



Roginsky [2] compared the rate of decomposition of permanganates of a series of metals and arranged them according to their increasing stability: for univalent ions,  $\text{Ag}^+$  ( $\sim 90^\circ\text{C}$ ),  $\text{Li}^+$  ( $\sim 100^\circ\text{C}$ ),  $\text{Na}^+$  ( $\sim 150^\circ\text{C}$ ),  $\text{K}^+$  ( $\sim 200^\circ\text{C}$ ),  $\text{Na}^+$  ( $\sim 150^\circ\text{C}$ ),  $\text{K}^+$  ( $\sim 200^\circ\text{C}$ ),  $\text{Rb}^+$  ( $\sim 290^\circ\text{C}$ ) and  $\text{Cs}^+$  ( $\sim 330^\circ\text{C}$ ); for bivalent ions,  $\text{Mg}^{2+}$  ( $110^\circ\text{C}$ ) and  $\text{Ba}^{2+}$  ( $170^\circ\text{C}$ ), this being exactly in accord with the series of deforming ions of Fajans and Joos [23]. For the permanganate with the least stability ( $\text{Li}^+$ ), the simple topochemistry was found to be maintained.

The topochemical nature of the decomposition of permanganates has been investigated by various authors [3–5]. Prout and Herley [6] have studied the thermal decomposition of lithium permanganate and they discussed the reaction in terms of the idealised equation



The decomposition of  $\text{NaMnO}_4$  was set out in terms of a similar equation.

Other authors have formulated such idealised equations for the thermal decomposition of Rb [7], Cs [6], and Ag [7] salts, namely



where M can be Rb, Cs or Ag.

It would seem that these compounds have not been studied as much as the potassium salt: however, Herbststein et al. [8,9] and Boldyrev et al. [10] recently looked at the decomposition of  $\text{RbMnO}_4$ ,  $\text{CsMnO}_4$  and of course  $\text{KMnO}_4$  (using various techniques), resulting in conflict between the two authors regarding the mechanism of decomposition of  $\text{KMnO}_4$ .

The thermal decomposition of  $\text{KMnO}_4$  occurs at a noticeable rate at temperatures ranging from 200 to  $280^\circ\text{C}$ . To describe the chemical reaction, most authors use the following schematic equation



the solid products being manganese dioxide and potassium manganate, and the gaseous product oxygen. Boldyrev et al. [10] consider the deviations from the above scheme to be related to secondary reactions.

In the work reported here the thermal decompositions of potassium, rubidium and caesium permanganates are reported using thermogravimetric techniques (TG) and differential thermal analysis (DTA), and the data are used to comment on the probable mechanism of decomposition. The studies are extended to cover the related compounds  $\text{K}_2\text{MnO}_4$  and  $\text{NaKMnO}_4$ .

## EXPERIMENTAL

### *Materials*

AnalaR grade potassium permanganate was supplied by proprietary chemical manufacturers. The remaining permanganates were prepared from this (as were also the manganates used in the decomposition studies) and recrystallised several times to ensure purity.

### *Preparation of samples*

The potassium permanganate samples were recrystallised as follows [11]. AnalaR  $\text{KMnO}_4$  (12.0 g) was dissolved in dust-free distilled water ( $100 \text{ cm}^3$ ,  $60^\circ\text{C}$ ) and rapidly filtered through glass wool (to remove any manganese dioxide). The filtrate was placed in an enclosure at  $25^\circ\text{C}$  for 6 h in the dark. The supernatant liquid was then decanted, the crystals rapidly dried, and the required crystals then selected by hand under an optical microscope ( $0.5 \times 1.00 \text{ mm}$  and  $1.0 \times 6.0 \text{ mm}$ ). G.P.R. grade potassium permanganate was also used for decomposition experiments in the state "as received", the crystals of size ( $1.0 \times 3.0 \text{ mm}$ ) also being hand-selected under a microscope. Crystals of rubidium permanganate ( $0.5 \times 2.5 \text{ mm}$ ) were obtained by the method described by Herley and Prout [12]. Rhombic bipyramidal crystals of caesium permanganate ( $0.30\text{--}0.50 \text{ mm}$ ) were prepared by the method of Prout and Herley [6]. Potassium manganate was prepared by the action of strong boiling caustic alkali solution (KOH) on potassium permanganate solid in the presence of small amounts of potassium nitrate. A compound with formula " $\text{NaKMnO}_4$ " was prepared by replacing the KOH with caustic soda. Recrystallisation was carried out several times.

