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ISOTHERMAL DSC STUDY OF THE THERMAL DECOMPOSITION OF POTASSIUM PERMANGANATE

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ABSTRACT

Potassium permanganate decomposes on heating in two discrete stages. The first stage (~ 290°C) is exothermic overall and the second (~ 620°C) is endothermic. Kinetic studies of the first stage of the decomposition in vacuum led to the introduction of the Prout–Tompkins equation ($\ln(\alpha/(1-\alpha)) = kt + c$) and a mechanism involving branching nuclei to account for this autocatalytic behaviour.

Isothermal DSC studies show that the first stage of the decomposition does not give the symmetrical exotherm expected for the Prout–Tompkins model, but consists of several overlapping exotherms, as well as a final endothermic contribution when product oxygen is removed by an inert carrier gas.

The effects of atmosphere, temperature and particle size on the DSC curves are reported and discussed in relation to the Prout–Tompkins model. Electron micrographs reveal some details of the decomposition mechanism.

INTRODUCTION

During a thermoanalytical study of the intersolid reactions in the antimony/potassium permanganate pyrotechnic system [1], we found it of interest to re-examine some aspects of the thermal decomposition of potassium permanganate. The Group I and II metal permanganates, especially $KMnO_4$, have been studied in great detail (ref. 2 and references therein), including a very recent thermoanalytical study [3], but there is still some controversy over the course of the decomposition. $KMnO_4$ decomposes in nitrogen in two discrete stages. The first stage occurs around 290°C (563 K), is exothermic overall and involves a mass loss of ~ 12%, while the second stage at ~ 620°C (893 K) is endothermic with a mass loss of ~ 3.5% of the original sample.

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Kinetic studies have been concerned with the first stage of the decomposition [4]

$$10\ KMnO_4(s) \rightarrow 2.65\ K_2MnO_4(s) + (2.35\ K_2O \cdot 7.35\ MnO_{2.05})(s) + 6\ O_2(g)$$

In vacuum, the temperature range over which decomposition occurs at a conveniently measurable rate [5,6] is 470–500 K, which is some 40 K lower than in nitrogen. The isothermal decomposition of $KMnO_4$ in vacuum is reported to give characteristic sigmoid curves of fractional decomposition, α, against time [2,6,7]. These curves conform to the Prout–Tompkins equation

$$\ln(\alpha/(1-\alpha)) = kt + c$$

Detailed mechanisms have been proposed to account for this autocatalytic behaviour [2,5,6] in terms of initiation of the reaction at lattice imperfections, followed by development of strain within the crystals, which then leads to cracking and the formation of new surfaces at which decomposition is rapid.

Conformity to the Prout–Tompkins equation is notoriously difficult to distinguish [8] from conformity to other models leading to sigmoid α–time curves, such as the Avrami–Erofeev model

$$[-\ln(1-\alpha)]^{1/n} = k't + c'$$

especially when $n = 3$ or 4. Recently a method has been published [9] which is suitable for analysing isothermal rate (i.e., $d\alpha/dt$) time curves, such as the output from isothermal DSC, without integration. Obedience to the Prout–Tompkins equation would be readily recognizable through the appearance of a very symmetrical exotherm [9]. Isothermal DSC, as well as scanning electron microscopy (SEM), have thus been used to follow the course of decomposition.

EXPERIMENTAL

A Perkin-Elmer DSC-2 differential scanning calorimeter was used. Samples were crimped in aluminium pans with pierced lids. The carrier gas was either nitrogen or oxygen at a pressure of 140 kPa.

Materials

Several preparations of potassium permanganate were used: (A) AnalaR, as received, (B) AnalaR, recrystallised from water, (C) and (D) samples of (A) and (B), respectively, ground to 75–125 μm diameter, (E) aged material, recrystallised ~ 15 years ago, and (F) powdered $KMnO_4$ ($< 53\ \mu$m) as used in pyrotechnic compositions [1].

