Thermochimica Acta, 26 (1978) 311–336
© Elsevier Scientific Publishing Company, Amsterdam – Printed in The Netherlands

THERMAL DECOMPOSITION KINETICS OF STRONTIUM PERMANGANATE TRIHYDRATE, CADMIUM PERMANGANATE HEXAHYDRATE AND CALCIUM PERMANGANATE PENTAHYDRATE CRYSTALS*

K. R. SAKURAI**, D. A. SCHAEFFER† AND P. J. HERLEY††
Department of Materials Science, State University of New York, Stony Brook, N. Y. 11794 (U.S.A.)

ABSTRACT

A thermogravimetric study of the kinetics of thermal nuclei formation and growth has been carried out for the dehydration and decomposition of single crystal strontium permanganate trihydrate, cadmium permanganate hexahydrate, and calcium permanganate pentahydrate. The isothermal dehydration of strontium permanganate trihydrate occurs in two stages between 50 and 100 °C. The dehydration kinetics suggest that the two dehydration stages are based on a single-step nucleation process followed by a growth process without nuclei overlap. The resulting activation energies are consistent with the proposed nucleation theory. For the dehydration kinetics of cadmium permanganate hexahydrate, an overlapping nucleation growth mechanism appears to be operating between 30 and 60 °C. The results are irreproducible for the dehydration of calcium permanganate pentahydrate at 100 °C.

The thermal decomposition studies indicate that the data of the sigmoidal, isothermal fractional decomposition vs. time curves are reproducible for whole and ground crystals of each dehydrated permanganate. All of the data plots contain an induction or slow rate period, an acceleratory and a decay period. The induction period can be shortened by irradiation with ^{60}Co γ-rays prior to decomposition. Activation energies obtained for all three materials for the various thermal decomposition periods are found to be similar to those published previously on other alkali and alkaline-earth permanganates.

---

[*] Presented at the 7th North American Thermal Analysis Society Conference, St. Louis, Missouri, September 25–28, 1977.

[**] Present address: Chemistry Department, University of Wisconsin, Milwaukee, Wisconsin 53201 (U.S.A.).

[†] Present address: SCM Glidden Metals Group, Research Laboratory, 11000 Cedar Avenue, Cleveland, Ohio 44106 (U.S.A.).

[††] To whom all correspondence should be addressed.

INTRODUCTION

The isothermal fractional decomposition, (i.e. α) vs. time curves for solid (crystals) and powdered lithium[1], sodium[1], potassium[2, 3], rubidium[3], caesium[4], barium[5] and silver[6] permanganates show three distinct decomposition periods. Over the first stage, the induction period, the fractional decomposition is linearly dependent on time, i.e.

$$\alpha = k_1 t + c_1 \tag{1}$$

where $\alpha = P(t)/P_f$. $P(t)$ is the pressure evolved in a closed system at time t and P_f is the final pressure at the completion of the reaction. The induction period is followed in succession by the second or acceleratory stage during which the decomposition rate accelerates markedly to an α value corresponding to the inflexion point. This point marks the onset of a third or decay period during which the reaction rate decays monotonically. For all of the above-mentioned permanganates, the data over the acceleratory and decay periods can be described by the Prout–Tompkins equation[2]

$$\log \frac{\alpha}{1-\alpha} = k_{2,3} t + c_{2,3} \tag{2}$$

(k_2, c_2 = acceleratory, k_3, c_3 = decay, periods). Equation (2) is based on the assumption that the product nuclei give rise to strain, which in turn causes microcracking and, thus, new surfaces at which decomposition might occur. Thus during the acceleratory period, the reaction proceeds in a branching manner into the crystal bulk. Ultimately, the branching mechanism would cease due to the interference of the branching planes. Upon completion of this sequence of events, the decomposition has reached the inflexion point of the α vs. t curve. Subsequently, the decomposition rate is controlled by the amount of unreacted material and a contracting interface mechanism predominates.

The role of strain induced during the thermal decomposition process was also observed in the decomposition of ammonium perchlorate[7–9], where the number of nucleation sites was markedly effected by the radiation-induced strain in the crystal prior to decomposition. For ammonium perchlorate, the decomposition process[10, 11] involves, initially, the slow formation and growth of random nuclei followed by growth with overlap. The kinetics of this process are described by the Avrami–Erofeyev analysis[12], i.e.

$$-[\log(1-\alpha)] + \frac{6\sigma N_0 k_5^3}{V_0 k_4^3}\left\{\exp(-k_4 t) - 1 + k_4 t - \left[\frac{(k_4 t)^2}{2.1}\right] + \left[\frac{k_4 t^3}{3.1}\right]\right\} \tag{3}$$

where σ is a shape factor, N_0 is the total number of potential nucleus-forming sites at $t = 0$, V_0 is the final volume, k_4 is the rate of nucleation and k_5 the (linear) growth rate of the decomposition sites. Equation (3), can be simplified by assuming that $k_4 t$ is small over the acceleratory period yielding

$$[-\log(1-\alpha)]^{1/4} = k_6 t \tag{4}$$

for the acceleratory period. For k_5t large, i.e. over the decay period, eqn. (3) becomes

$$[-\log(1-\alpha)]^{1/3} = k_7t \tag{5}$$

The literature apparently contains no reports on the kinetics of the dehydration or isothermal decomposition of strontium, cadmium or calcium permanganates. It is thus of interest to investigate the dehydration and isothermal decomposition kinetics of strontium, cadmium and calcium permanganates to determine if the decomposition kinetics were similar to the decomposition of other permanganates or if there occurs a random nucleation process such as that postulated for eqns. (3)–(5).

