

## A kinetic and mechanistic study of the thermal decomposition of copper(II) permanganate

Andrew K. Galwey <sup>a,\*</sup> Samir A.A. Fakiha <sup>b</sup> and K. M. Abd El-Salaam <sup>b</sup>

<sup>a</sup> *School of Chemistry, The Queen's University of Belfast, Belfast, Northern Ireland BT9 5AG, UK*

<sup>b</sup> *Chemistry Department, Umm Al-Qura University, P.O. Box 3711, Makkah Al-Mukaramah, Saudi Arabia*

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### Abstract

The thermal decomposition of copper(II) permanganate has been studied between 335 and 370 K. Isothermal yield–time curves for the evolution of product oxygen (1.27 mol O<sub>2</sub> per mol Cu(MnO<sub>4</sub>)<sub>2</sub>) were sigmoid shaped and data fitted the Avrami–Erofe'ev equation ( $n = 2$ ):  $[-\ln(1 - \alpha)]^{1/2} = kt$ , between  $0.03 < \alpha < 0.93$  (where  $\alpha$  is the fractional reaction). The activation energy for decomposition was  $115 \pm 15$  kJ mol<sup>-1</sup>.

In the mechanistic discussion presented it is concluded that anion breakdown occurred at the interface between the crystalline reactant and an ill-crystallized, probably several constituent, disorganized mixture of residual products. Permanganate anion breakdown is believed to follow electron transfer to a Cu<sup>2+</sup> ion ( $\rightarrow$ Cu<sup>+</sup>) that is subsequently reoxidized. A principal motivation for the work was as a route for the preparation of a non-stoichiometric, imperfect, microcrystalline mixture of transition metal oxides. The product of the present reaction is being investigated to determine its value as a precursor for the preparation of active heterogeneous oxidation catalysts.

### INTRODUCTION

Binary transition metal oxide phases possess chemical properties that make them potentially valuable as heterogeneous oxidation catalysts and such phases have been suggested as possible replacements for the more expensive platinum metals [1, 2]. Binary oxides can be prepared by heating powder mixtures of the appropriate constituents but severe heating conditions are usually required [3]. This is undesirable because the high temperatures cause diminution of the product area. Moreover, and probably more significantly, the annealing processes involved may destroy the specialist imperfection structures, particularly those located in the surfaces, that are the probable sites of catalytic activity. There may also be difficulties of

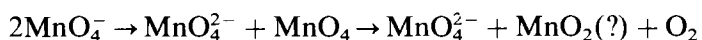
\* Corresponding author.

controlling deviations from stoichiometry; oxygen excess or deficiency may be responsible for the semiconducting properties (n or p type) of these solids.

A useful alternative approach to the preparation of two-cation oxide phases is to co-precipitate an appropriate mixture of thermally unstable salts of the required cations and calcine the solid product at a relatively low temperature. Insoluble intermediates used in this method have included carbonates and oxalates (finely powdered), hydroxides (good cation mixing may be achieved in a precipitated gel, which may initially be almost amorphous) and nitrates (where the subsequent decomposition proceeds under oxidizing conditions).

Mindful of these constraints upon the methods most usually applied, we describe here a novel and potentially valuable approach to the preparation of binary metal oxide catalysts. These phases may be alternatively prepared by the low temperature thermal decomposition of a salt containing an appropriate transition metal cation together with a thermally unstable but highly oxidized anion. The present article is concerned with the pyrolysis of  $\text{Cu}(\text{MnO}_4)_2$ ; we have reported previously [4] a similar study of  $\text{Ni}(\text{MnO}_4)_2$  decomposition. Compared with other methods available for the preparation of binary oxide phases, the temperatures required for the initial steps in anion breakdown are exceptionally low (about 370 K). Because the transition metals in the precursor compound are present in homogeneous distribution at the ionic level, no diffusive mixing is required to form the double oxide. It is also possible that the crystal structure formed under mild reaction conditions may be different from that formed by a higher temperature preparation. Certainly the surface area and imperfection structures may be expected to be greater and more numerous in materials only mildly heated. Such solids may be annealed to an acceptable stability before use. There is also the possibility that the breakdown step of the oxidized anion may result in some retention of locally oxidized species which may enhance the catalytic activity of the solid in heterogeneous reactions.