RESULTS AND DISCUSSION

Effect of preparation and pretreatment

The decomposition of $KMnO_4$ is known to be sensitive to the preparation and the pretreatment of the reactant. This is confirmed by the results of dynamic (10 K min^{-1}) and isothermal (520 K) DSC runs in nitrogen, shown in Figs. 1–3. Recrystallisation results in a sharpened exotherm (Fig. 1), while grinding broadens the exotherms of both preparations. In the isothermal runs, although it is not always easy to establish the position of the baseline, several features appear that are not evident from the dynamic runs. Firstly,

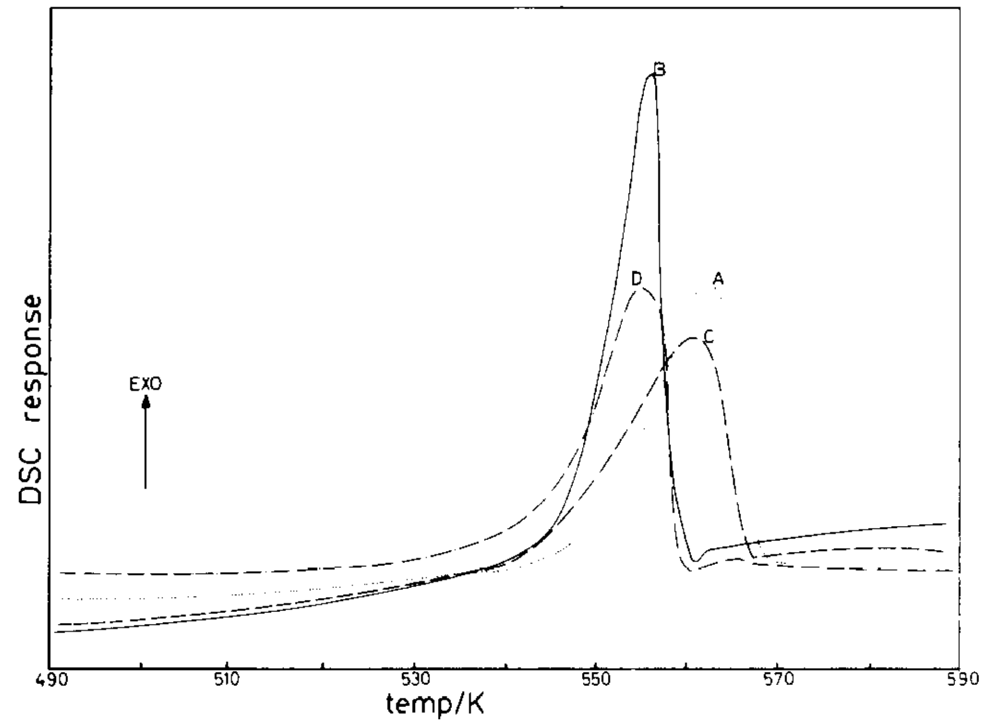

Fig. 1. Dynamic DSC scans on different samples of $KMnO_4$ at 10 K min^{-1} in nitrogen: (A) AR 5.82 mg; (B) recrystallised 6.49 mg; (C) AR crushed 6.34 mg; (D) recrystallised, crushed 5.86 mg.

