Thermochimica Acta, 92 (1985) 149-152
Elsevier Science Publishers B.V., Amsterdam

ISOTHERMAL DSC STUDY OF THE THERMAL DECOMPOSITION OF POTASSIUM PERMANGANATE

Michael E. Brown*, Kathryn C. Sole and Michael W. Beck
Chemistry Department, Rhodes University, Grahamstown, 6140 South Africa

ABSTRACT

Potassium permanganate decomposes on heating in two stages. The first stage (~290 °C) is exothermic overall and the second (~620 °C) is endothermic. The Prout-Tompkins model is often used to describe the kinetics of the first stage. 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 electron micrographs reveal some details of the decomposition mechanism.

INTRODUCTION

The thermal decomposition of potassium permanganate has been studied in considerable detail [1,2 and references therein], but is still a source of controversy. Decomposition in nitrogen is in two discrete stages. The first (~290 °C) is exothermic overall (mass loss ~12%), while the second (~620 °C) is endothermic (mass loss ~3.5% of original). Isothermal kinetic studies [3,4] of the first stage in vacuum, report characteristic sigmoid curves of fractional decomposition, α, against time [1,4,5]. These curves conform to the Prout-Tompkins equation: $\ln(\alpha/(1-\alpha)) = kt + c$. Detailed mechanisms account for this autocatalytic behaviour [1,2,4] in terms of initiation of the reaction at crystal imperfections and development of strain which leads to cracking and the formation of new surfaces at which decomposition is rapid.

Conformity to the Prout-Tompkins equation is difficult to distinguish [6] from conformity to other sigmoid-curve models. Isothermal rate-time curves [7], such as the output from isothermal DSC, should give very symmetrical exotherms if the Prout-Tompkins model is obeyed.

EXPERIMENTAL

A Perkin-Elmer DSC-2 was used. Samples were crimped in aluminium pans with pierced lids. The carrier gas was N_2 or O_2 at 140 kPa. Several preparations of $KMnO_4$ 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 μm).

Proceedings of ICTA 85, Bratislava

RESULTS AND DISCUSSION

Effect of preparation and pretreatment: The decomposition of $KMnO_4$ is known to be sensitive to preparation and pretreatment Isothermal (520 K) DSC runs in nitrogen (Figs 1 and 2) show that decomposition in nitrogen is complex, involving several overlapping stages, some of which appear to be endothermic. Recrystallization sharpens while grinding broadens the exotherms. 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 [7]. The trace for a single crystal (fig. 2) shows irregular heat evolution, accompanied by erratic fragmentation of the crystal (observable 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: In oxygen the later endothermic contributions are absent (Fig. 3) and the exotherms for crushed material are smoother and more symmetrical. The average overall enthalpy of decomposition in oxygen (-11.4 ± 1.2 kJ mol^{-1}) is greater than that in nitrogen (-9.3 ± 0.6 kJ mol^{-1}), while the average mass-loss in oxygen (10.3 ± 1.1%) is slightly lower than in nitrogen (11.5 ± 0.6%).

Effect of temperature: Isothermal DSC runs (515 to 530 K) on sample A (Fig. 4) in nitrogen may be compared with similar runs in oxygen (Fig. 5). Endothermic contributions, beyond the rate maxima, are absent in oxygen. Complete kinetic analysis of such irregularly shaped curves is not feasible, but apparent zero-order rate coefficients, based either on (i) the reciprocals of times taken to reach maximum rates (t_{max}), or (ii) for reaction to be completed (t_{end}), or (iii) upon the actual maximum rate of heat evolution, give "apparent activation energies" of from 123 (iii) to 158 (i) kJ mol^{-1} in N_2 and from 160 (iii) to 191 (i) kJ mol^{-1} in O_2. Crushing the samples lowers these values. Prout and Tompkins [4] reported 162 kJ mol^{-1} for decomposition of crystals and 146 kJ mol^{-1} for ground material, in vacuum.

Electron microscopy: SEM examination of $KMnO_4$ crystals, before and after partial decomposition, showed that even before heating, most of the crystals had irregular surface cracking (Fig. 6(b)). Smooth surfaces could be obtained by careful recrystallization and storage (Fig. 6(a)). The operating conditions of the SEM did not affect the sample surface. Partially decomposed crystals show characteristic cracking and peeling off of layers of material (Fig. 6(c)) before total shattering occurs. No differences were observed for decomposition in different atmospheres. The thickness of the layers of partially decomposed material and the average size of the mozaic blocks formed, varied from sample to sample.

CONCLUSIONS

The first stage of the $KMnO_4$ decomposition has been shown to be complex. Decomposition starts with a small endotherm, which may arise from removal of water trapped in the crystal, or from endothermic decomposition of defective surface material. The major part of the decomposition consists of several overlapping and irregular exothermic processes, associated with the irregular cracking and peeling of layers of partially decomposed material, observed using SEM. Traces for polycrystalline samples are averages of the irregular processes observed for single crystals. The major part of reaction is similar in both N_2 and O_2, as is to be expected since O_2 is a product of decomposition. When product oxygen can be removed by 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 may be dissociation of a "higher" to a "lower" complex K, Mn-oxide. The measured mass-losses and enthalpies of decomposition support the suggestion of a different final process. As the temperature increases, or as the material is crushed, resolution of the overlapping exotherms decreases and the DSC curve approaches the symmetry associated with the sigmoid models. Conformity of the kinetics to the Prout-Tompkins equation can thus only be expected when sufficient averaging of the actual processes occurring is taking place. SEM observations support the qualitative interpretation of the Prout-Tompkins model [3,4].