### EQUIPMENT

#### *TG Thermobalances*

Thermogravimetric analyses recorded in this study were undertaken using commercial Stanton—Redcroft instruments, namely models TR1, TRO1 (with a differential thermal attachment for DTA) and TG-750.

#### *DTA units*

The endothermic and exothermic changes which occurred during thermal decomposition were detected using Netzsch DTA (high temperature  $1300^\circ\text{C}$  and low temperature  $1000^\circ\text{C}$ ) units, and the Stanton—Redcroft DTA attachment to the TRO1 thermobalance. Decompositions were carried out either in air or a controlled atmosphere of dry nitrogen ( $100 \text{ cm}^3 \text{ min}^{-1}$ ).

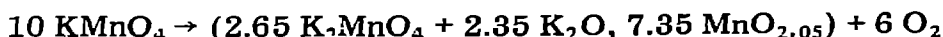
#### *Procedure*

The thermal analyses of potassium, rubidium and caesium permanganate were investigated by TG in the temperature range  $25\text{--}900^\circ\text{C}$ . The atmospheres used were air, oxygen, nitrogen and carbon dioxide (all at flow rates of  $25 \text{ cm}^3 \text{ h}^{-1}$ ). DTA was undertaken using whole and ground crystals of G.P.R. and AnalaR  $\text{KMnO}_4$ ,  $\text{K}_2\text{MnO}_4$  (fine crystals), and  $\text{NaKMnO}_4$ .

### RESULTS

It was found that no difference was observed between "as received" AnalaR samples and those recrystallised. A similar result was observed by

Herbstein et al. [8]. AnalaR potassium permanganate crystals began to decompose between 220 and 300°C, the decomposition starting at 220°C at a heating rate of ca. 5°C min<sup>-1</sup> in a dynamic air atmosphere (25 cm<sup>3</sup> h<sup>-1</sup>). This observation agrees well with previous work [8,13,14]. The percentage weight change was almost independent of atmosphere (11–12%). The idealised decomposition equation in air was assumed to be that of Herbstein et al. [8], namely



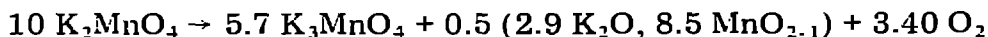
showing a percentage weight loss for this stage of ca 12% in agreement with this equation.

In the temperature range 300–500°C a small gradual weight loss (1–2%) was observed for samples decomposed in oxygen, air and nitrogen. This additional weight loss agrees well with the results of others [8,10,15].

The effect of changing the atmosphere, e.g. nitrogen (25 cm<sup>3</sup> h<sup>-1</sup>) to oxygen (25 cm<sup>3</sup> h<sup>-1</sup>), changed the decomposition temperature only slightly,  $T_{\text{O}_2} > T_{\text{N}_2}$  by 50°C. The reaction products (using the TG-750 instrument only) when controllably cooled to ambient temperature in dry air (25 cm<sup>3</sup> h<sup>-1</sup>) did not change weight.

Using the TRO1 type balance when the decomposition was performed in static air and a small amount of carbon dioxide was gently directed towards the top of the sample holder, caused a gain in weight to appear on the TG curve in the temperature range 380–430°C. This weight gain did not occur if carbon dioxide was excluded, although of course there would be a small amount of carbon dioxide in the atmospheric air. This observation resembles the effect found by Herbstein et al. [8].