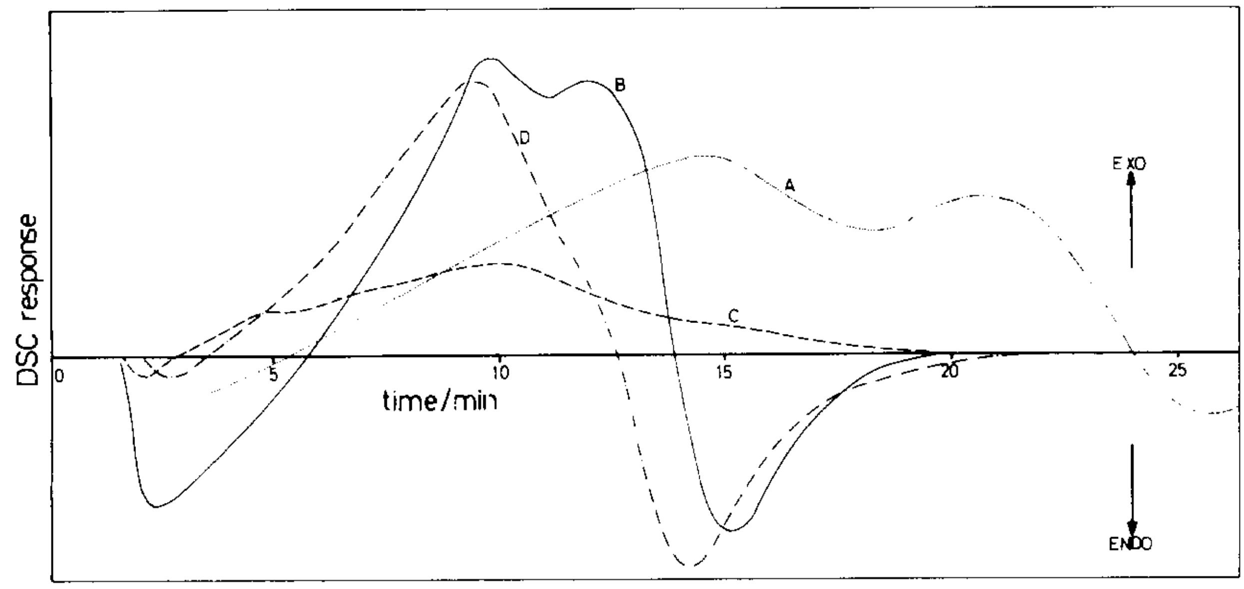

Fig. 2. Isothermal DSC scans on different samples of $KMnO_4$ at 520 K in nitrogen: (A) AR 10.52 mg; (B) recrystallised 10.15 mg; (C) AR crushed 7.50 mg; (D) recrystallised, crushed 10.13 mg.

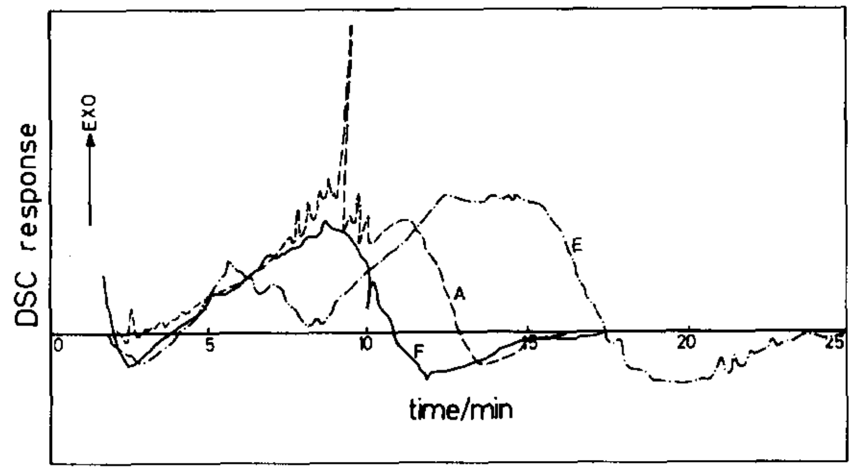

Fig. 3. Isothermal DSC scans on some further samples of $KMnO_4$ at 520 K in nitrogen: (F) powder 7.73 mg; (A) AR single crystal 5.04 mg; (E) aged sample 9.77 mg.

the decomposition in nitrogen is a complex reaction involving several overlapping stages, some of which appear to be endothermic. At this temperature the shapes of the isothermal traces do not even approximate to the symmetrical rate/time curve required by the Prout–Tompkins model [9]. In the dynamic runs (Fig. 1), there are only very small endothermic contributions and this illustrates the danger of studying complex reactions, where the mechanism of reaction may change with temperature, by nonisothermal methods. The isothermal scan on a 5 mg single crystal (Fig. 3) shows the irregular nature of the heat evolution, accompanied by erratic fragmentation of the crystal (which can be observed using hot-stage microscopy). This sort of signal would not be observed under the averaging conditions of thermogravimetry or accumulated pressure measurement.

Effect of atmosphere

When the above runs are repeated in an oxygen atmosphere, the dynamic runs (Fig. 4) are similar to Fig. 1, but the later endothermic contributions to