In order to examine the effects of ^{60}Co gamma rays on the subsequent isothermal decomposition process, it is necessary to understand the decomposition kinetics of the unirradiated material. Ionizing radiation markedly affects the decomposition kinetics of permanganates[1]. With increasing gamma-ray dose, the induction period is shortened, the rates of the acceleratory and decay periods increases and the overall time of decomposition is shortened without altering the overall activation energy of the decomposition process(es). Hence the kinetics of nucleation and growth during the thermal dehydration and decomposition of strontium, cadmium and calcium permanganates will be investigated as a function of temperature, particle size and gamma-ray preirradiation. A comparison would then be possible with the previous results of kinetic data from the other permanganates.

EXPERIMENTAL

Crystal preparation

The strontium, cadmium and calcium permanganates were synthesized from silver permanganate crystals. The silver permanganate was prepared as follows: 67.5 g of silver nitrate ("Baker Analyzed" Lot 45088, J. T. Baker Chemical Company) was dissolved in 100 ml of distilled water at room temperature, and 62.5 g of potassium permanganate (ASC reagent, Cont. 35952 Hall Lab. Prod.) in 500 ml of distilled water was added so that the following reaction took place stoichiometrically.

$$AgNO_3 + KMnO_4 \rightarrow AgMnO_4\downarrow + KNO_3 \tag{6}$$

The resulting mixture was cooled slowly to 5 °C in an ice bath, followed by filtration at 5 °C through a sintered glass funnel (ASTM 40-60C) to obtain silver permanganate, a dark-purple amorphous precipitate. Using eqn. (6), the percentage yield was 94.2%. The amorphous precipitate was recrystallized by evaporation from an aqueous solution in air yielding crystals which were approximately (4.0 × 2.0 × 2.0) mm in size. These crystals were then stored in a vacuum desiccator using Drierite as a desiccant.

(i) *Synthesis of strontium permanganate trihydrate.* 1.75 g of strontium chloride hexahydrate ($SrCl_2 \cdot 6H_2O$) (Baker Analyzed, Lot 37259, J. T. Baker Chemical Company) was dissolved in 30 ml of distilled water at room temperature. A stoichiometric quantity of silver permanganate, 30 g dissolved in 400 ml of distilled water, was added according to the equation

$$\mathrm{SrCl_2 \cdot 6H_2O(aq.) + 2\ AgMnO_4 \rightarrow Sr(MnO_4)_2 \cdot 3H_2O(aq.) + 2\ AgCl\downarrow} \qquad (7)$$

This solution was then rapidly filtered using a sintered glass funnel (ASTM 40-60C). The resulting filtrate, which contained no traces of Ag^+ or Cl^-, was concentrated by evaporation in air for five days. Large (3.0 × 3.0 × 3.0 mm) hygroscopic single crystals were obtained. The percentage yield calculated from eqn. (7) for the hydrated crystals was 94.2% ± 2%.

(ii) *Synthesis of cadmium permanganate hexahydrate.* After 1.99 g of barium chloride dehydrate was dissolved in 50 ml of distilled water, a 10 M solution of silver permanganate was slowly added and the resulting solution filtered through a sintered glass funnel (ASTM 40-60C) at room temperature. A solution containing 1.84 g of cadmium sulphate (Baker Analyzed, Lot 9480, J. T. Baker Chemical Company) dissolved in 70 ml of distilled water was then added to the above filtrate to produce the reaction

$$\mathrm{CdSO_4 + Ba(MnO_4)_2 + \rightarrow Cd(MnO_4)_2 \cdot 6H_2O(aq.) + BaSO_4\downarrow} \qquad (8)$$

The resulting solution was filtered with Whatman No. 4 filter paper, the filtrate containing no detectable traces of barium, silver, chloride or sulfate ions. The filtrate was evaporated at 35°C in air for two days and this was followed by a prolonged evaporation at room temperature for two weeks. The resulting dark-violet crystals were hygroscopic with rhombohedral symmetry. Their sizes ranged between 5.0 × 4.0 × 2.0 mm and 0.5 × 0.3 × 0.2 mm. The percentage yield of hydrated solid was 89.2 ± 8% as calculated from eqn. (8).

