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THE CATALYTIC EFFECT OF ADDITIONS ON THE RATE OF THERMAL DECOMPOSITION OF PERMANGANATES

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ABSTRACT

The catalytic effect of additions on the rate of thermal decomposition of potassium permanganate ($KMnO_4$) were investigated using TG in an atmosphere of air. The additives used were potassium manganate (K_2MnO_4), potassium hypomanganate (K_3MnO_4), the phase "$K_4Mn_7O_{16}$", manganese dioxide (MnO_2), zinc oxide (ZnO) and cuprous oxide (Cu_2O).

The crystals of $KMnO_4$ were found to produce an S-type α—t plot, capable of analysis using a Prout and Tompkins type equation, with an initial acceleratory period being replaced by a deceleratory period over half of the decomposition.

The addition of MnO_2 to the system is simply to eliminate the acceleration period and produce a process whereby the rate is deceleratory throughout. The phase "$K_4Mn_7O_{16}$" had a similar effect. The manganate and manganate—permanganate compounds are clearly demonstrated to have a negative catalytic effect upon the acceleratory period.

The introduction of a solid phase oxide to the system was to decrease the effect of the initial slow acceleratory reaction with an increase in the overall importance of the deceleratory process. These oxides do not eliminate the initial slow acceleratory periods, but all produce their catalytic effect on the deceleratory rate process.

An additional study regarded the effect of UV light on the decomposition of $AgMnO_4$ and $KMnO_4$. The Prout and Tompkins and Avrami—Erofeev equations were applied to the $AgMnO_4$ α—t data. The change in the values of the rate constants were observed to be fractionally increased in the decay region. However, the difference in the rate constants seemed to be insufficient to suggest that the UV had any effect on the kinetics. In the case of $KMnO_4$, however, irradiation with UV almost doubled the rate.

At 110°C photodecomposition proceeds by successive absorption of two photons by a permanganate ion followed by thermal ionization. Above 200°C there is appreciable ionization of MnO_4^- in the absence of UV, however, when UV is incident some MnO_4^- ions are optically excited, resulting in an internal electronic transition promoting an electron to a level below that of the conduction band. From this level it is promoted thermally into the conduction band.

INTRODUCTION

The thermal decomposition of potassium permanganate ($KMnO_4$) occurs at a noticeable rate at 200°C. The schematic equation

$$2\ KMnO_4 \rightarrow K_2MnO_4 + MnO_2 + O_2$$

is used by most authors to describe the reaction. This indicates that the thermal decomposition of permanganate is redox in nature.

It was observations of the process of decomposition of $KMnO_4$ that led to the discovery of topochemical autocatalysis [1]. The spontaneous disintegration of the salt, the starting material in this reaction, led to the first attempts at explaining autocatalytic maxima [2], which are characteristic of topochemistry. It was also in the study of this same reaction that the concept of the role of spontaneous heating in topochemical reactions was first formulated — a concept used in the explanation of the phenomena of inverse catalysis [3].

The fundamental cause of spontaneous acceleration in the break-down of permanganate is the catalytic action of their decomposition products. Kinetic equations derived on the theory of the reaction being localised on the boundary surfaces between the reaction products and the remaining undecomposed part of the crystals were apparantly in good agreement with experimental findings [4]. Observations on the kinetics of $KMnO_4$ decomposition have been reported in various studies [2,5—13].

The great advantage of permanganate as a material for topochemical research is the possibility of a comparative study, at moderate temperatures, of the decomposition kinetics of a series of related compounds having an unstable anion in common, but differing one from another in the nature and size of the cation [3], which does not directly participate in the reaction.

It has been shown elsewhere that the decomposition of permanganate may be represented as a break-down of the MnO_4^- anion with formation of free gaseous oxygen and simultaneous reduction of heptavalent manganese to the tetravalent state [7]. Here a cation with a single or double charge, while remaining unaltered, may act as a special kind of catalyst. This brings to light interesting possibilities of research on elementary catalytic effects exerted by individual atoms in the crystal lattice or, of more interest here, the catalytic influence of foreign solid substances on the permanganate decomposition reaction.

Much disagreement has resulted in the past regarding whether manganese dioxide (MnO_2) had any catalytic effects on the decomposition reaction [1,3,8]. At that time the final products of the reaction were uncertain, but all authors agreed that MnO_2 was one of them.