The present report focuses exclusively on the kinetics and the mechanism of the thermal decomposition of  $\text{Cu}(\text{MnO}_4)_2$  and further work in prospect will be concerned with characterizing the catalytic properties of the solid reaction products. While there have been many studies of the decompositions of permanganates that contain strongly electropositive cations [3], including Li, Na, K [5], Rb [6], Cs [7] and Ba, there have been fewer concerned with transition metal permanganates except for silver [3] and recent studies of the nickel salt [4, 8]. The thermal reactions of  $\text{KMnO}_4$  [5], which is much more stable than the present salt, are probably the most intensively studied of the permanganates [3]. This reaction is identified [5] as a nucleation and growth process in which the rate limiting step is probably electron transfer within the anionic sub-lattice

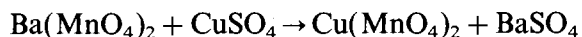


The constituent phases of the residue have not yet been satisfactorily characterized. The possibility that such materials may possess catalytic activity is an important motive for undertaking the present study.

## EXPERIMENTAL

### *Reactant preparation*

Copper(II) permanganate was prepared as suggested by Baran and Aymonino [9]. Almost saturated aqueous solutions containing barium permanganate and copper(II) sulphate in 2:1 molar ratio were slowly mixed together at ambient temperature



The barium sulphate precipitate was removed by filtration. The solvent was partially evaporated at 290 K and the crystals obtained by filtration were salt **1**. A second identical preparation that resulted in the evaporation of a higher portion (but not all) of the water yielded salt **2**. During the again identical preparation of salt **3** the water was evaporated at about 330 K. Each dried reactant was stored in a dark bottle before kinetic studies.

The water of crystallization retained in all three salts was significantly less than the hexahydrate expected [9]. This is considered to be unimportant here because the present work was concerned with the thermal decomposition of the anion only. Most, if not all, of the constituent water was lost from the reactant samples during preparative drying, preliminary evacuation and subsequent heating to reaction temperature. Similar behaviour was reported for nickel permanganate [4]. Electron microprobe analyses of the reactant salts and representative samples of the residues from completed decompositions confirmed the expected reactant compositions: the mean elemental ratio Cu:Mn was  $1.00:1.97 \pm 0.10$ .

### *Kinetic measurements*

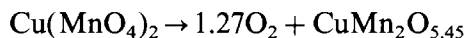
All kinetic studies were completed in a conventional glass vacuum apparatus in which the extent of salt decomposition was measured from the evolved pressure of non-condensable (at 78 K, a liquid N<sub>2</sub> trap was maintained) product oxygen. Each reactant sample (20–40 mg, weighed  $\pm 0.2$  mg) was evacuated for 1 h before being admitted to the constant temperature ( $\pm 0.7$  K) heated zone. Gas pressures were measured at prespecified time intervals, by a Baratron MKS 222B gauge (0–10 Torr, read with an accuracy of  $\pm 0.001$  Torr) and data (pressure, time, temperature) values were stored in the memory of the controlling computer. Values of  $\alpha$ , the fractional reaction ( $\alpha = p/p_f$ ), were calculated for each measured pressure ( $p$ ) reading and the pressure corresponding to the completed reaction  $p_f$ . Values

of functions ( $f(\alpha)$ ) applicable to appropriate rate expressions ( $f(\alpha) = kt$ ) used for the kinetic analyses of solid-state reactions [3] were also calculated. Results could be obtained in the form of tabulated data or as graphs suitable for the identification of the rate equation most satisfactorily fitting the measured  $\alpha$ -time values. All experiments were isothermal. Rate studies were also completed in the absence of the 78 K cold trap for decompositions proceeding in a small water vapour pressure [4]. The apparatus and experimental methods have been described in a previous article [10].