(iii) *Synthesis of calcium permanganate pentahydrate.* 3.68 g of calcium chloride (Baker Analyzed, Lot 20089, J. T. Baker Chemical Company) was dissolved in 50 ml of distilled water and then added to 15.0 M solution of silver permanganate. The following reaction occurred.

$$\mathrm{CaCl_2 + 2\ AgMnO_4 + \rightarrow Ca(MnO_4)_2 \cdot 5H_2O(aq.) + 2\ AgCl\downarrow} \qquad (9)$$

The product solution was stored in the dark for approximately 12 h. The silver chloride precipitate was filtered using an ASTM (40-60C) sintered glass funnel. The filtrate, calcium permanganate solution, contained no detectable traces of chloride or silver ions. It was concentrated in air at 35°C for five days and then allowed to cool to room temperature. The resulting crystals were black-purple in color and needle-like in shape and approximately 2 × 0.2 × 0.2 mm in size. The percentage yield was 91.0 ± 0.2% as calculated from eqn. (9).

In this study, both whole (pristine) crystals and powdered material were investigated. Whole crystals were used as prepared. Powdered material was obtained by crushing and grinding whole crystals in an agate pestle and mortar to a sieved fineness to pass through a B.S. sieve of 225 mesh/sq. in. (i.e. ~65 μm).

The purities of the crystals have been determined by conventional analytical (oxalate) titration techniques. The average percentage purity for three determinations on each permanganate were $Sr(MnO_4)_2 \cdot 3H_2O$ 93.7 ± 2%; $Cd(MnO_4)_2 \cdot 6H_2O$ 96.2 ± 2%; and $Ca(MnO_4)_2 \cdot 5H_2O$ 95.9 ± 2%. The percentage thermal decomposition after dehydration for $Sr(MnO_4)_2$ was calculated based on eqn. (10) (where A = Sr, Cd or Ca) to be 91.7 ± 1% for powders and 90.9 ± 2% for whole crystals. For $Cd(MnO_4)_2$,

$$A(MnO_4)_2 \rightarrow AMnO_4 + MnO_2 + O_2\uparrow \qquad (10)$$

the percentage decomposition for whole crystals is 92.8 ± 1.3% and 93.3 ± 1.1% for powders. For powdered $Ca(MnO_4)_2$ crystals the percentage yield was 92.4 ± 1%. At best, eqn. (10) is an over-simplification. Complex stoichiometric reactions have been observed in the decomposition products of other permanganates[15] and it is probable that similar reactions are occurring during these decomposition reactions. Also the decomposition process could contain a retention region, i.e. a small quantity of unreacted permanganate might remain after decomposition. However, the probability that this would occur is small since after decomposition each sample was tested by dissolving it in water and in all cases the typical purple permanganate color was not observed.

Apparatus

The thermobalance used for these studies was a Perkin Elmer TGS-1 which incorporated a Cahn RG electrobalance with a dry nitrogen gas flow control unit operated at 10 psi. The data was recorded continuously using a Perkin-Elmer two-pen recorder, Model 52. The data was obtained in the form of line plots. The points shown in the subsequent figures are for illustrative purposes only. Many more data points were utilized for the kinetic analysis and the data was analyzed using a best fit computer program. The fractional decomposition, α, was obtained from the relationship $\alpha = (W_i - W_t)/(W_i - W_f)$ where W_i = initial weight, W_f = final weight and W_t = weight at time, t.

Procedure

The thermobalance was stabilized prior to thermal decomposition at room temperature for 48 h. The samples, which ranged in weight from 0.5 to 6.0 mg, were placed on platinum pans in the thermobalance and the decomposition chamber was sealed. To remove any traces of moisture and air from the chamber, dry, high-purity nitrogen gas was passed through the chamber prior to, and continuously during, the decomposition. The furnace heating rate was set at 320°C/min in order to raise the temperature as rapidly as possible to a pre-set constant value, which was then maintained automatically to ± 0.5°C. The recorder scanning rate was pre-set at 5 mm/min.

Irradiations were carried out at ambient temperature at Brookhaven National Laboratory with 1.1 and 1.3 MeV ^{60}Co gamma-rays. In order to avoid any contamination, the samples were encapsulated in air in glass ampoules prior to irradiation.

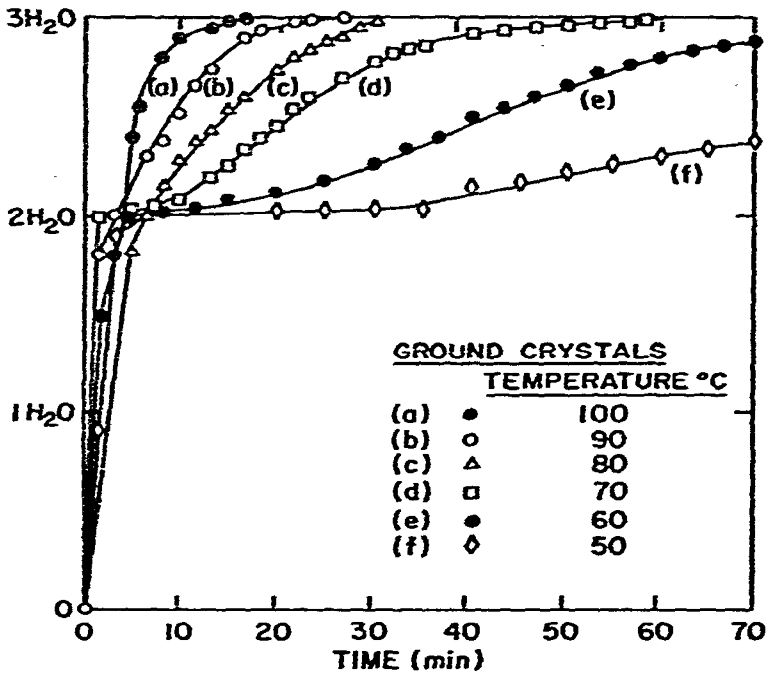

Fig. 1. Isothermal dehydration of powdered strontium permanganate trihydrate crystals between 50 and 100°C.