In 1928 Roginsky and Schultz [3] showed that not only MnO_2, but the addition of some oxides, as for example NiO and Cu_2O, accelerate the process of chemical decomposition of $KMnO_4$. This was confirmed by Moles and Crespi [1]. However, Hinshelwood and Bowen [2] believed that MnO_2 was ineffective.

Measurement of the electron work function of the permanganate and that of the additives, under conditions close to those where the process of thermal decomposition takes place, has shown that the additives accelerating the decomposition have greater work functions compared with permanganate (e.g., at 180°C for $KMnO_4$ 4.7—4.9 eV). It has been found that the value is less for manganate.

In accordance with this and the thermal decomposition scheme of Boldyrev [13], MnO_2 should be an acceptor of electrons and hence catalyse the reaction, whereas manganate should act as a donor of electrons and thus inhibit the thermal decomposition [14].

Boldyrev [13] has shown that the actual addition of MnO_2 accelerates the decomposition of $KMnO_4$, but additions of K_2MnO_4 retard it. However, as to the catalytic effect of MnO_2 on the rate of thermal decomposition, various publications contain contradictory data. Thus Simchen [15] did not detect any catalytic effect of MnO_2. Boldyrev [16], however, indicated that the dioxide does influence the decomposition, but also stated that the effectiveness of the influence of the additive relates to its prehistory and preparation.

Boldyrev [16] extended his studies to investigating the nature of the effect of manganate (K_2MnO_4) and manganate-permanganate (K_3MnO_4) on the thermal decomposition of $KMnO_4$ and then tried to further explain the autocatalytic phenomena in terms of the electronic action of these compounds.

In this study we investigate the effect of various additives on the potassium permanganates and then note the influence the additives have on the thermal decomposition. The results are then explained in terms of a modification to Boldyrev's published mechanism for this type of reaction.

EXPERIMENTAL

Materials

The AnalaR grade potassium permanganate used was supplied by a proprietory chemical manufacturer.

Preparation of samples

The potassium permanganate ($KMnO_4$) samples were recrystallised several times to ensure purity. The recrystallisation procedure was as follows. AnalaR $KMnO_4$ (12.0 g) was dissolved in dust-free distilled water (100 cm^3, 60°C) and then rapidly filtered through glass wool (to remove any manganese dioxide). The filtrate was placed in an enclosure at 25°C for 6 h in the dark. The supernatent liquid was decanted, the crystals rapidly dried, and then ground in an agate mortar.

Potassium manganate was prepared by the action of strong boiling caustic alkali solution (KOH) on AnalaR potassium permanganate solid in the presence of small amounts of potassium nitrate according to the method described in the literature [17]. The product was filtered from the supernatent liquor after evaporating the volume to half its initial value. The colour of the resulting solid was dark green. Water was added to the solid (25 cm^3), the mixture cooled in ice and potassium manganate (K_2MnO_4) was filtered by suction in a sintered-glass funnel and dried over phosphorus pentoxide (P_2O_5) in a dessicator.

Preparations were isolated from the products of the thermal decomposition of ground $KMnO_4$ (AnalaR) and K_2MnO_4. In all these cases the decomposition was performed on a Stanton—Redcroft TR1 thermobalance. Details of the isolation procedure may be found in Herbstein et al. [11].

Initially, $KMnO_4$ samples were heated to 25°C in an atmosphere of air, hence the decomposition product would comprise of K_2MnO_4 and the phase given the "non-committal label" [11,12] "$K_4Mn_7O_{16}$". The decomposed sample consists of soluble and insoluble portions. For the isolation of the insoluble portion, the product (ca. 1 g) was stirred for 1 h at 25°C with 20% KOH (50 cm^3). After being filtered off, the insoluble portion was treated again in a similar manner. This portion was then dried and stored in a dessicator over P_2O_5. The insoluble portion was assumed to be related to the "$K_4Mn_7O_{16}$" phase, i.e. 2.35 K_2O, 7.35 $MnO_{2.05}$ [11,12].

Further $KMnO_4$ samples were decomposed in air, but the temperature was increased to 600°C. The product was separated into the soluble and insoluble portions by treatment with 45% KOH at —10°C. The resulting solution was deep blue in colour, indicating the presence of MnO_4^{3-} ions, while the insoluble residue was a blue-black powder, similar to that obtained before as regards appearance but not necessarily identical in nature.