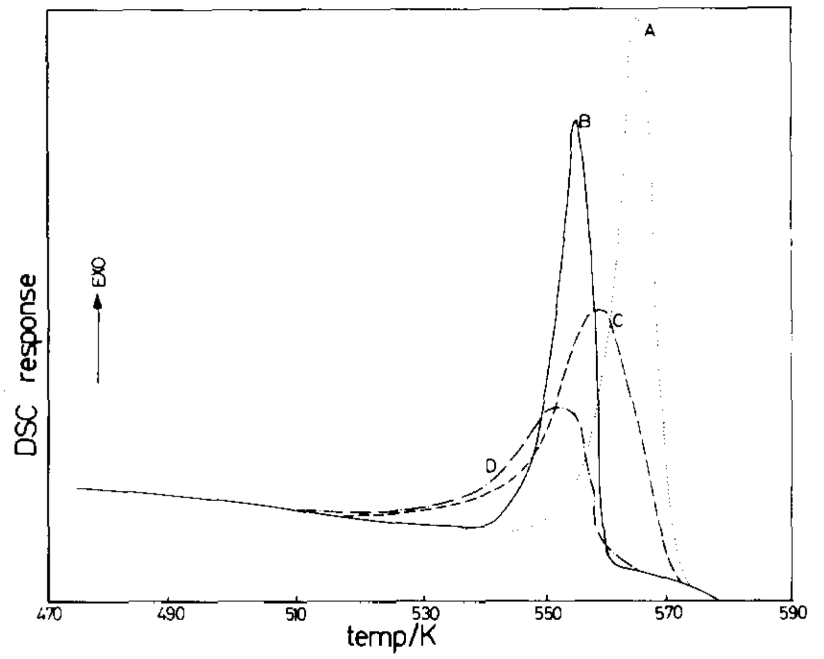

Fig. 4. Dynamic DSC scans on different samples of $KMnO_4$ at 10 K min^{-1} in oxygen: (A) AR 8.94 mg; (B) recrystallised 7.56 mg; (C) AR crushed 8.98 mg; (D) recrystallised, crushed 5.60 mg.

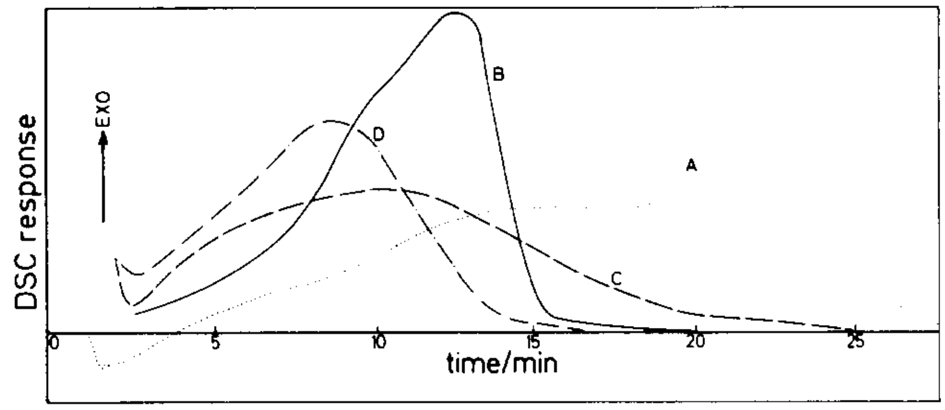

Fig. 5. Isothermal DSC runs on different samples of $KMnO_4$ at 520 K in oxygen: (A) AR 8.23 mg; (B) recrystallised 8.27 mg; (C) AR crushed 8.29 mg; (D) recrystallised, crushed 9.33 mg.

the reaction are absent in the isothermal runs (Fig. 5) and the exotherms for crushed material approach a smoother and more symmetrical shape. The overall enthalpies of decomposition in oxygen are also greater than those in nitrogen (measured from dynamic runs), see Table 1, while the average mass loss on decomposition in oxygen is slightly lower than in nitrogen.

Herbstein et al. [4] reported a value of 12.1% for the mass loss in nitrogen and $\Delta H = -10.5$ kJ mol^{-1}. Mass-loss measurements can be affected by the tendency of the product of the first stage of the decomposition to react with atmospheric CO_2 and H_2O [4].

Effect of sample mass

When increasing masses of the AnalaR sample (A) are decomposed isothermally in nitrogen (Fig. 6), the shape of the exotherm changes and the final endothermic contribution is decreased. Two effects could be operating as the sample mass increases: impedance of removal of product oxygen and/or self-heating of the sample during the exothermic reaction. Similar experiments in oxygen (Fig. 7) show a more regular increasing response with increasing sample mass.

TABLE 1

Enthalpies of decomposition of $KMnO_4$

Sample	ΔH (kJ mol^{-1}) (± 0.7 kJ mol^{-1})	
	In nitrogen	In oxygen
(A) AR	−9.9	−13.1
(B) recrystallised	−8.4	−10.1
(C) AR crushed	−9.5	−12.1
(D) recrystallised crushed	−9.2	−11.2
(F) powder		−10.3
Average mass loss	11.5 ± 0.6%	10.3 ± 1.1%

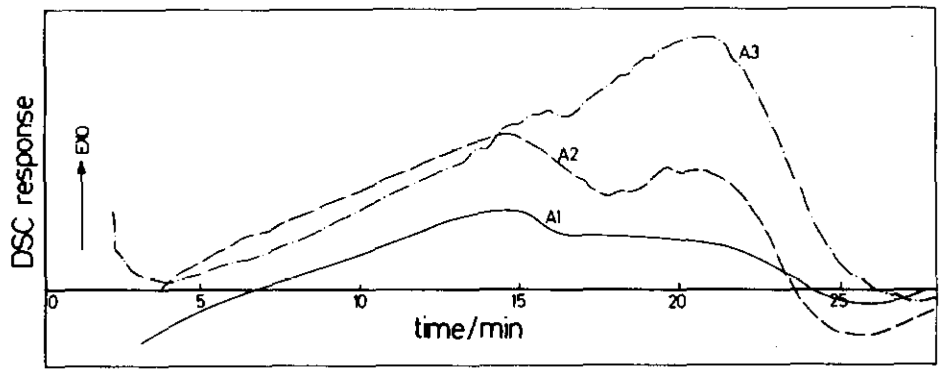

Fig. 6. Effect of sample mass on isothermal DSC runs on AR $KMnO_4$ at 520 K in nitrogen: (A1) 5.48 mg; (A2) 10.52 mg; (A3) 14.95 mg.