RESULTS

Strontium permanganate trihydrate

For *whole* crystals the isothermal dehydration kinetics were investigated at 100°C. The resulting data were found to be largely irreproducible and markedly dependent on the surface conditions. The α vs. time curves showed a monotonic decay with completion times ranging from 25 to 50 min. One probable reason for the observed irreproducibility could be the presence of occluded water. It was also observed that the crystals undergo no external change during the dehydration process.

On the other hand, the dehydration kinetics of *ground* crystals were reproducible and were investigated in the temperature range from 50 to 100°C (see Fig. 1). It was found that 66% of the total weight of the hydrated water was removed before 5 min had elapsed. These curves indicate that 2 of the 3 water molecules were removed rapidly on heating. The remainder continued evolving over a longer time period. On completion of the dehydration process, for example, after 40 min at 80°C, there was no external change in the crystal morphology.

Activation energies were determined for these two distinct processes in the powdered material as follows. The rate of initial rapid dehydration process was approximated by a linear relationship of the form of eqn. (1), i.e.

$$\alpha = k_1 t + c_1$$

TABLE 1

DEHYDRATION KINETIC RATE CONSTANTS FOR STRONTIUM PERMANGANATE TRIHYDRATE, POWDERED CRYSTALS

Rate equation	*Dehydration kinetic rate constant (min⁻¹)*					
	50°C	*60°C*	*70°C*	*80°C*	*90°C*	*100°C*
Linear (for initial 2 water molecules)	0.150	0.220	0.334	0.308	0.309	0.604
A–E decay (for final water molecules)		0.00300	0.00291	0.00283	0.00275	0.00268

and the monotonic decay of the slower period was analyzed using the Avrami–Erofeyev equation at large times, eqn. (5). The resulting rate constants are tabulated in Table 1. The activation energies were found to be 6.6 ± 0.1 kcal/mole for the process of removing the two water molecules and 13.8 ± 2.1 kcal/mole for the removal of the final water molecule.

Strontium permanganate

The isothermal decomposition of pristine dehydrated material was carried out directly after each dehydration and was investigated using both whole and powdered crystals over the temperature range 120°–145°C.

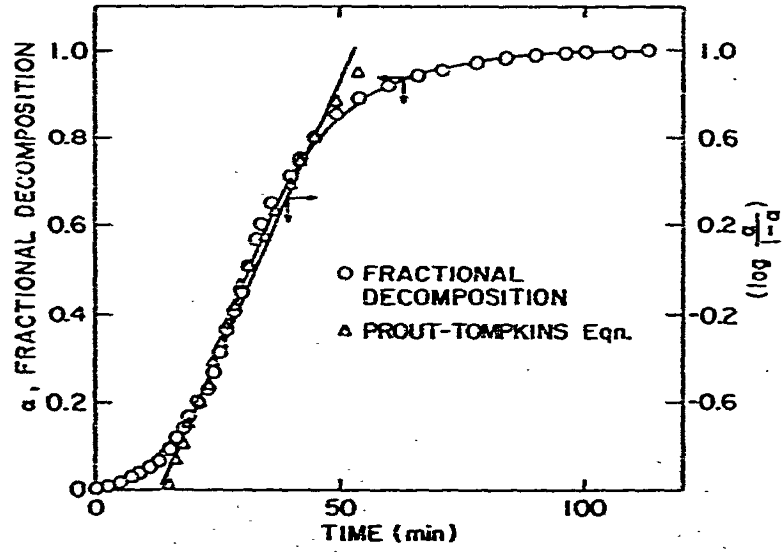

Fig. 2. Fractional decomposition, $\alpha = (W_i - W_t)/(W_i - W_f)$, versus time curve for whole crystals of dehydrated strontium permanganate thermally decomposed at 135°C. The figure also shows the Prout–Tompkins analysis of the data. This demonstrates the applicability of this equation to the experimental curve.