The above isolation procedure was performed on the products of the decomposition of K_2MnO_4 (600°C in air). The insoluble portion was assumed to have the composition suggested by Herbstein et al. [11,12].

Potassium manganate-permanganate (K_3MnO_4) was prepared by co-precipitation of permanganate and manganate from caustic alkaline solution (45%, KOH at —10°C). The resulting solution was deep blue in colour, indicating the presence of MnO_4^{3-}, and the solid formed was filtered using a sintered-glass crucible, and dried in a dessicator. All samples prepared by the above methods were stored under conditions eliminating the possibility of their decomposition under the influence of heat and light.

Manganese dioxide (commercial reagent, mesh size 10—18) was used as an additive both in the state "as received" or after being powdered in an agate mortar. Zinc oxide and cuprous oxide were used as additives in the form of fine powders which were then mechanically mixed with ground $KMnO_4$ crystals.

These chemicals, as most of the others mentioned here, were the purest form sold by the manufacturers.

Measurement of surface areas of samples and catalytic additives

A very quick single point method was employed. The method used was of an empirical nature using a similar apparatus to that described by Klyachko-Gurvich [18]. The apparatus has also been described by Dollimore et al. [19].

Thermogravimetric techniques

Ground crystals of AnalaR $KMnO_4$ were decomposed on a Stanton—Redcroft TG-750 thermobalance (10 mg samples and surface area ca. 0.4 $m^2\ g^{-1}$). The temperature range at which the instrument was capable of accurately monitoring the weight change (while the reaction was sufficiently fast enough to go to completion within 1 h) was found to be 220—245°C.

Mechanical mixtures of powdered $KMnO_4$ (90% by weight, surface area ca. 0.4 m^2 g^{-1}) and powdered MnO_2 (10% by weight, surface area ca. 100 m^2 g^{-1}), powdered $KMnO_4$ and MnO_2 (10% by weight, mesh size 10—18), powdered $KMnO_4$ and K_2MnO_4, powdered $KMnO_4$ and K_3MnO_4, powdered $KMnO_4$ and "$K_4Mn_7O_{16}$" phases (isolated from $KMnO_4$ and K_2MnO_4 decomposition products) and finally powdered $KMnO_4$ and MnO_2 (obtained by decomposing $Mn(NO_3)_2$ at 170°C) were also subjected to a similar series of isothermal and TG experiments. The zinc and cuprous oxide additives (10% by weight) were also mechanically ground with powdered $KMnO_4$ (90% by weight) and subjected to isothermal study at two different temperatures.

RESULTS AND DISCUSSION

The isothermal heating (200°C) results found from this investigation of the addition of catalytic additives to $KMnO_4$ (ground) are shown in Fig. 1. Figure 1A shows the plot of α vs. t found when a study was made of the decomposition of a mechanically mixed mixture of powdered $KMnO_4$ (90% by weight, surface area ca. 0.4 m^2 g^{-1}) and powdered MnO_2 (10% by weight, surface area 100 m^2 g^{-1}). Figure 1B resulted from a similar study but mesh size 10—18 MnO_2 (10% by weight) was used. Figure 1C shows the plot found when the MnO_2 was replaced by the soluble portion of the product of $KMnO_4$ thermal decomposition and Fig. 1D that for AnalaR ground $KMnO_4$ crystals (0.4 m^2 g^{-1}) was decomposed at the same temperature but with no additive.

Mechanical mixtures of ground AnalaR potassium permanganate and potassium manganate (prepared as described earlier) showed the same effect