## RESULTS AND DISCUSSION

### *Reaction stoichiometry*

The present work was exclusively concerned with the first step in anion breakdown, for which the kinetic studies were completed between 335 and 370 K. Measurements of product pressures corresponding to initial evolution of water from reactants after evacuation gave yields that corresponded to  $\text{Cu}(\text{MnO}_4)_2 \cdot 1.7\text{--}4.1\text{H}_2\text{O}$ . This is ascribed to vacuum dehydration of the expected hexahydrate [9]. Yields of product gases not condensed at 78 K corresponded to  $1.27 \pm 0.05$  mol  $\text{O}_2$  per mol  $\text{Cu}(\text{MnO}_4)_2$ , after due allowance for the constituent water. The stoichiometry of the reaction studied can, therefore, be represented as



The oxygen yield is somewhat less than that ( $1.54\text{O}_2$ ) measured for the decomposition of  $\text{Ni}(\text{MnO}_4)_2$  [4].

### *Reaction kinetics*

The kinetic study of the isothermal decomposition of  $\text{Cu}(\text{MnO}_4)_2$  was completed between 335 and 370 K. Representative  $\alpha$ -time plots are shown in Fig. 1 which are sigmoidal and, in this respect, resemble the reactions of other metal permanganates [3]. The dominant feature of the present behaviour is the constant reaction rate during the median region, approximately  $0.2 < \alpha < 0.8$ . Acceleratory and deceleratory behaviour was not prominent, contrasting with the extended acceleratory characters of the decompositions of  $\text{RbMnO}_4$  [6] and  $\text{CsMnO}_4$  [7]. Induction periods to reaction were short. The most satisfactory representation of the rate data was by the Avrami–Erofe'ev equation ( $n = 2$ )

$$[-\ln(1 - \alpha)]^{1/2} = kt \quad (1)$$

Figure 2 shows eqn. (1) plots using the results in Fig. 1. A single rate constant was applicable during the greater part of this reaction, and the linear fit usually extended between  $0.03 < \alpha < 0.93$ . In a small number of

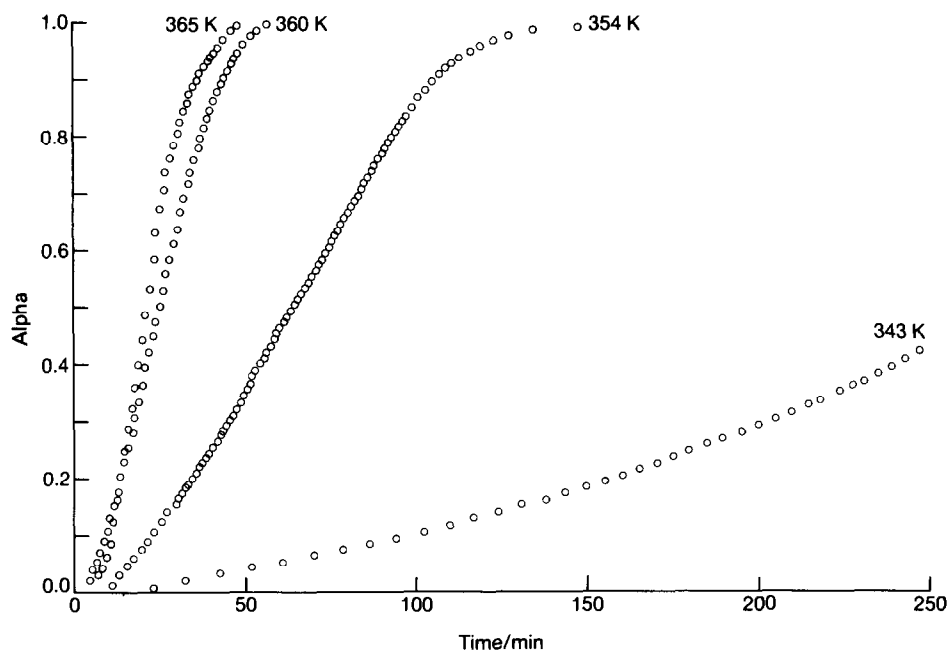


Fig. 1. Isothermal  $\alpha$ -time plots for the thermal decompositions of copper(II) permanganate (salt 3) at 343, 354, 360 and 365 K. Curves showed sigmoid shape but the acceleratory and deceleratory regions were not pronounced; the dominant feature was the median period of constant reaction rate. Induction periods were short.