TABLE 2

THERMAL DECOMPOSITION KINETIC RATE CONSTANTS FOR STRONTIUM PERMANGANATE, WHOLE CRYSTALS

Analysis	*Thermal decomposition kinetic rate constant* ($\textit{min}^{-1}$)				
	145°C	*140°C*	*135°C*	*130°C*	*125°C*
P–T (accel. period)	0.152	0.102	0.0530	0.0280	0.0180
	0.166	0.100	0.0530	0.0330	0.0110
	0.152	0.113	0.0590	0.0290	0.0250
P–T (decay period)	0.201	0.096	0.0530	0.0280	0.0260
	0.199	0.0960	0.0570	0.0220	0.0190
	0.189	0.101	0.0500	0.0290	0.0200
A–E (accel. period)	0.0270	0.0185	0.00940	0.00490	0.00340
	0.0290	0.0190	0.00940	0.00520	0.00390
	0.0270	0.0180	0.00980	0.00480	0.00330
A–E (decay period)	0.0140	0.0110	0.00690	0.00410	0.00270
	0.0170	0.0120	0.00750	0.00450	0.00300
	0.0110	0.0100	0.00690	0.00400	0.00270
Linear (induction period)	0.0216	0.0190	0.0110	0.00660	0.00450
	0.0215	0.0250	0.0100	0.00810	0.00410
	0.0216	0.0180	0.00900	0.00600	0.00550

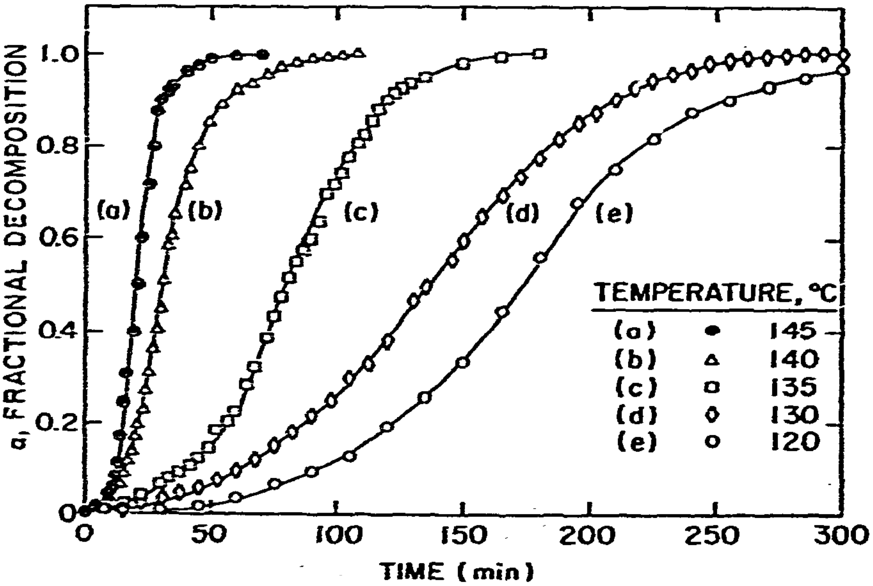

Fig. 3. Fractional decomposition, $\alpha = (W_i - W_t)/(W_i - W_f)$, versus time curves for whole crystals of dehydrated strontium permanganate isothermally decomposed between 120 and 145°C.

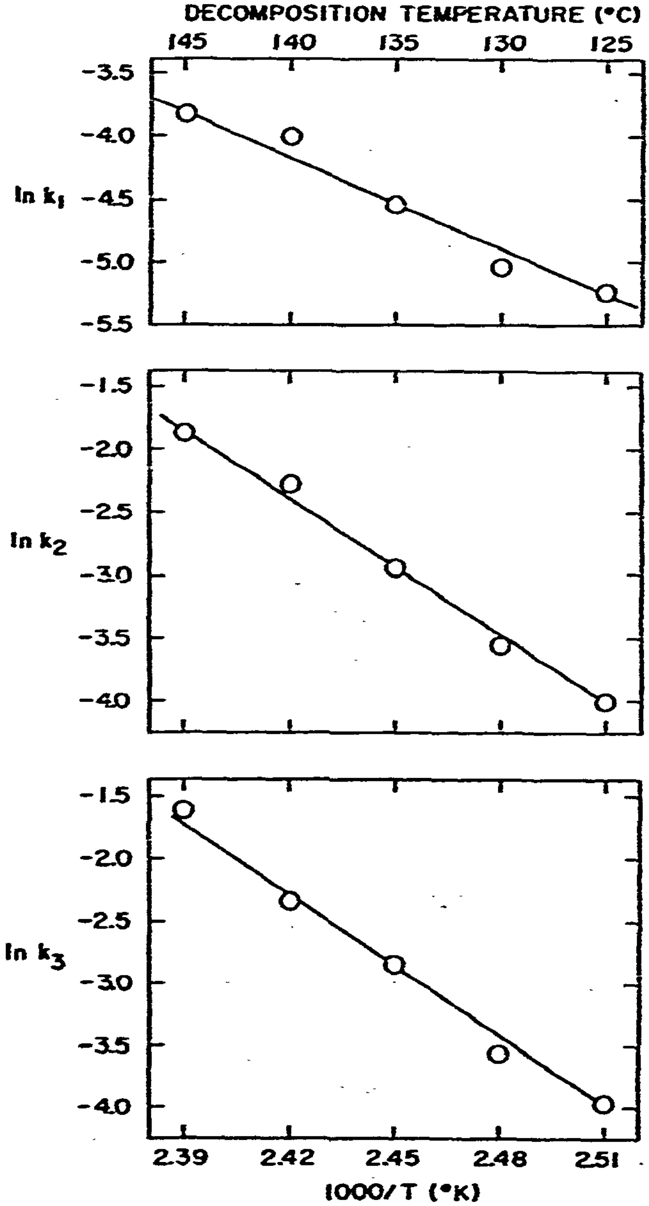

Fig. 4. Plots of ln[k_1 (induction), k_2 (acceleration) and k_3 (decay)] versus $1/T$ K for the thermal decomposition of whole crystals of dehydrated strontium permanganate.