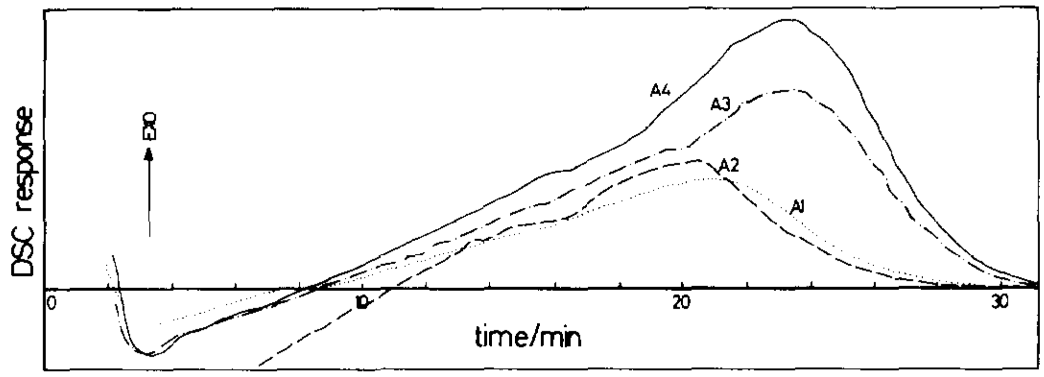

Fig. 7. Effect of sample mass on isothermal DSC runs on AR $KMnO_4$ at 520 K in oxygen: (A1) 4.26 mg; (A2) 7.27 mg; (A3) 10.27 mg; (A4) 13.77 mg.

It is possible that the initial endothermic contribution for the isothermal decomposition involves removal of water trapped during crystallisation, or decomposition of very defective sample, as these contributions are observed both in nitrogen and in oxygen.

Effect of temperature

A series of isothermal DSC runs at different temperatures (515–530 K) on $KMnO_4$, sample A (Fig. 8) and crushed $KMnO_4$, sample C (Fig. 9) in nitrogen may be compared with similar runs in oxygen (Figs. 10 and 11). The effect of crushing the sample is clearly seen as altering the shape of the complex exotherm and decreasing the time taken for the rate of decomposition to reach a maximum. The endothermic contributions, observed beyond the rate maxima in runs in nitrogen, are absent in oxygen. Complete kinetic analysis of such irregularly shaped curves is not feasible, but apparent

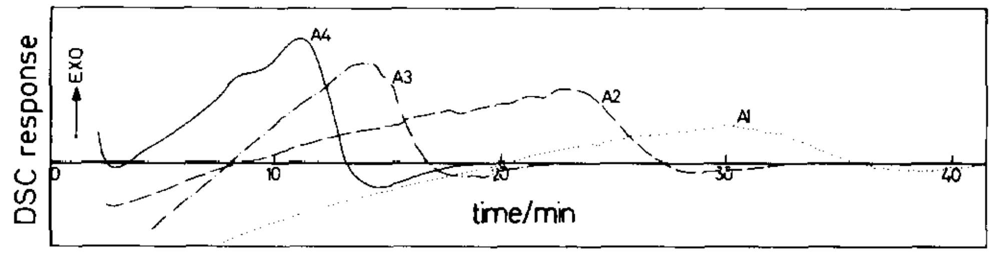

Fig. 8. Effect of temperature on isothermal DSC runs on AR $KMnO_4$ in nitrogen: (A1) 515 K, 8.17 mg; (A2) 520 K, 7.98 mg; (A3) 525 K, 7.92 mg; (A4) 530 K, 7.98 mg.

