbed by melting/decomposition of $KHSO_4$, no exotherm would appear in the DTA curves of these reactions.

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