Heating to higher temperatures resulted in a weight loss at ca. 600°C, the exact temperature depending on the atmosphere, e.g. oxygen ca. 700°C, air ca. 620°C and nitrogen ca. 540°C. In all cases the percentage total weight loss was found to be between 5 and 6%. Assuming that the idealised decomposition equation found by Herbstein et al. [8] is to be applied to the reaction at this stage, namely



then it is noted that the weight loss theoretically found is 5.5% (this value corresponds to the experimentally observed value in the present study).

Similar observations were found in the case of rubidium and caesium salts for the first stage, but the reaction temperatures were higher, in the order Cs > Rb > K, i.e. Rb (290–330°C) and Cs (310–350°C); the exact value depending on the experimental conditions, i.e.  $T_{\text{O}_2} > T_{\text{air}} > T_{\text{N}_2}$  — with about 40°C difference in decomposition temperature when oxygen replaced nitrogen as the atmosphere (25 cm<sup>3</sup> h<sup>-1</sup>). These observations agree well with previous results for the rubidium salt [8] but no reports of TG work on caesium permanganate were found in the literature. In both cases the percentage weight loss for the first stage was found to be ca. 10%, previous work [11] quoted 9.36% for the rubidium salt.

Herbstein et al. [8] put forward an idealised decomposition equation for

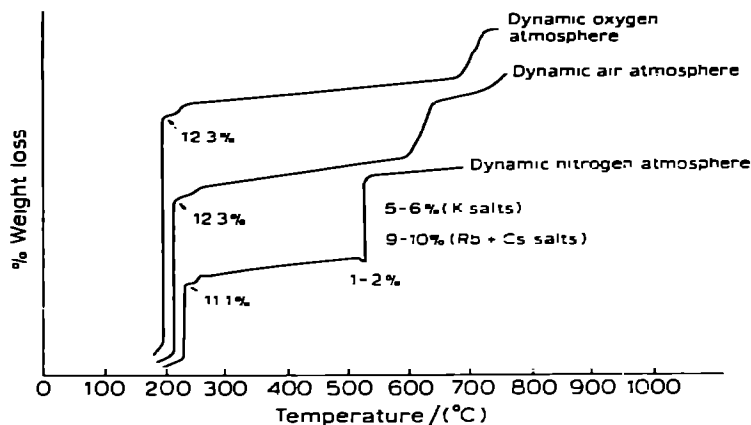
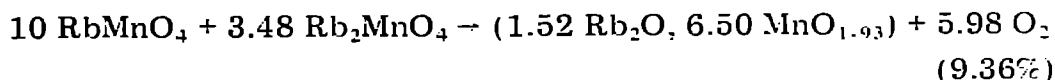


Fig. 1. A typical TG plot of some group I permanganates in different atmospheres ( $O_2$ ,  $N_2$  and Air). Heating rate  $10^\circ C \text{ min}^{-1}$ . Note: weight loss axis not to scale.

$RbMnO_4$  in an atmosphere of air at  $315^\circ C$ , namely



In our experiments on this salt at higher temperatures (i.e.  $>315^\circ C$ ) there was a noticeable weight loss at ca.  $800^\circ C$  for the rubidium salt and ca.  $850^\circ C$  for the caesium salt, i.e.  $810\text{--}820^\circ C$  in dynamic air ( $RbMnO_4$ ) and  $840\text{--}860^\circ C$  ( $CsMnO_4$ ). In both cases 9–10% weight loss occurred. The decomposition temperatures in different atmospheres were of the order  $T_{O_2} > T_{air} > T_{N_2}$ . A typical TG plot of permanganate decomposition is shown in Fig. 1.