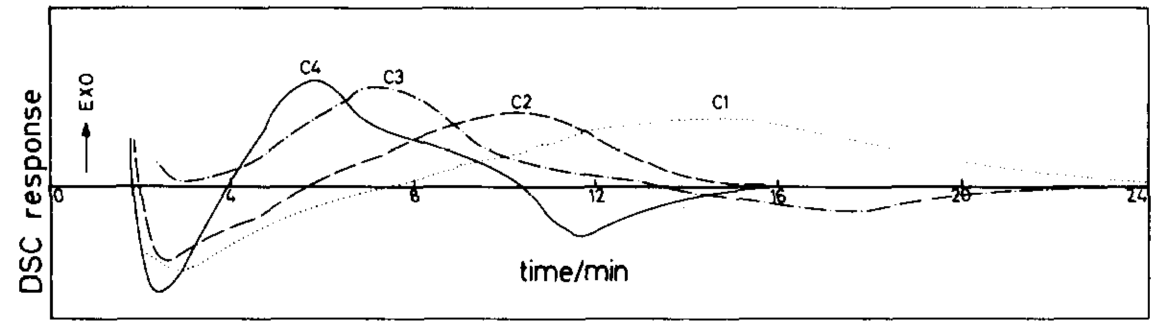

Fig. 9. Effect of temperature on isothermal DSC runs on crushed $KMn0_4$ in nitrogen: (C1) 515 K, 8.00 mg; (C2) 520 K, 8.23 mg; (C3) 525 K, 8.67 mg; (C4) 530 K, 8.47 mg.

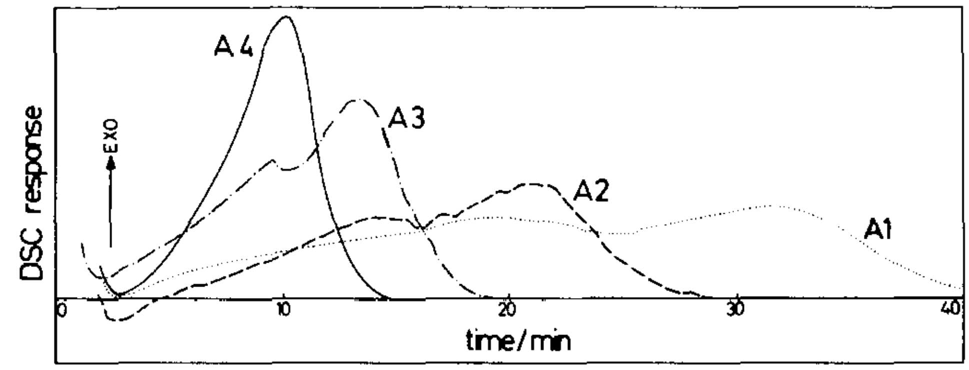

Fig. 10. Effect of temperature on isothermal DSC runs on AR $KMn0_4$ in oxygen: (A1) 515 K, 8.73 mg; (A2) 520 K, 8.48 mg; (A3) 525 K, 8.88 mg; (A4) 530 K, 8.22 mg.

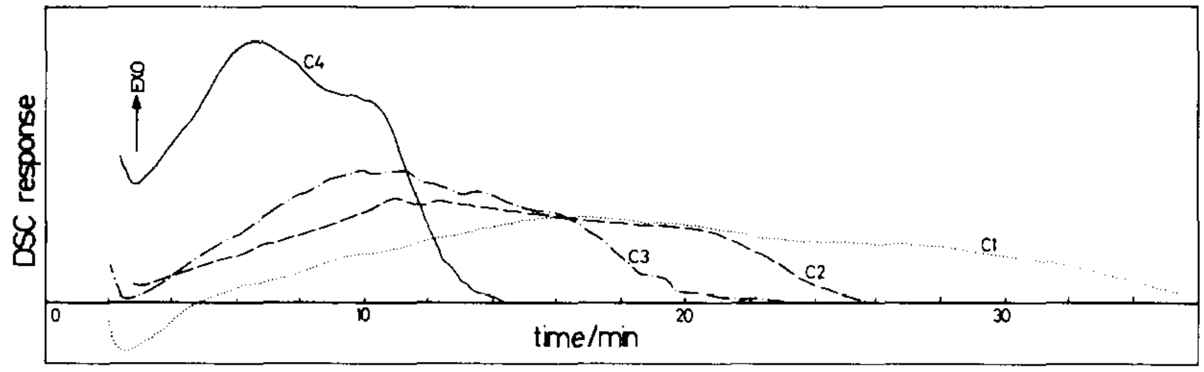

Fig. 11. Effect of temperature on isothermal DSC runs on crushed $KMn0_4$ in oxygen: (C1) 515 K, 8.31 mg; (C2) 520 K, 8.53 mg; (C3) 525 K, 8.10 mg; (C4) 530 K, 8.40 mg.