For *whole* crystals, a typical α vs. t curve is shown in Fig. 2 for a decomposition temperature of 135 °C. The resulting sigmoidal curve contains a small linear induction period and an inflexion point at approximately $\alpha = 0.5$. Excellent reproducibility was observed for the whole crystals as can be seen in the values of the rate constants listed in Table 2. The effect of decomposition temperatures on the α vs. t curves for temperatures ranging from 120° to 145°C is shown in Fig. 3.

The Prout–Tompkins equation (P–T), eqn. (2), was applied to the data and the

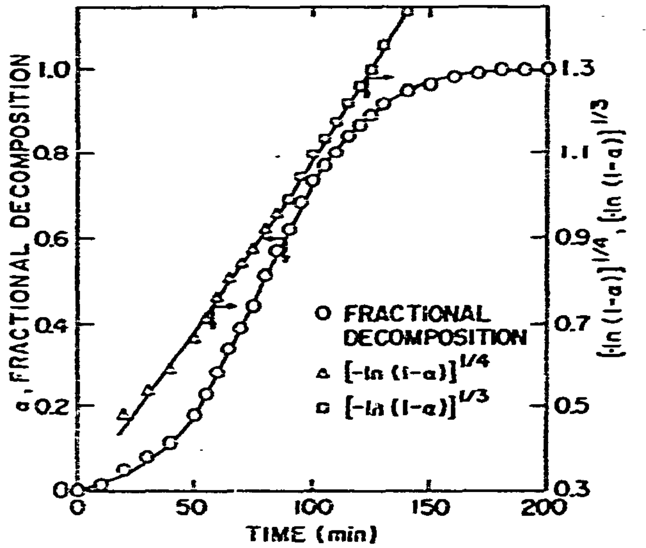

Fig. 5. Fractional decomposition, $\alpha = (W_i - W_t)/W_i - W_f)$, versus time curve for powdered dehydrated strontium permanganate crystals thermally decomposed at 130°C. The figure also shows the Avrami–Erofeyev analysis of the data. This demonstrates the applicability of this equation to the experimental curve.

TABLE 3

THERMAL DECOMPOSITION KINETIC RATE CONSTANTS FOR DEHYDRATED STRONTIUM PERMANGANATE POWDERED CRYSTALS

Kinetic analysis	*Thermal decomposition kinetic rate constant (min⁻¹)*					
	145°C	*140°C*	*135°C*	*130°C*	*125°C*	*120°C*
P–T (accel. period)	0.310	0.155	0.0833	0.0500	0.0290	0.0228
	0.330	0.162	0.0800	0.0500	0.0280	0.0240
	0.301	0.143	0.0851	0.0490	0.0340	0.0210
P–T (decay period)	0.165	0.0860	0.0600	0.0400	0.0330	0.0200
	0.173	0.0930	0.0591	0.0450	0.0300	0.0210
	0.161	0.0881	0.0622	0.0390	0.0330	0.0200
A–E (accel. period)	0.0580	0.0184	0.0153	0.00872	0.00417	0.000312
	0.0621	0.0190	0.0174	0.00804	0.00426	0.000361
	0.0541	0.0180	0.0152	0.00879	0.00401	0.000302
A–E (decay period)	0.0152	0.0132	0.0120	0.00816	0.00333	0.00197
	0.0191	0.0129	0.0156	0.00900	0.00290	0.00165
	0.0130	0.0138	0.0113	0.00790	0.00335	0.00181
Linear (induction period)	0.0249	0.0209	0.00830	0.0150	0.0133	0.00250
	0.0210	0.0310	0.0190	0.0160	0.0122	0.00270
	0.0251	0.0200	0.0170	0.0155	0.015	0.00210

extent of fit was $0.09 < \alpha > 0.90$ (see Fig. 2). The Avrami–Erofeyev equation (A–E) was also applied to the data, but the fit was not as extensive as for the P–T equation, particularly when examined over the entire temperature range. Nevertheless, rate constants for both the acceleratory and decay periods were determined for both equations and are listed in Table 2 together with the rate constants determined from the (linear) induction period. These rate constants were used to calculate the activation energies. The plots of $\ln k_{1,2,3}$ vs. $1/T$ K for the induction, acceleratory and decay periods (Fig. 4) gave activation energies of 25.9 ± 3.5, 34.9 ± 2.2 and 32.2 ± 2.4 kcal/mole, respectively.