DTA showed that the first decomposition for permanganates is exothermic and the second endothermic. A typical DTA plot for AnalaR  $KMnO_4$  is shown in Fig. 2. The first peak occurred between 200 and  $300^\circ C$  and the second peak between 500 and  $700^\circ C$ ; the exact decomposition temperature

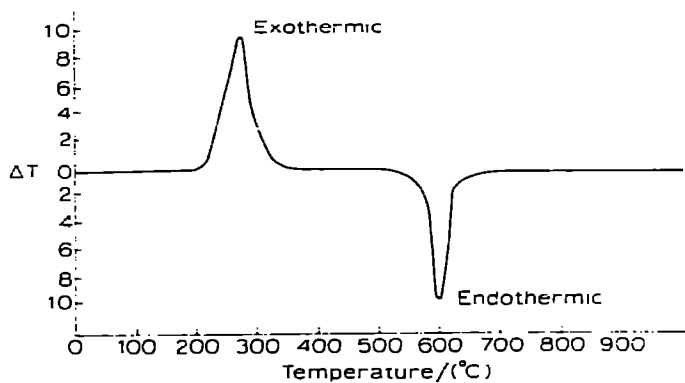


Fig. 2. A typical DTA plot of AnalaR potassium permanganate in dynamic air.

TABLE 1

DTA results using the Stanton—Redcroft attachment to TR01 thermobalance

Sample wt. (mg)	Temp. of exothermic peak (°C)	Peak ht. (arbitrary units)	Temp. of endothermic peak (°C)	Peak ht. (arbitrary units)
A. G.P.R. $\text{KMnO}_4$ crystals in static air, heated at $10^\circ\text{C min}^{-1}$				
50	260	12	620	4
80	260	16	620	5
130	265	24	620	8
150	265	36	620	13
180	265	37	620	13
210	265	38	620	13
270	265	39	620	13
350	270	42	620	13
B. G.P.R. $\text{KMnO}_4$ crystals in static air, heated at $10^\circ\text{C min}^{-1}$ , preheated at $160^\circ\text{C}$ for 12 h				
50	275	12	575	4
140	270	36	585	12
200	260	38	580	13

detected depending on the atmosphere used and the unit employed, e.g. in the range  $230$ – $270^\circ\text{C}$  for the first decomposition stage, and  $580$ – $620^\circ\text{C}$  for the second stage using the same atmosphere (static air) but different units.

Table 1 shows the results found when G.P.R.  $\text{KMnO}_4$  crystals "as received" were decomposed on the Stanton—Redcroft DTA assembly (to the TR01 thermobalance). The temperature of the first decomposition ( $260$ – $270^\circ\text{C}$ ) was found to be only slightly dependent on sample concentration and independent for the second decomposition ( $620^\circ\text{C}$ ).

Results observed for G.P.R. "as received" and recrystallised AnalaR  $\text{KMnO}_4$  are compared in Tables 1A and 2A, respectively. It is evident that for the decomposition of recrystallised AnalaR samples, a second (small) endothermic peak was observed at  $125^\circ\text{C}$ , which was not observed for G.P.R. samples. The nature of this small peak is unknown, but has been observed previously [3].

Table 2B shows the results found when recrystallised AnalaR  $\text{KMnO}_4$  crystals were preheated at  $160^\circ\text{C}$  for 12 h before decomposing. The small endothermic peak at  $125^\circ\text{C}$  was still clearly evident and appears to be independent of the amount of  $\text{KMnO}_4$  crystals used.

Ground crystals of G.P.R.  $\text{KMnO}_4$  (recrystallised, surface area  $0.4\text{ m}^2\text{ g}^{-1}$ ) decomposed on the Netzsch DTA units showed the first decomposition to occur at ca.  $236^\circ\text{C}$  (in static air) and the second at ca.  $580^\circ\text{C}$  (also in static air). Table 3 shows both peaks to be independent of initial sample concentration.