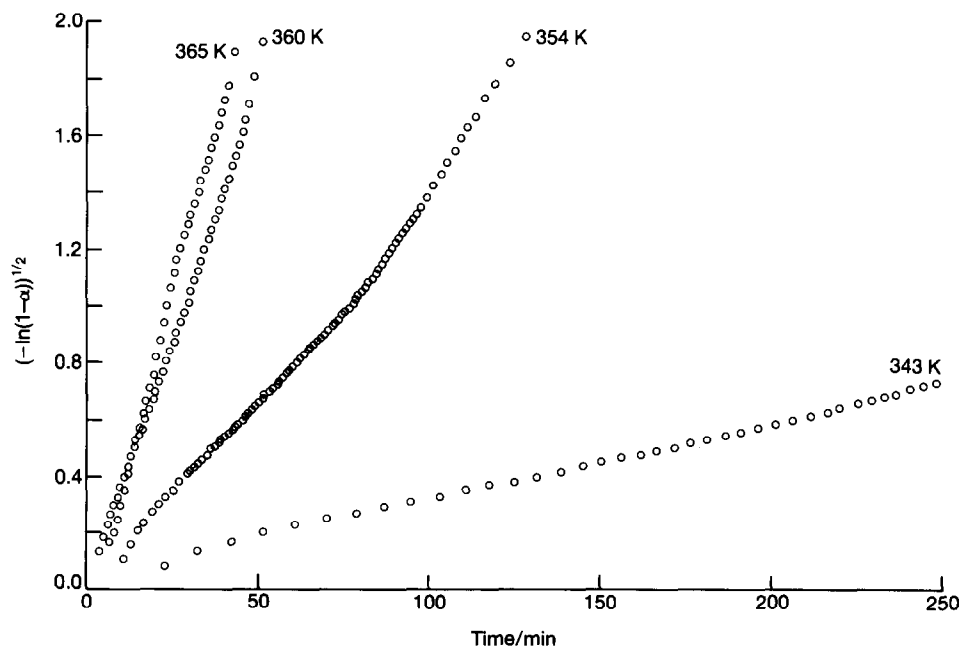


Fig. 2. Plots of  $[-\ln(1-\alpha)]^{1/2}$  against time for the same experiments as shown in Fig. 1, showing the fit of data to eqn. (1).

experiments there was a slight, but perceptible, deviation from linearity when the rate became relatively slower in the range  $\alpha \approx 0.6$ – $0.7$  (see 354 K plot in Fig. 2). However, later this deviation was compensated and the rate again obeyed eqn. (1).

Using the Avrami–Erofe'ev ( $n = 2$ ) eqn. (1) rate constants, the calculated activation energy for this reaction was  $115 \pm 15 \text{ kJ mol}^{-1}$ . There was some scatter of points on the Arrhenius plot, resulting in the relatively large uncertainty value. The thirty rate constants measured (ten for each of the three preparations studied) were close to the same mean line. Satisfactory reproducibility was obtained for the three different preparations. Sixteen of these rate constants were measured for the evolution of oxygen only (using a 78 K trap). These values were not detectably different from the fourteen reactions in which no cold trap was maintained and reaction proceeded in small pressures of water vapour.

This pattern of kinetic results resembles that reported for the nickel salt in that the same rate eqn. (1) was obeyed but, for the present reactant, a single rate constant was applicable throughout (almost) the whole reaction. Unlike  $\text{Ni}(\text{MnO}_4)_2$ , however, the kinetic characteristics of the copper salt were not appreciably influenced by the presence of water vapour. The copper salt was the less stable; direct comparisons of reaction rates showed that decomposition proceeded at comparable rates some 25–30 K below those for the nickel salt. Our kinetic investigations, representing measurements concerned with similar ranges of reaction rates, were completed between  $\text{Cu}(\text{MnO}_4)_2$ , 335 to 370 K ( $115 \pm 15 \text{ kJ mol}^{-1}$ ), and  $\text{Ni}(\text{MnO}_4)_2$ , 356 to 400 K ( $100 \pm 5 \text{ kJ mol}^{-1}$ ) (activation energies shown in brackets).