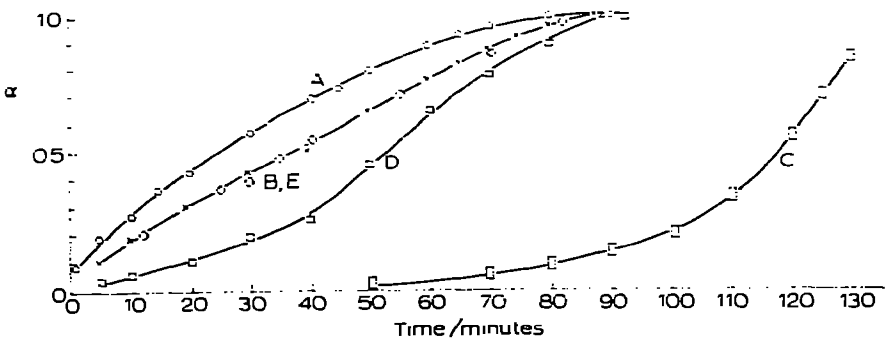

Fig. 1. α—t plots showing the catalytic effect of additives on the decomposition of $KMnO_4$ at 220°C. A, Powdered $KMnO_4$ crystals + 10% MnO_2 powder; B, powdered $KMnO_4$ crystals + 10% MnO_2 (mesh size 10—18); C, powdered $KMnO_4$ crystals + 10% of the "soluble portion" of the decomposition product of $KMnO_4$ thermal decomposition (up to 900°C); D, powdered $KMnO_4$ crystals only; E, as C with the exception that "insoluble portion" used.

on the rate of decomposition as that for the soluble portion of the product of the $KMnO_4$ thermal decomposition (see Fig. 1C). The final products of the thermal decomposition of $KMnO_4$ have been discussed earlier [27] and are thought to be K_3MnO_4 and a phase considered as "$K_4Mn_7O_{16}$". Earlier in this present study it was mentioned that the products found after the decomposition of $KMnO_4$ could be separated into soluble and insoluble fractions using KOH under certain conditions. The insoluble fraction was a bluish-black powder and the caustic filtrate was dried and both samples used as catalyst additives.

These additives were mechanically mixed with the ground $KMnO_4$ samples as described above. The results found in the case of the solid obtained from the caustic filtrate produced the α—t plot already mentioned (see Figure 1C). The bluish-black powder produced similar results to Fig. 1B (i.e. shown in Fig. 1E).

It is seen from Fig. 1 that the crystals of $KMnO_4$ (curve D) produced an S-type α—t plot, capable of analysis using a Prout and Tompkins type equation, with an initial acceleratory period being replaced by a deceleratory period over half of the decomposition. The addition of MnO_2 to the initial system is simply to eliminate the acceleration period of decomposition and produce a process whereby the rate is deceleratory throughout (curves A and B). It should be noted that the insoluble produced portion, which would seem to be the "$K_4Mn_7O_{16}$" phase, has a similar effect (curve E). The soluble portion of the decomposition process is clearly demonstrated to have a negative catalytic effect upon the acceleratory portion of the decomposition process. These soluble fractions of the decomposition process are actually the manganate and manganate-permanganate compounds.

The positive catalytic effect of the MnO_2 phase is clearly seen as an elimination of the initial slow acceleratory mechanism and its replacement by a deceleratory process. The Arrhenius parameters for the decomposition of potassium permanganate has been discussed in other studies [6,8,20--27]. Here the objective is simply limited to an indication that a change of kinetic mechanism is clearly involved.

Figures 2 and 3 show the effects that some metal oxides have on the ther-

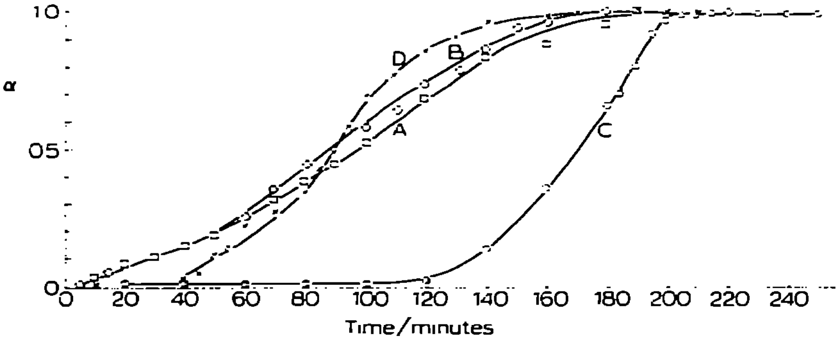

Fig. 2. α—t plots for $KMnO_4$ decomposed at 215°C. A, $KMnO_4$ (ground crystals) + 10% Cu_2O; B, $KMnO_4$ (ground crystals) + 10% ZnO; C, $KMnO_4$ (whole crystals 0.5 × 1.0 mm); D, $KMnO_4$ (ground crystals).

