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MOLTEN POTASSIUM PYROSULFATE: THE REACTIONS OF SEVEN METAL OXALATES

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ABSTRACT

The reactions of $Li_2C_2O_4$, $Na_2C_2O_4$, $K_2C_2O_4 \cdot H_2O$, $CaC_2O_4 \cdot H_2O$, ZnC_2O_4, $La_2(C_2O_4)_3$ and $K_2TiO(C_2O_4)_2 \cdot 2H_2O$ with $K_2S_2O_7$ were investigated using thermal methods of analysis. Reaction products were analysed by various techniques. It was found that anhydrous oxalates reacted with $K_2S_2O_7$, evolving a mixture of CO_2 and CO with the formation of K_2SO_4 and the corresponding metal sulfates, which, in the reactions of ZnC_2O_4 and $K_2TiO(C_2O_4)_2 \cdot 2H_2O$, probably existed as $K_2[Zn(SO_4)_2]$ and $K_4[Ti(SO_4)_4]$, respectively. Water was found to be an additional product in the hydrated metal oxalate reactions. The stoichiometries of these reactions have been established from the thermogravimetric and acidimetric results.

INTRODUCTION

Molten $K_2S_2O_7$ was shown to act as a Lux–Flood acid when it was found to be converted into K_2SO_4 after accepting oxide ions from such Lux–Flood bases as hydroxides, carbonates, nitrites and nitrates, etc. [1,2]. The $K_2S_2O_7$ melt also exhibited oxidising properties by converting a number of metals into the corresponding metal cations [3], halides into halogen [4] and lower valent sulfur-oxo anions into sulfates [5] with the evolution of SO_2 as the main reduction product. On the other hand, oxalate has been reported to act as a reducing agent, not only in the well-known aqueous volumetric analysis [6], but also in nitrate [7,8] and nitrite [9] melts. The basic character of oxalate, i.e. as a donor of oxide ions, has been demonstrated [10] during the acid–base potentiometric titrations in molten nitrate by its reaction with such Lux–Flood acids as $NaPO_3$ and $K_2Cr_2O_7$. It was therefore of a great academic interest to investigate the reactivity of such a reducing/basic species as oxalate with an oxidising/acidic melt like $K_2S_2O_7$. This paper now reports the investigations of the reactions of seven metal oxalates with the molten $K_2S_2O_7$.

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EXPERIMENTAL

Materials

$K_2S_2O_7$ was prepared by decomposing E. Merck $K_2S_2O_8$ (98%) at 280°C for 4 h. The aqueous solution of the product showed the absence of persulfate by starch–iodide as well as $MnSO_4$ tests [11]. The melting point of the product was found to be 415°C, as compared with 410°C earlier reported in the literature [12]. Acidimetric analysis showed $98.9 \pm 0.8\%$ $K_2S_2O_7$.

ZnC_2O_4 was precipitated by adding a solution of $(NH_4)_2C_2O_4$ to a hot solution of $ZnSO_4 \cdot 7H_2O$. The precipitate was filtered, washed with cold water and dried in an oven at 120°C. The titrimetric analysis using a standard $KMnO_4$ solution indicated $56.63 \pm 1.20\%$ oxalate content (Calculated for ZnC_2O_4; $C_2O_4^{2-}$, 57.38%). $Li_2C_2O_4$ (BDH, L.R.), $Na_2C_2O_4$ (BDH, Analar, 99.9%), $K_2C_2O_4 \cdot H_2O$ (E. Merck, 99%), $CaC_2O_4 \cdot H_2O$ (BDH, Analar 98%), $K_2TiO(C_2O_4)_2 \cdot 2H_2O$ (BDH, Analar, 98.5%) and $La_2(C_2O_4)_3$ (Koch-Light, 99.9%) were used as received.

Procedure and analysis

Approximately 10 g of purified $K_2S_2O_7$ was heated isothermally at 450°C in pyrex test tubes with B19 joints, which fitted snugly into an electric furnace connected to an Ether Transitrol Controller. About 0.5 g of a reactant was added onto the molten $K_2S_2O_7$ from the side arm of the reaction test tube. On completion of each reaction, the solidified melts were examined by Raman spectroscopy to detect the presence of sulfate and after dissolving in water, the remaining amount of pyrosulfate was determined by titrating the solution against a standard NaOH solution and, by difference, the amount of pyrosulfate consumed in the reaction was calculated.

For gas analysis, reactions were carried out by heating $K_2S_2O_7$ and a reactant in Pyrex test tubes at 450°C under a vacuum. Gaseous products were identified by mass spectrometry and infrared spectroscopy. Thermogravimetric and differential thermal analysis results were obtained by heating $K_2S_2O_7$ and a reactant (10 : 1 mass ratio) in silica crucibles at 2°C min^{-1} under a current of oxygen-free dry nitrogen. All analyses are reported as averages of four to six determinations.