For *ground* crystals, a typical α vs. t curve at 130°C is shown in Fig. 5 with the appropriate kinetic analysis. Again, the reproducibility was observed to be good as evidenced by a comparison of the rate constants observed from 3 runs at each decomposition temperature (see Table 3). The effect of temperature on the α vs. t curves for the range 120–145°C for ground material is shown in Fig. 6. These curves all exhibited a linear induction period. However, unlike the whole crystals, the inflexion point did not correspond with $\alpha = 0.5$ and thus the P–T analysis[2] was inapplicable. Attempts were made to fit the exponential law over the acceleratory period

$$\ln \alpha = k_8 t + c_8 \tag{11}$$

and, for the decay period, the unimolecular law

$$\ln(1 - \alpha) = k_9 t + c_9 \tag{12}$$

was applied. In addition, the A–E equation was fitted over the whole curve. The best fit was obtained using the A–E equation. The range of fit for the A–E equation

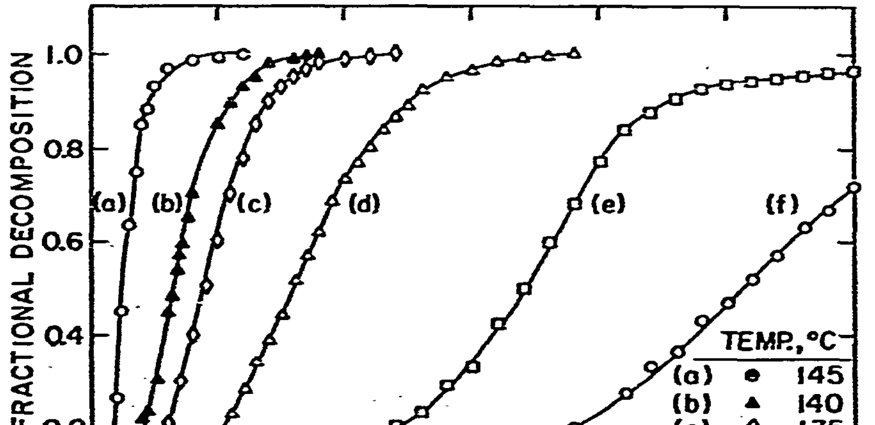

Fig. 6. Fractional decomposition, $\alpha = (W_i - W_t)/(W_i - W_f)$, versus time curves for powdered dehydrated strontium permanganate crystals isothermally decomposed between 120 and 145°C.

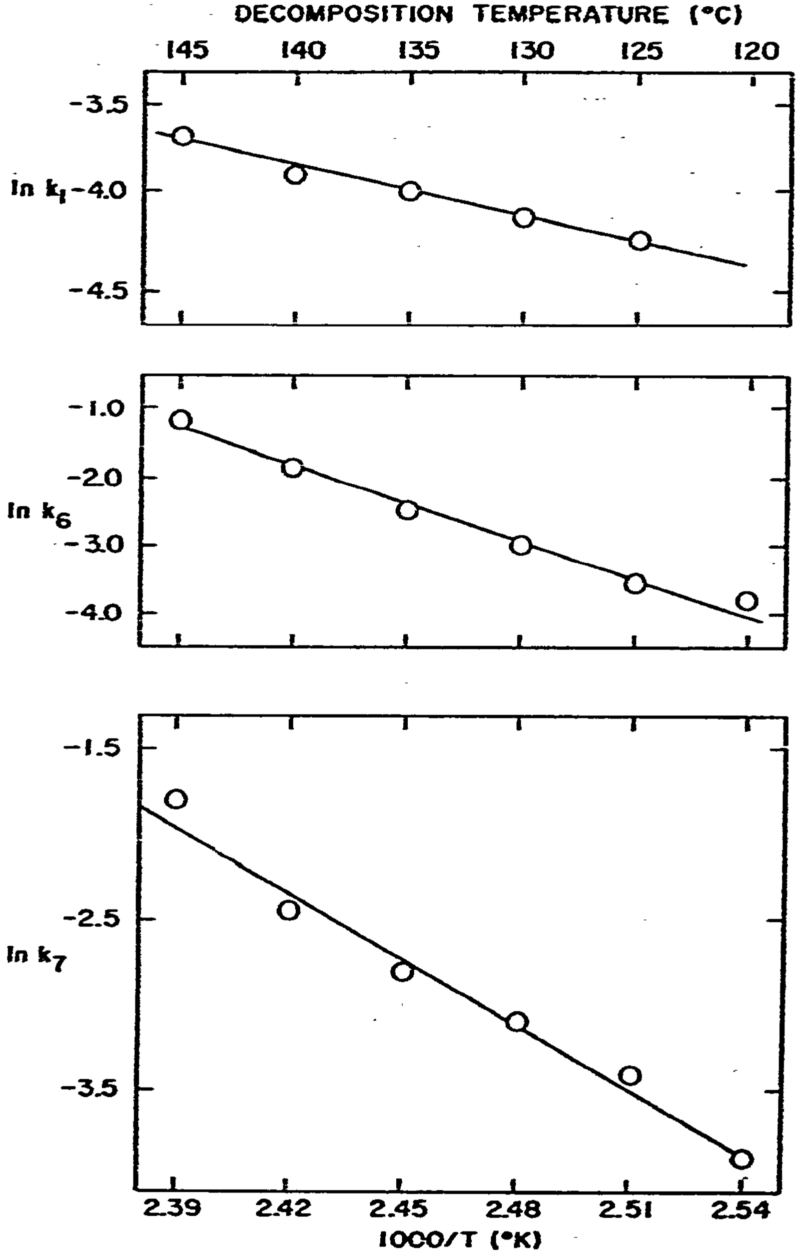

Fig. 7. Plots of ln (rate constants) versus 1/T K for the induction (k_1), acceleratory (k_6) and decay (k_7) periods of the thermal decomposition of powdered dehydrated strontium permanganate crystals.