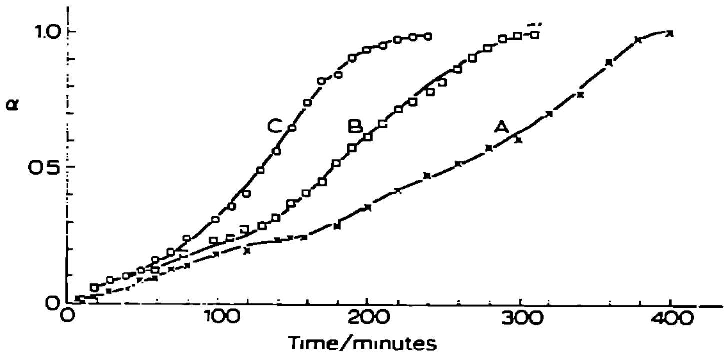

Fig. 3. α—*t* plots for the decomposition of $KMnO_4$ in the presence of additives at 200°C. A, $KMnO_4$ ground crystals; B, $KMnO_4$ ground crystals + 10% Cu_2O; C, $KMnO_4$ ground crystals + 10% ZnO.

mal decomposition of $KMnO_4$ at two different temperatures. Zinc oxide was chosen since it is a typical n-type semiconductor and cuprous oxide since it is p-type. It is evident from Figs. 2A, B and 3B and C that the oxides show catalytic properties regarding the decomposition; however, at higher temperatures the effect of both metal oxides is smaller.

Here again the introduction of a solid phase oxide to the system is to decrease the effect of initial slow acceleratory reaction with an increase in the overall importance of the deceleratory process. However, it must be observed that the same kind of effect may be achieved by grinding the $KMnO_4$ crystals (see Fig. 3). In Fig. 4 the comparison is made using ground $KMnO_4$ crystals in each run and the catalytic effect of the solid oxide phases is clearly seen. It must be noted that these oxides do not eliminate the initial slow acceleratory period as does MnO_2, and that it still describes the initial decomposition process up to about $\alpha = 0.3$. An important observation is, therefore, that these oxide additives (Cu_2O, ZnO, MnO_2 phases) all produce their catalytic effect on the deceleratory rate process.

An additional experiment using $AgMnO_4$ crystals (0.5 × 4.0 mm) was

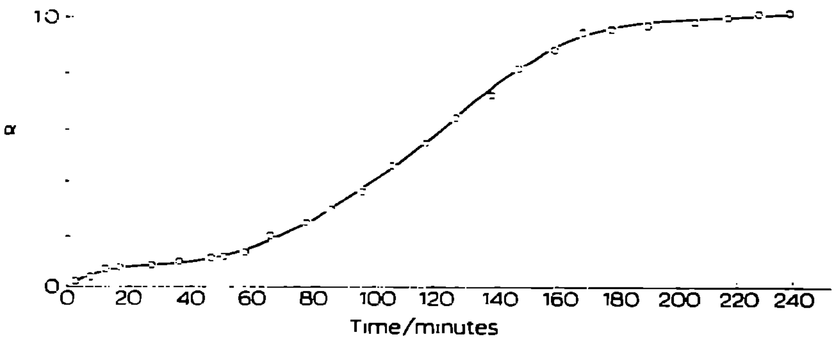

Fig. 4. α—*t* plot for large $AgMnO_4$ crystals pre-irradiated with UV light prior to decomposition at 110°C.

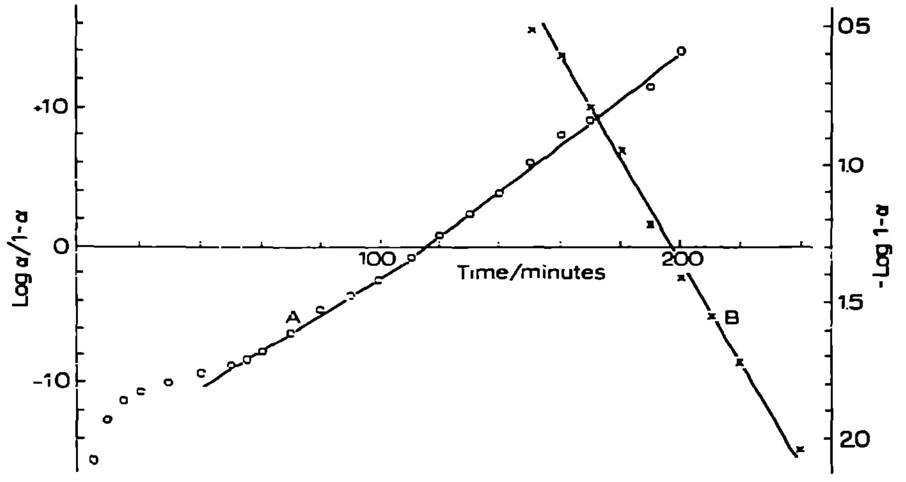

Fig. 5. The decomposition of $AgMnO_4$ crystals at 110°C and pre-irradiated with UV light. A, Prout and Tompkins plot; B, first-order decay plot.