Physical measurements

Thermogravimetry (TG) was carried out on a Stanton TR01 thermobalance, and differential thermal analysis (DTA) on a Rigaku–Denki Thermoflex modular thermal analysis apparatus. Raman, infrared and mass spectra were obtained on a SPEX Ramalog laser Raman spectrometer, a

Perkin–Elmer 1430 Ratio Recording Infrared Spectrophotometer and a JEOL JSM D100 Mass Spectrometer, respectively.

RESULTS AND DISCUSSION

Gaseous products of the reactions of the anhydrous metal oxalates with $K_2S_2O_7$ were found by mass spectrometry and infrared spectroscopy to contain a mixture of CO_2 and CO, while those of the hydrated metal oxalates showed the presence of H_2O in addition to the above gases. Raman spectra of the solidified reaction products showed a band at 982 ± 2 cm^{-1}, characteristic of sulfate, even in excess of $K_2S_2O_7$ [13]. However, the Raman spectra of the reaction products of ZnC_2O_4 and $K_2TiO(C_2O_4)_2 \cdot 2H_2O$ contained additional bands at 1004 ± 2 and 940 ± 2 cm^{-1}, respectively. The presence of these additional bands may be taken to indicate the existence of sulfato complexes in these reactions, because the symmetry of the free sulfate ion is distorted on complex formation and this gives rise to an additional band [14]. This conclusion is further supported by the presence of $K_2[Zn(SO_4)_2]$ and $K_4[Ti(SO_4)_4]$ complexes in the reaction products of $ZnO + K_2S_2O_8$ and $TiO_2 + K_2S_2O_8$, respectively [15,16].

The thermogravimetric and the acidimetric results of the reactions of oxalates with $K_2S_2O_7$ are shown in Table 1. The thermogravimetric results show a comparison between mass losses experimentally determined and those calculated for the following reaction stoichiometries:

$$Li_2C_2O_4 + K_2S_2O_7 \rightarrow Li_2SO_4 + K_2SO_4 + CO_2 + CO \qquad (1)$$

$$Na_2C_2O_4 + K_2S_2O_7 \rightarrow Na_2SO_4 + K_2SO_4 + CO_2 + CO \qquad (2)$$

$$K_2C_2O_4 \cdot H_2O + K_2S_2O_7 \rightarrow 2K_2SO_4 + CO_2 + CO + H_2O \qquad (3)$$

$$CaC_2O_4 \cdot H_2O + K_2S_2O_7 \rightarrow CaSO_4 + K_2SO_4 + CO_2 + CO + H_2O \qquad (4)$$

$$ZnC_2O_4 + K_2S_2O_7 \rightarrow K_2[Zn(SO_4)_2] + CO_2 + CO \qquad (5)$$

$$La_2(C_2O_4)_3 + 3K_2S_2O_7 \rightarrow La_2(SO_4)_3 + 3K_2SO_4 + 3CO_2 + 3CO \qquad (6)$$

$$K_2TiO(C_2O_4)_2 \cdot 2H_2O + 3K_2S_2O_7 \rightarrow K_4[Ti(SO_4)_4] + 2K_2SO_4 + 2CO_2 + 2CO + 2H_2O \qquad (7)$$

Products on the right-hand side of the above equations are well supported by the qualitative results of Raman, infrared and mass spectrometric methods, and by the quantitative results obtained by thermogravimetry. The molar ratios of reactants on the left-hand side of the equations are based on the acidimetric results, as shown in the last column of Table 1. Thus, the thermogravimetric and the acidimetric results support each other.

Sulfur dioxide was found to be absent from the gaseous products, as was sulfite from the solid products. The absence of the reduction products of

TABLE 1

Thermogravimetric and acidimetric results of the reactions of oxalates with $K_2S_2O_7$

Metal oxalate	Temperature range (°C)	Temperature of maximum rate (°C)	Mass loss (%)		Molar ratio of pyrosulfate/oxalate
			Found	Calculated	
$Li_2C_2O_4$	350–440	396	72.40±1.92	70.57	1.00±0.03
$Na_2C_2O_4$	376–412	396	52.49±0.87	53.73	0.96±0.05
$K_2C_2O_4 \cdot H_2O$	384–500	458	48.95±1.83	48.92	1.04±0.04
$CaC_2O_4 \cdot H_2O$	372–422	416	59.17±0.58	60.82	1.02±0.04
ZnC_2O_4	288–389	308	46.38±1.91	46.94	0.94±0.02
$La_2(C_2O_4)_3$	360–460	388	39.80±1.76	39.85	2.85±0.12
$K_2TiO(C_2O_4)_2 \cdot 2H_2O$	326–410	360	53.80±1.38	50.82	3.29±0.10

The first mass loss in the hydrated metal oxalate reactions was due to water, for which temperature values are not shown in this table.

pyrosulfate indicates that an oxidation–reduction process did not take place in these reactions. The presence of CO_2, CO and sulfate in the products indicates that only acid–base reactions took place in the oxalate–pyrosulfate systems. The metal oxalates acted as Lux–Flood bases, evolving CO_2 and CO and donating oxide ions to pyrosulfate, which was converted into sulfate.