zero-order rate coefficients, based either on the reciprocals of times taken to reach maximum rates (t_{max}) or for reaction to be completed (t_{end}), or upon the actual maximum rate of heat evolution (corrected for sample mass), may be used in Arrhenius-type plots to quantify the temperature dependence of the reaction rate by quotation of "apparent activation energies". The values of activation energies have been shown not to depend too critically on the kinetic model used [8,10]. Some values, obtained by weighted least-squares analysis, are given in Table 2. The values in oxygen are generally higher than those in nitrogen, and values for crushed material are lower than for crystals. This last finding is in agreement with the results of Prout and Tompkins [6]. Their values for the decomposition of $KMn0_4$ in vacuum were: whole crystals 161–162 kJ mol^{-1} and ground crystals 144–148 kJ mol^{-1}. These are closest to the apparent activation energies in N_2 based on $1/t_{max}$.

TABLE 2

Apparent activation energies for the decomposition of $KMnO_4$ (for calculation, see text)

Sample	Atm.	Apparent activation energy (kJ mol^{-1})		
		Max. rate	$1/t_{max}$	$1/t_{end}$
AR	N_2	158 ± 35	158 ± 15	123 ± 11
Crushed	N_2	63 ± 11	141 ± 8	95 ± 20
AR	O_2	191 ± 13	172 ± 13	160 ± 7
Crushed	O_2	178 ± 37	136 ± 30	140 ± 20