A further DTA experiment was attempted using fine crystals of the compound labelled  $\text{NaKMnO}_4$ . Table 4A shows the results of the DT analysis of this compound. Six endothermic peaks were observed, the peak at  $133^\circ\text{C}$  probably corresponds to the unknown peak of Peters et al. [14] which was

TABLE 2

DTA results using a Stanton—Redcroft DTA attachment to TR01 thermobalance

Sample wt. (mg)	Temp. of exothermic peak (°C)	Peak ht. (arbitrary units)	Temp. of endothermic peak (°C)	Peak ht. (arbitrary units)
<b>A. AnalaR KMnO<sub>3</sub> crystals in static air, heated at 10°C min<sup>-1</sup></b>				
140	270	37	620	12
			125	3
170	275	39	620	13
			125	3
200	280	45	620	15
			125	3
<b>B. AnalaR KMnO<sub>4</sub> crystals in static air, heated at 10°C min<sup>-1</sup> preheated at 60°C for 12 h</b>				
140	301	34	620	12
			125	3
250	300	45	620	14
			125	3

found earlier for AnalaR KMnO<sub>4</sub>. The peak at 603°C probably relates to the decomposition of K<sub>2</sub>MnO<sub>4</sub> to K<sub>3</sub>(MnO<sub>4</sub>)<sub>2</sub> [8]. Table 4B shows that after preheating the specimen, peak C was no longer observed, but a second peak emerged at ca. 500°C; the remaining peaks were observed in the same position as for the sample which was not preheated. The DTA showed that the majority of the sample decomposed at ca. 360°C.

TABLE 3

DTA using the Netzsch DTA units. Recrystallised G.P.R. KMnO<sub>4</sub> ground crystals in static air, heated at 10°C min<sup>-1</sup>

Conc. of KMnO <sub>4</sub> (%)	Temp. of exothermic peak (°C)	Peak ht. (arbitrary units)	Temp. of endothermic peak (°C)	Peak ht. (arbitrary units)
<b>A. Low temperature instrument</b>				
80	230	15	580	5
100	236	22	580	7
200	236	29	580	10
250	236	32	580	10
300	236	45	580	15
500	236	(Off scale)	580	(Off scale)
<b>B. High temperature instrument</b>				
40	236	1	580	1
120	236	3	580	1
200	236	9	580	3
250	236	12	580	4
500	236	(Off scale)	580	(Off scale)

TABLE 4

Stanton—Redcroft attachment to TR01 thermobalance

Endothermic peak	Temp. of endothermic peak ( $^{\circ}\text{C}$ )	Peak ht. (arbitrary units)
<i>A. Recrystallised "NaKMnO<sub>4</sub>" (fine crystals) in static air, heated at 10<math>^{\circ}\text{C min}^{-1}</math> (sample weight 100 mg)</i>		
A	133	8
B	241	10
C	270	4
D	365	20
E	494	7
F	602	8
<i>B. Recrystallised "NaKMnO<sub>4</sub>" (fine crystals) in static air, heated at 10<math>^{\circ}\text{C min}^{-1}</math> preheated, at 160<math>^{\circ}\text{C}</math> for 12 h</i>		
A	133	7
B	241	12
C	—	—
D	365	20
E	476	7
	494	5
F	603	8
<i>C. Recrystallised K<sub>2</sub>MnO<sub>4</sub> (fine crystals) in static air, heated at 10<math>^{\circ}\text{C min}^{-1}</math> (sample wt = 100 mg)</i>		
	600	40
<i>D. Recrystallised K<sub>2</sub>MnO<sub>4</sub> (fine crystals) in static air, heated at 10<math>^{\circ}\text{C min}^{-1}</math>, preheated at 160<math>^{\circ}\text{C}</math> for 12 h (sample wt. = 100 mg)</i>		
	603	40

Table 4C and D shows the DTA results of thermally decomposing doubly recrystallised K<sub>2</sub>MnO<sub>4</sub> in an atmosphere of static air. The effect of preheating the sample did not produce any observable change in the DTA.