Acid–base nature of a reaction can also be ascertained by the differential thermal analysis study. Lux–Flood acid–base reactions in molten salts are accompanied by an exothermal process, as do the 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 [17], but also in molten salt systems [18,19].

The DTA curve of $K_2S_2O_7$ alone showed two endotherms at 328 and 415°C, assigned to its crystal structure change and melting point, respectively [12]. The DTA curves of the reaction mixtures showed two endotherms and an exotherm in most cases. Table 2 shows maximum temperature values for the DTA peaks of $K_2S_2O_7$ alone and those of the reaction mixtures. By comparing these results, it can be concluded that the values of the exothermal peak shown in column 3 of Table 2 may be taken to represent temperatures at which Lux–Flood acid–base reactions took place between oxalates and $K_2S_2O_7$. However, the DTA curves of the reactions of ZnC_2O_4 and $K_2TiO(C_2O_4)_2 \cdot 2H_2O$ contained no exotherms. This could be due to an endothermal process of equal energy taking place simultaneously with the acid–base exothermal process. This would have created a thermal neutrality in the region and caused the disappearance of the expected exotherms of these reactions. Such an endothermal process could have arisen due to the formation and the dissolution of sulfato complexes, indicated by the Raman spectra, to be present in the products of these reactions. The

TABLE 2

Differential thermal analysis results

Reactant	T_{max} values (°C) for the major DTA peaks		
	Endotherm	Endotherm	Exotherm
$K_2S_2O_7$ alone	328	415	–
$Li_2C_2O_4$	330	416	425
$Na_2C_2O_4$	328	414	404
$K_2C_2O_4 \cdot H_2O$	328	416	424
$CaC_2O_4 \cdot H_2O$	328	410	416
ZnC_2O_4	328	416	–
$La_2(C_2O_4)_3$	332	416	442
$K_2TiO(C_2O_4)_2 \cdot 2H_2O$	324	410	–

other reason for the absence of the exotherms could be that the acid–base reactions would have taken place during the melting of $K_2S_2O_7$, and the exotherms would have disappeared in the melting endotherm.

In addition to three major DTA peaks described in Table 2, the hydrated metal oxalates also showed dehydration endotherms in their DTA curves when heated alone or with $K_2S_2O_7$. Thus, for example, the DTA curves of the reactions of $K_2C_2O_4 \cdot H_2O$, $CaC_2O_4 \cdot H_2O$ and $K_2TiO(C_2O_4)_2 \cdot 2H_2O$ showed endothermal peaks at 100, 200 and 110°C, respectively, with the mass losses due to water in their TG curves at the corresponding temperatures. These thermal results indicate that water of crystallisation is not used up for the hydrolysis of pyrosulfate under these conditions and thus do not support the general belief that pyrosulfate is instantaneously hydrolysed by water [20] as shown in equation (8):

$$S_2O_7^{2-} + H_2O \rightarrow 2H^+ + 2SO_4^{2-} \qquad (8)$$

It may also be concluded that, in the study of reactions using $K_2S_2O_7$ as a medium, a reactant can either be used in hydrated or anhydrous form.

The relative basicity or reactivity of the oxalates in $K_2S_2O_7$ may be assessed either by the values of the initial reaction temperature at which mass losses took place, or by the values of maximum temperature at which exothermal peaks appeared due to acid–base reactions. Because of the acid–base nature of the reactions, a method based on the DTA study appears to be better than that based on the thermogravimetric study. Unfortunately, a comparison of the relative basicity or reactivity could not be made with confidence in all cases on the basis of the DTA study because the exothermal process was affected by other thermal processes, as clearly noted in the reactions of ZnC_2O_4 and $K_2TiO(C_2O_4)_2 \cdot 2H_2O$. The following order of basicity or reactivity of the oxalates in $K_2S_2O_7$ can be proposed on the basis of initial reaction temperatures shown in Table 1: Zn > Ti > Li > La > Ca > Na > K.

Oxalate was found to behave as a reducing species in nitrate [7,8] and nitrite [9] melts, but, in pyrosulfate, it acted as a Lux–Flood base. This seems to be due to different nature of the reaction media.

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