### *Reaction mechanism*

The observed obedience of  $\text{Cu}(\text{MnO}_4)_2$  decomposition to the Avrami–Erofe'ev eqn. (1) resembles the behaviour of other solid permanganates, including those of the alkali metals [3, 5–7], silver [3] and nickel [4]. This is evidence that suggests a nucleation and growth mechanism. Attempts to confirm this by observations using the scanning electron microscope were unsuccessful. No progressive changes in texture with increasing  $\alpha$  values could be found. The irregularities and diversities of features examined could not be distinguished or characterized as reactant or as product and comparisons between samples could not be related to extents of chemical change. There was evidence that the reactant was unstable in the electron beam.

The chemistry of the oxides of manganese is complicated [11]; these phases may be non-stoichiometric and for some compositions different crystallographic structures exist. The phases present depend also on the other cations that are present [12]. The decomposition products of  $\text{KMnO}_4$  [5] (the system most completely characterized) have not as yet been identified in detail. The compositions of the components present in the residue

from the present reaction have not been determined but, from the overall composition  $\text{CuMn}_2\text{O}_{5.45}$ , we conclude that this contains manganese in more than one oxidation state ( $?\text{CuMnO}_4$  (manganate is often a product of permanganate breakdown) +  $?\text{Mn}_2\text{O}_3$ ). Clearly the present reaction temperatures (less than 380 K) are well below the range required for crystallization of manganese oxides [11]. We conclude, therefore, that the residue is an assemblage containing at least two (probably more) phases that include materials that are non-stoichiometric, microcrystalline, poorly crystalline or possibly even amorphous and with high surface area. The role of this ill-defined material in salt breakdown will be discussed below. These composite phases, however, exhibit many of the features that are regarded as desirable in heterogeneous catalysts. These contain high concentrations of defects and imperfections in high area mixtures of transition metal oxides. Accordingly, this material is being investigated as a potentially versatile precursor for the preparation of active heterogeneous oxidation catalysts.

The reaction interface [3], the active zone of chemical change that advances into the undecomposed salt during reaction, is envisaged as the contact between crystalline  $\text{Cu}(\text{MnO}_4)_2$  and the ill-defined, several phase, product assemblage. Electron transfer has been identified [3] as an essential step in  $\text{MnO}_4^-$  anion breakdown. This may occur at the boundary of the reactant crystal by transfer to the cation constituents ( $\text{Cu}^{2+}$ ,  $(?)\text{Mn}^{3+}$ ) of the product with which it is in direct contact. Following breakdown of the  $\text{MnO}_4$  radical, with subsequent oxygen release, the manganese oxide will be accommodated into a residual phase. The  $\text{Cu}^{2+}$  ion is a possible electron acceptor. Under reducing conditions copper(I) intermediates have been identified [10] in decomposition of copper(II) carboxylates. Here rapid reoxidation ( $\text{Cu}^+ \rightarrow \text{Cu}^{2+}$ ) can be expected.

The relatively facile reaction of  $\text{Cu}(\text{MnO}_4)_2$  occurs at temperatures more than 100 K below the ranges for decompositions of alkali permanganates [3, 5–7]. This could be a consequence of the less electropositive cation, for a rate process in which electron transfer controls reaction rate. We believe that here copper reduction occurs before breakdown of the  $\text{MnO}_4$  from which the electron was received. Decomposition of the comparable, but slightly less reactive, nickel salt could similarly proceed through cation reduction, if it is accepted that permanganate is a sufficiently strong oxidizing agent to result in the transitory formation of  $\text{Ni}^{3+}$  ions. This may then receive an electron from a reactant  $\text{MnO}_4^-$  ion.

We conclude, therefore, that  $\text{Cu}(\text{MnO}_4)_2$  decomposition proceeds in the vicinity of an interface composed of a contact between crystalline reactant and poorly crystallized product. Electron transfer, possibly accompanied by transitory reduction of the copper is followed by permanganate anion breakdown and oxygen release. The disorganized and non-stoichiometric product is regarded as a potentially valuable precursor for the preparation of active heterogeneous oxidation catalysts. Future studies will investigate this possibility.

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