DT analysis of RbMnO<sub>4</sub> and CsMnO<sub>3</sub> was undertaken in an atmosphere of static air (using Stanton—Redcroft DTA attachment to TR01 thermobalance). The first decomposition was shown to be exothermic, the second endothermic, no other peaks were observed. The decomposition temperatures observed correspond well with the TG results shown in Fig. 1.

## DISCUSSION

The thermal decomposition of KMnO<sub>4</sub> and K<sub>2</sub>MnO<sub>4</sub> (also CsMnO<sub>4</sub>, RbMnO<sub>4</sub>, K<sub>2</sub>MnO<sub>4</sub>, and Rb<sub>2</sub>MnO<sub>4</sub>) can be considered as redox reactions in which oxygen from the oxy-anions is oxidised to molecular oxygen, while the oxidation number of the manganese in the oxy-anion is either reduced



by one in the oxy-anions concerned (e.g. from Mn(VII) to Mn(VI) in passage from  $\text{MnO}_4^-$  to  $\text{MnO}_4^{2-}$ ) or to Mn(IV) in the “ $\text{K}_4\text{Mn}_7\text{O}_{16}$ ” phase.

According to Herbstein et al. [8], in  $\text{KMnO}_4$  and ca. 250°C Mn—O bonds are broken in 73% of the  $\text{MnO}_4^-$  ions; on average, 1.6 Mn—O bonds are broken in each of these permanganate ions. Electrons are transferred to the remaining 27% of the permanganate ions, which are reduced to  $\text{MnO}_4^{2-}$  with only a small change in their tetrahedral shape [16]. In  $\text{K}_2\text{MnO}_4$  at ca. 600°C, Mn—O bonds are broken in 43% of the  $\text{MnO}_4^{2-}$  ions; on average 1.6 Mn—O bonds are broken in each of these manganate ions, which are reduced to  $\text{MnO}_3^{2-}$ . The structure of the hypomanganite ion is not known, but Herbstein et al. [8] consider it to be possibly tetrahedral. The percentage values for bonds broken, etc. given by Herbstein et al. [8] are subject to other constraints that could be imposed on the experimental system.

To describe the chemical reaction for the thermal decomposition of  $\text{KMnO}_4$  at 205–280°C, most authors use the schematic equation



and it has been generally accepted [5,8,11,14,17] that products of the decomposition in air at ca. 200°C are manganate, “ $\text{K}_4\text{Mn}_7\text{O}_{16}$ ” phase and oxygen. This is referred to as the “Herbstein” mechanism. However, Boldyrev et al. [10] have recently suggested that the crystalline phase  $\text{K}_3(\text{MnO}_4)_2$  is formed in the first stages of the decomposition and that  $\text{K}_2\text{MnO}_4$  is produced in a later stage, i.e. the “Boldyrev” mechanism. If this is so, then all earlier studies of the thermolysis of  $\text{KMnO}_4$ , especially of Prout and Tompkins type, will have to be re-interpreted.

Herbstein and Weissman’s [9] results placed in doubt the results of Boldyrev et al. [10], since their experiments confirmed the accepted description of the course of the thermal decomposition.

However, Boldyrev et al. [18] recently carried out detailed investigations (in the range 200–215°C) for the purpose of proving experimentally the question regarding the existence of  $\text{K}_3(\text{MnO}_4)_2$ . The results confirmed their previous conclusions and they believe that the observations can be considered to be a firmly established experimental fact.

Much of the observed TG results found for  $\text{KMnO}_4$  in this present study are compatible with the results of Herbstein et al. [8]; however, their interpretation cannot be accepted without extensive X-ray studies.

The situation regarding the thermal decomposition of  $\text{RbMnO}_4$  and  $\text{CsMnO}_4$  according to Herbstein et al. [8] is qualitatively similar to that of  $\text{KMnO}_4$ , but having no quantitative correspondence. The TG results from this present study also corresponded to the TG observations of Herbstein et al. [8].