undertaken to demonstrate the effect of irradiation by UV light on permanganate samples. The permanganate was exposed to UV light for 60 min prior to decomposition at 110° C. Figure 4 shows the α—t plot which resulted.

The Prout and Tompkins equation

$$\log \alpha/1 - \alpha = k_n t + c$$

and the Avrami—Erofeev equation

$$\log (1 - \alpha) = kt + c$$

may be applied to the α—t data obtained from Fig. 4. The plots are shown in Fig. 5. Table 1 summarises the k values observed and compares them with those obtained previously for a non-irradiated sample when decomposed at the same temperature. k_1 and k_2 refer to the two linear regions found from applying the Prout and Tompkins equation and k_3 to the decay period where in the latter the Avrami—Erofeev equation is more generally applicable.

The change in values of the rate constants is observed to be very frac-

TABLE I

Comparison of the kinetics between $AgMnO_4$ crystals decomposed with and without UV pre-irradiation at 110°C

Samples	Rate constants [a] (Min^{-1})		
	k_1	k_2	k_3
Non-irradiated crystals	0.013	0.016	0.019
UV irradiated crystals	0.014	0.017	0.018

[a] Rate constants k_1 and k_2 refer to the two linear regions where the Prout and Tompkins equation was applied. Rate constant k_3 refers to the decay period where the Avrami—Erofeev equation was applied.

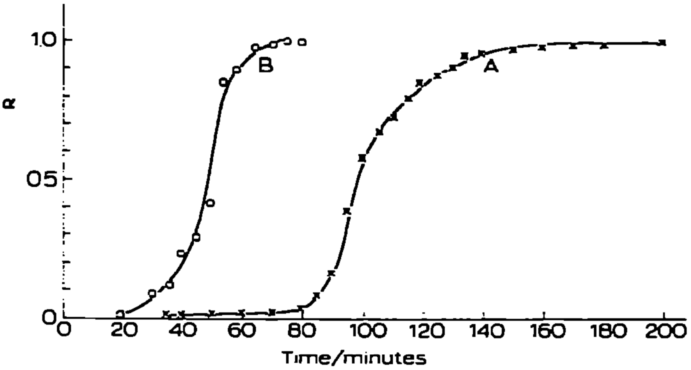

Fig. 6. α—t plots for the decomposition of a single crystal of $KMnO_4$ at 214°C. A, Decomposed without radiation; B, decomposed and simultaneously irradiated with UV light.

tionally increased in the acceleratory region and decreased in the decay region. However, the difference in the rate constants seems to be insufficiently large to suggest that the UV light had any effect on the reaction kinetics. Similar results were found by Prout and Tompkins [28].

Figure 6 shows the results observed when a single crystal of $KMnO_4$ (1.0 × 6.0 mm) was decomposed and simultaneously irradiated with UV light from a mercury-halogen arc (see curve B). Curve A shows a similar crystal which was thermally decomposed without irradiation. Both crystals used in this study were carefully selected (using a microscope to ensure reproducibility). The rate of the thermal decomposition is seen to almost double when the crystal was irradiated.

It follows from previous considerations that the thermal decomposition of permanganate is a typical redox reaction; however, Roginsky and Schultz [3] proved that the rate of thermal decomposition of permanganate changes in the presence of additions of such oxides which are generally active in redox catalysis. It is therefore assumed that considerable importance in thermal decomposition may be attributed to the excitation and transition of the electron.

Boldyrev [16] found $KMnO_4$ to an n-type semiconductor and thus much importance may be considered regarding the effect of metal oxide catalytic additives on the decomposition. Boldyrev [16] measured the work function of MnO_2, K_2MnO_4 and K_3MnO_4, and concluded that the additives accelerating the decomposition have a greater work function compared with $KMnO_4$. Thus, in accelerating the decomposition the manganese dioxide acts as an acceptor of electrons, whereas manganate and hypomanganate act as donors of electrons and thus inhibit the thermal decomposition. Figure 1 shows the results obtained using MnO_2. It is clearly seen that this oxide greatly influences the decomposition, but the effectiveness of influence is seen to depend on its prehistory, i.e. surface area (see Fig. 1A—D).