REFERENCES

1. J.S. Booth, D. Dollimore and G.R. Heal, Thermochim. Acta, 39 (1980) 281,293
2. A.Z. Moghaddam and G.J. Rees, Fuel, 63 (1984) 653.
3. M.E. Brown, D. Dollimore and A.K. Galwey, "Reactions in the Solid State", Comprehensive Chemical Kinetics, Vol. 22, Elsevier, Amsterdam, 1980.
4. E.G. Prout and F.C. Tompkins, Trans. Faraday Soc., 40 (1944) 488.
5. K.R. Sakurai, D.A. Schaeffer and P.J. Herley, Thermochim. Acta, 26 (1978) 311.
6. M.E. Brown and A.K. Galwey, Thermochim. Acta, 29 (1979) 129.
7. M.E. Brown and A.K. Galwey, "Thermal Analysis", Proceedings of the 7th ICTA, Kingston, Canada, 1982, Wiley-Heyden, Chichester, 1982, Vol. 1, p58-64.

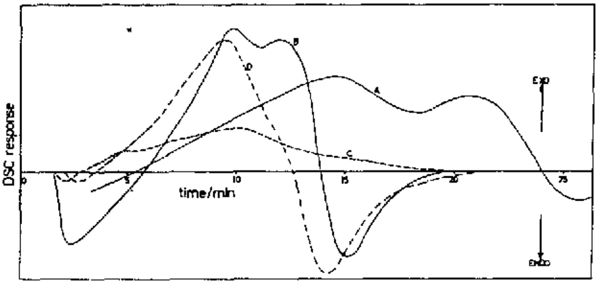

Fig. 1· Isothermal DSC scans on different samples of $KMnO_4$ at 520 K in nitrogen A. AR B. recrystallised C. AR crushed D. recryst., crushed

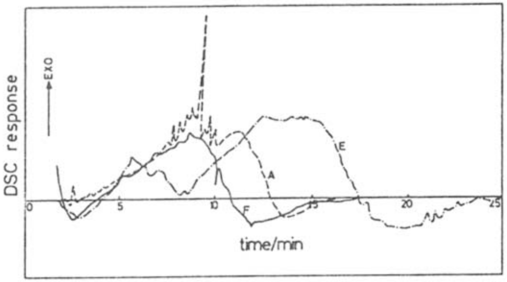

Fig. 2: Isothermal DSC scans on some further samples of $KMnO_4$ at 520 K in nitrogen A. AR single crystal E. aged sample F. powder

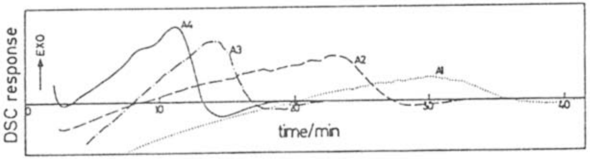

Fig. 4: Effect of temperature on isothermal DSC runs on AR $KMnO_4$ in nitrogen A1: 515 K A2: 520 K A3. 525 K A4: 530 K

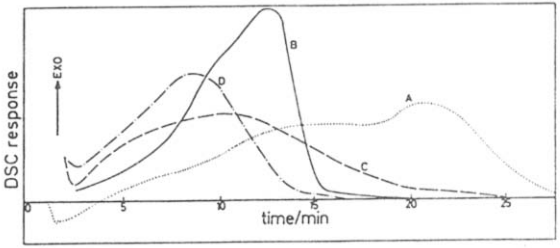

Fig. 3: Isothermal DSC scans on different samples of $KMnO_4$ at 520 K in oxygen A. AR B. recrystallised C. AR crushed D. recryst., crushed

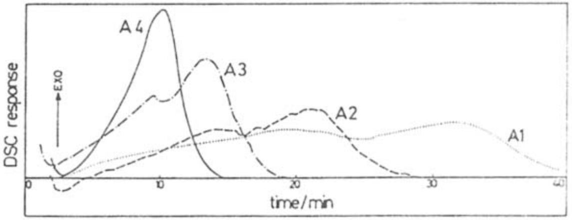

Fig. 5: Effect of temperature on isothermal DSC runs on AR $KMnO_4$ in oxygen A1: 515 K A2: 520 K A3: 525 K A4: 530 K

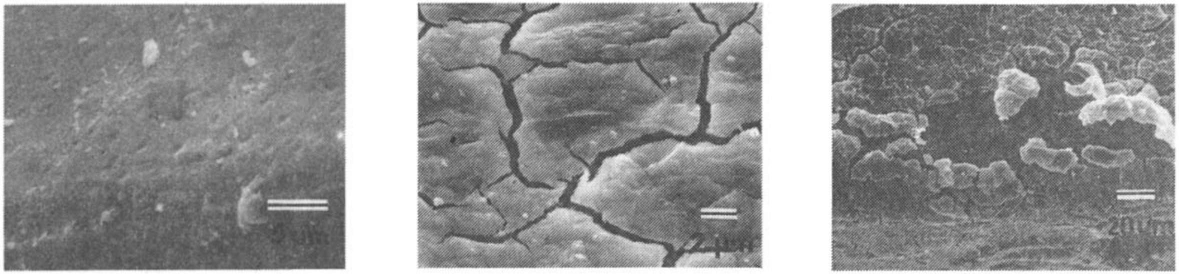

Fig. 6: (a) $KMnO_4$ crystal before decomposition (b) surface decomposition on storage (c) partially decomposed