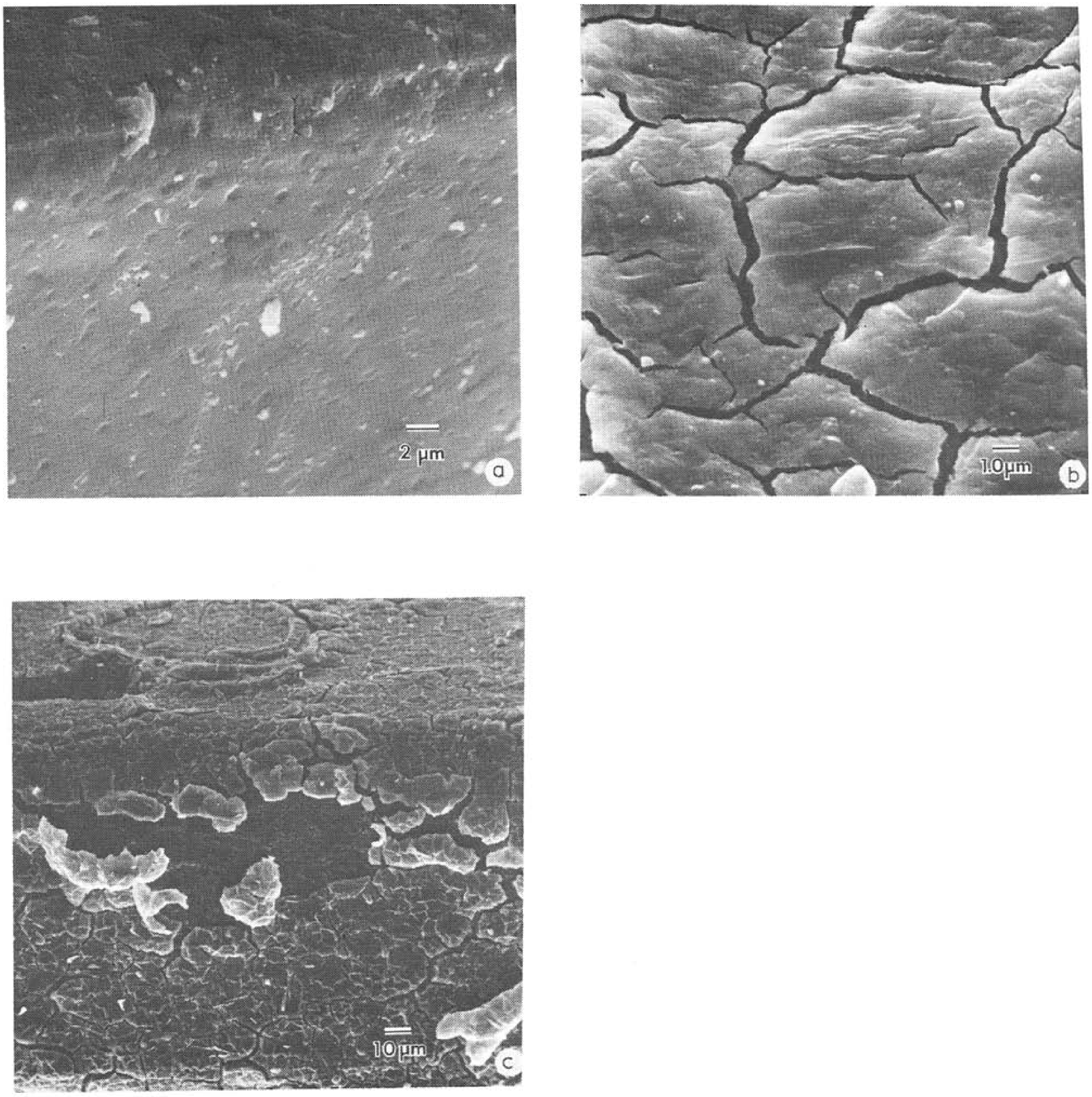

Fig. 12. Scanning electron micrographs of (a) a $KMnO_4$ crystal before decomposition; (b) a $KMnO_4$ crystal showing surface decomposition during storage; (c) a partially decomposed $KMnO_4$ crystal showing the characteristic cracking and peeling which precedes shattering.

Electron microscopy

Selected single crystals of $KMnO_4$, before and after partial decomposition, were thinly coated with gold and examined by SEM. Samples were partially decomposed on a hot-stage microscope in air, or in the DSC in N_2 or in O_2. Even before being heated, most of the crystals examined showed much irregular surface cracking (Fig. 12b). Initially smooth surfaces are obviously desirable for detecting the changes brought about by thermal decomposition. Careful recrystallisation and storage in the dark resulted in smoother surfaces (Fig. 12a). No changes in these relatively smooth surfaces were observed after prolonged exposure to the low pressures in the electron microscope, or in the electron beam at 30 kV (twice the accelerating voltage normally used), so it can be assumed that the coating process and the operating conditions of the SEM do not affect the sample surface.

Partially decomposed crystals show characteristic cracking and peeling off of layers of material (Fig. 12c). The extent of decomposition before total shattering of the crystals occurs is low, so it is unlikely that the material that peels off in the early stages is completely decomposed. No significant differences were observed for decomposition in different atmospheres. The thickness of the layers of partially decomposed material and the average size of the mosaic blocks formed, varied from sample to sample. Some areas of rounded surface suggest the possibility of some localised melting [11].

CONCLUSIONS

Isothermal DSC studies on various preparations of $KMnO_4$ have shown that the first stage of the decomposition, which has previously been assumed to be a single exothermic process, is in fact far more complex. Decomposition of some, but not all samples, starts with a small endothermic process which may arise from removal of water trapped in the crystal, or from endothermic decomposition (see below) of very defective surface material. The decomposition which follows, and which accounts for the major part of the reaction, is exothermic, but there are several overlapping exothermic processes, indicating an irregular evolution of heat. This can be associated with the irregular cracking and peeling of layers of partially decomposed material observed using SEM. The isothermal DSC trace for a single crystal (5 mg) (Fig. 3, curve A) is very irregular and shows that the traces for polycrystalline samples are averages of the individual processes.

Comparison of the isothermal traces at different temperatures in nitrogen (Fig. 8) and in oxygen (Fig. 10) shows that the major part of reaction is similar in both atmospheres, as is to be expected since O_2 is a product of the $KMnO_4$ decomposition. When conditions are such, however, that the product oxygen can be removed by the inert carrier gas, i.e., towards the end of a slow decomposition in N_2 of a small sample mass, a final endothermic contribution is observed. This endothermic process may be dissociation of a "higher" to a "lower" complex K, Mn-oxide [4]. The measured mass losses and enthalpies of decomposition both support the suggestion of a different final process which occurs when oxygen can be removed. Detection of differences in the solid products formed was not possible because of their strong affinity for water and CO_2 [4].

Examination of Fig. 10 shows that as the temperature increases, resolution of the overlapping exothermic processes decreases and the DSC curve begins to approach the symmetry associated with the sigmoid models [9], e.g., Fig. 10, curve A4. The shapes of the isothermal DSC curves also change when the material is crushed (Figs. 9 and 11) and it thus appears that conformity of the kinetics of the thermal decomposition of $KMnO_4$ to the Prout–Tompkins equation (or even to the Avrami–Erofeev equation) can be expected only when sufficient averaging of the actual processes occurring is taking place through use of small particles, relatively rapid decomposition rates or sensors with slow responses.

SEM observations support the qualitative interpretation of the Prout–Tompkins model [5,6], but identification of kinetic parameters with specific processes may not be justified [12]. The observed peeling and shattering of crystals tends to support the suggestion of Protashchik [13] that the sites of initial decomposition are within, rather than at, the surfaces of crystals.

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