Figure 1C shows the effect of the "$K_4Mn_7O_{16}$" phase and K_3MnO_4 (and K_2MnO_4) on the thermal decomposition, the rate being drastically reduced in the case of K_3MnO_4 (and K_2MnO_4) but the phase "$K_4Mn_7O_{16}$" did not produce any more increase in the rate than for the case of pure MnO_2.

Roginsky and Schultz [3] originally found the rate of evolution of oxygen from $KMnO_4$ to be autocatalytically accelerated. Boldyrev [16] discussed this autocatalytic nature in terms of the catalytic effect the solid product "$K_4Mn_7O_{16}$" has on the reaction, but the reaction will be concurrently inhibited by K_3MnO_4 (and K_2MnO_4).

Simchen [15] found the "$K_4Mn_7O_{16}$" phase as not accelerating the reaction. This probably relates to the fact of the history of the additives having remarkable influence on the effectiveness of the additives, i.e. can influence the transition and excitation of the electron.

Regarding the studies performed investigating the action of ZnO and Cu_2O on the $KMnO_4$ decomposition; at lower temperatures both semiconductors were found to accelerate the decomposition but at higher temperature the effect of both oxides is reduced. Interpretation of these observations would require a study of the electronic work functions of the additives or the possible contact potentials between the additive and the permanganate particles.

The results regarding the pre-irradiation of permanganate prior to thermal decompositio : showed that no subsequent change resulted, but when irradiated and decomposed simultaneously the rate of thermal decomposition of $KMnO_4$ at 214°C was considerably faster than the unirradiated sample.

Boldyrev et al. [14] discussed such results in terms of the following mechanism. Photodecomposition in the temperature range 110—180°C was considered to proceed by the successive absorption of two photons by a permanganate ion followed by thermal ionization, i.e.

$$MnO_4^- \xrightarrow[2h\nu]{} (MnO_4^-)^{**} \rightarrow MnO_4^0 + e^-$$

This mechanism is capable of being modified to apply for the simultaneous case.

Above 200°C, Boldyrev et al. [29] showed that there is appreciable ionization of MnO_4^- in the absence of UV light; however, when the UV light is incident to the reactant some MnO_4^- ions are optically excited, resulting in an internal electronic transition promoting an electron to a level below that of the conduction band. From this level it is promoted thermally into the conduction band.

The simultaneous mechanism is considered as

$$MnO_4^- \xrightarrow[h\nu]{} (MnO_4^-)^*$$

then

$$(MnO_4^-)^* \rightarrow MnO_4^0 + e^-$$

thus the two parallel reactions are responsible for the creation of MnO_4^0 radical during the simultaneous reaction.

Prout and Lownds [10] discussed the observed increase in the rate of reaction by UV irradiation by restating the Prout and Tompkins mechanism in terms of a layer of products formed on the surface and that physical stresses at the interface cause crystal fracture and consequent acceleration of the reaction.

It is seen that irradiation with UV light during thermal decomposition accelerates the formation of the surface layer and the duration of the initial slow reaction is shortened. In the acceleratory period nucleation on the fresh surfaces occurs at an increased rate during the simultaneous irradiation and decomposition as compared with the thermal decomposition.

CONCLUSIONS

This investigation into the catalytic effect of additions on the rate of thermal decomposition of permanganates has demonstrated that:

(1) on the addition of MnO_2 to the $KMnO_4$ system the acceleration period of the decomposition was eliminated and produced a process whereby the rate was deceleratory throughout (see Fig. 1A and B);

(2) the insoluble portion of the $KMnO_4$ decomposition products ($K_4Mn_7O_{16}$ phase) was found to produce a similar effect (see Fig. 1E);

(3) the soluble portion of the decomposition process demonstrated a negative catalytic effect upon the acceleratory portion of the decomposition process (the manganate and manganate-permanganate compounds),

(4) the positive catalytic effect of the MnO_2 phase was clearly seen as an elimination of the initial slow acceleratory mechanism and its replacement by a deceleratory process. The objective was limited here to indicate that a change of kinetic mechanism was involved;