The decomposition temperatures found show that the appropriate order of thermal stability for the group I salts are  $\text{M}_3(\text{MnO}_4)_2 > \text{M}_2\text{MnO}_4 > \text{MMnO}_4$  if the Herbstein decomposition mechanism is assumed. The same order of stability was found by comparison of lattice energies calculated by the Kapustinskii equation [19] (e.g.  $\text{KMnO}_4$ , 585;  $\text{K}_2\text{MnO}_4$ , 1756; and  $\text{K}_3(\text{MnO}_4)_2$ , 3511 kJ mole<sup>-1</sup>).

However, Erenburg et al. [20] have recently studied the thermolysis of

$\text{CsMnO}_4$  and  $\text{RbMnO}_4$  in air (no TG data given) by X-ray diffraction. The primary product in all experiments were the manganates. In this respect their behaviour differs sharply from that of  $\text{KMnO}_4$  if the Boldyrev et al. [18] thermal decomposition mechanism is considered.

The DTA results from this present study showed that the first decomposition stage for permanganate is exothermic and the second endothermic. Pirisi and Mattu [21] found the exothermic decomposition of  $\text{KMnO}_4$  to begin at  $275^\circ\text{C}$ , the maximum in the decomposition peak was found at  $295^\circ\text{C}$  and the end of the stage occurred at  $300^\circ\text{C}$ . The data results shown in this study compare well with previous work [8,14,21] and also the TG results given in Fig. 1.

The results showed that when general purpose reagent "as received" crystals were decomposed, only two decomposition stages could be found, but when an extremely pure sample was used a very small endothermic peak was also noticed at ca.  $125^\circ\text{C}$ . It is evident from the TG, DTA and X-ray diffraction (combined in some cases) studies on permanganates that doubt exists regarding the products of the decomposition [8–10,18,20,22]. The cause of the endotherm at ca.  $125^\circ\text{C}$  is not known.

Results for the decomposition of pure potassium permanganate showed the decomposition to occur at ca.  $600^\circ\text{C}$ ; these observations are comparable to those of Herbstein et al. [8], but the work of Boldyrev et al. [10,18] again puts doubt on any interpretation. Samples of the compound " $\text{NaKMnO}_4$ " showed extremely complex DTA patterns; the peaks could not be interpreted since the true structure of the compound was not determined. However, the Na : K ratio was determined 1 : 1. It is evident that the bulk of the sample decomposed at ca.  $365^\circ\text{C}$ . DTA results of  $\text{RbMnO}_4$  and  $\text{CsMnO}_4$  were comparable to those of Herbstein et al. [8,9] and Erenburg et al. [20].

## CONCLUSION

In the actual mechanism of the reaction the original simpler views of Prout and Tompkins have been replaced by two alternative mechanisms, one by Herbstein and the other by Boldyrev. The two may be potentially reconciled, however, by noting that Herbstein did not attribute all his decomposition process to the one mechanism. The possibility exists that both mechanisms exist side by side.

If, however, the view point of Boldyrev is taken, then all the earlier studies of the thermal decomposition of  $\text{KMnO}_4$  will have to be re-interpreted.

The thermal decomposition of  $\text{KMnO}_4$  has been shown experimentally to consist of two stages. The exact nature of the products of the thermal decomposition are, however, still uncertain (with the exception that oxygen is released). The difference between the mechanism proposed by Boldyrev and that by Herbstein has already been shown, but the structure of the phase " $\text{K}_4\text{Mn}_7\text{O}_{16}$ " (proposed in both mechanisms as a product of the first and second stages) is unknown, and it must be asked whether these products are structurally identical or not.

Two stages are shown to exist in the thermal decomposition of  $\text{RbMnO}_4$  and  $\text{CsMnO}_4$ . The reaction is analogous to that of  $\text{KMnO}_4$  but the exact nature of the products is also still uncertain (with the exception that oxygen is again released).

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