(5) the effect of metal oxides on the thermal decomposition was demonstrated by zinc oxide (a typical n-type semiconductor) and cuprous oxide (a typical p-type semiconductor). Figures 2A, B and 3B and C show how the oxides affected the rate of decomposition of $KMnO_4$. The important observation was therefore that these oxide additives all produced their catalytic effect on the deceleratory rate process;

(6) considerable importance in the thermal decomposition may be attributed to the excitation and transition of the electron. $KMnO_4$ is known to be an n-type semiconductor [16] and the additives accelerating the decomposition have a much greater work function compared with $KMnO_4$ [17]. In accelerating the decomposition, the MnO_2 acts as an acceptor of electrons whereas manganate and hypomanganate act as donors of electrons and thus inhibit the decomposition.

REFERENCES

1 E. Moles and M. Crespi, Z. Phys. Chem., 100 (1922) 337.
2 C.N. Hinshelwood and K. Bowen, Philos. Mag., 40 (1920) 569.
3 S.Z. Roginsky and Ye.I. Schultz, Ukr. Khim. Zh., 3 (1928) 177.
4 S.Z. Roginsky, Zh. Fiz. Khim., 12 (1938) 427.
5 S.Z. Roginsky and Ye.I. Schultz, Z. Phys. Chem., Abt. A, 138 (1928) 21.
6 E.G. Prout and F.C. Tompkins, Trans. Faraday Soc., 40 (1944) 488.
7 S.Yu. Yelovich, S.Z. Roginsky and Ye.I. Shumuk, Izv. Akad. Nauk. S.S.S.R., Otd. Khim. Nauk., 5 (1950) 469.
8 B.V. Erofeev and I.I. Smirnova, J. Phys. Chem., U.S.S.R., 26 (1952) 1233.

9 S.Z. Roginsky, Trans. Faraday Soc., 34 (1938) 959.
10 E.G. Prout and C.M. Lownds. J. Inorg. Nucl. Chem., Lett., 9 (1973) 617.
11 F.H. Herbstein, G. Ron and A. Weissman, J. Chem. Soc. A, (1971) 1821.
12 F.H. Herbstein, G. Ron and A. Weissman, J. Chem. Soc., Dalton Trans., (1973) 1701.
13 V.V. Boldyrev, Russ. Chem. Rev., 42 (1973) 523.
14 V.V. Boldyrev, G.B. London and V.K. Zhuravlev, Phys. Status Solidi, 30 (1968) K13.
15 E.A. Simchen, Bull. Soc. Chim. Fr., 5 (1954) 638.
16 V.V. Boldyrev, Phys. Chem. Solids, 30 (1969) 1215.
17 S.Z. Roginsky, Trans. Faraday Soc., 34 (1938) 959. C.N. Hinshelwood and K. Bowen, Philos. Mag., 40 (1920) 569; Proc. R. Soc. London, Ser. A, 99 (1921) 203.
18 A.L. Klyachko-Gurvich, Izv. Akad. Nauk. S.S.S.R., Otd. Khim. Nauk, (1961) 1884. Engl. Trans. 1756 (1961).
19 D. Dollimore, P. Spooner and A. Turner, Surf. Technol., 4 (1976) 121.
20 E.G. Prout, J. Inorg. Nucl. Chem., 7 (1958) 368.
21 E.G. Prout and P.J. Herley, J. Phys. Chem., 66 (1962) 961.
22 A.K. Galwey, J. Chem. Educ., 37 (1960) 98.
23 I.I. Smirnova, Zh. Fiz. Khim., 30 (1956) 2649.
24 B.V. Erofeev, Zh. Fiz. Khim., 25 (1951) 1098.
25 V.A. Protashchik and B.V. Erofeev, Dokl. Akad. Nauk. B. S.S.R., 10 (1966) 658.
26 V.A. Protashchik, Vestsi. Akad. Nauk. B. S.S.R., Ser. Khim. Navuk. 4 (1966) 46.
27 J.S. Booth, D. Dollimore and G.R. Heal, Thermochim. Acta, 39 (1980) 281.
28 E.G. Prout and F.C. Tompkins, Trans. Faraday Soc., 41 (1945) 468.
29 V.V. Boldyrev. A.P. Voronin. T.A. Nevolina and V.V. Morusin. J. Solid State Chem., 20 (1977) 327.