extended from $0.05 < \alpha > 0.60$ over the acceleratory period and $0.60 < \alpha > 0.97$ over the decay period. These ranges were consistent for all the temperatures studied. This fit enabled the respective rate constants to be obtained for the induction, acceleratory and decay period (see Table 3). The resulting activation energy plots of ln $k_{1,6,7}$ vs. $1/T$ K are shown in Fig. 7. The activation energies determined from these

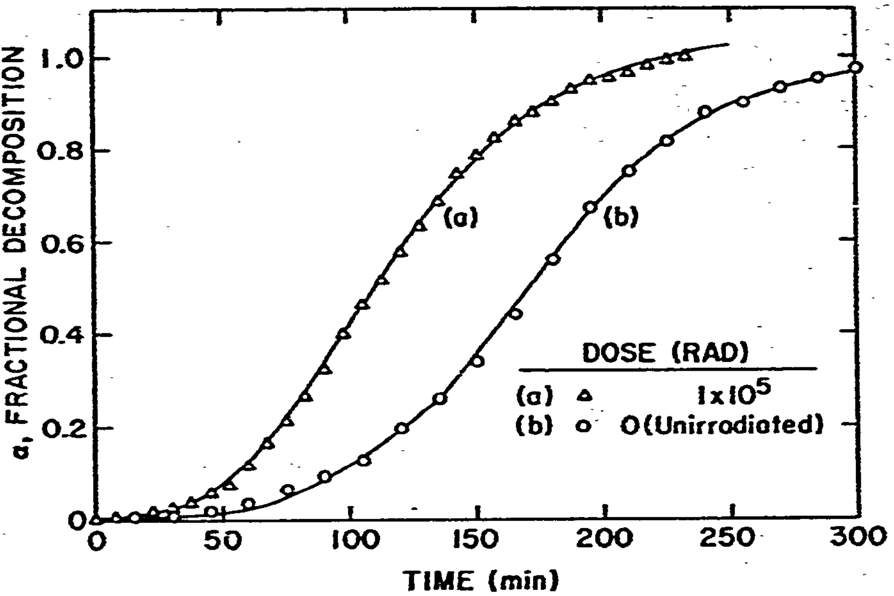

Fig. 8. The effect of a 1 × 10^5 rad gamma-ray dose on the subsequent thermal decomposition of whole crystals of dehydrated strontium permanganate at 120°C. The plot shows the fractional decomposition, $\alpha = (W_i - W_t)/(W_i - W_f)$.

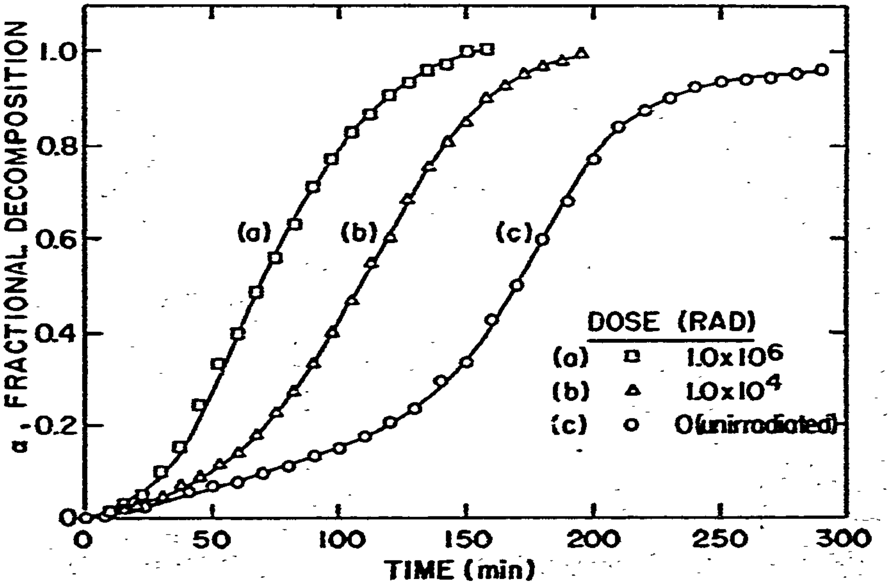

Fig. 9. The effect of gamma-ray doses of 1 × 10^6 and 1 × 10^4 rad on the subsequent thermal decomposition of powdered dehydrated strontium permanganate crystals. The plot shows the fractional decomposition $\alpha = (W_i - W_t)/(W_i - W_f)$, versus time for ground crystals decomposed at 125°C.

plots were 29.5 ± 3.1, 33.7 ± 3.1 and 32.6 ± 2.7 kcal/mole for the induction, acceleratory and decay periods, respectively.

A preliminary investigation was carried out of the effects of ^{60}Co γ-ray irradiation on the subsequent thermal decomposition process. For whole and ground

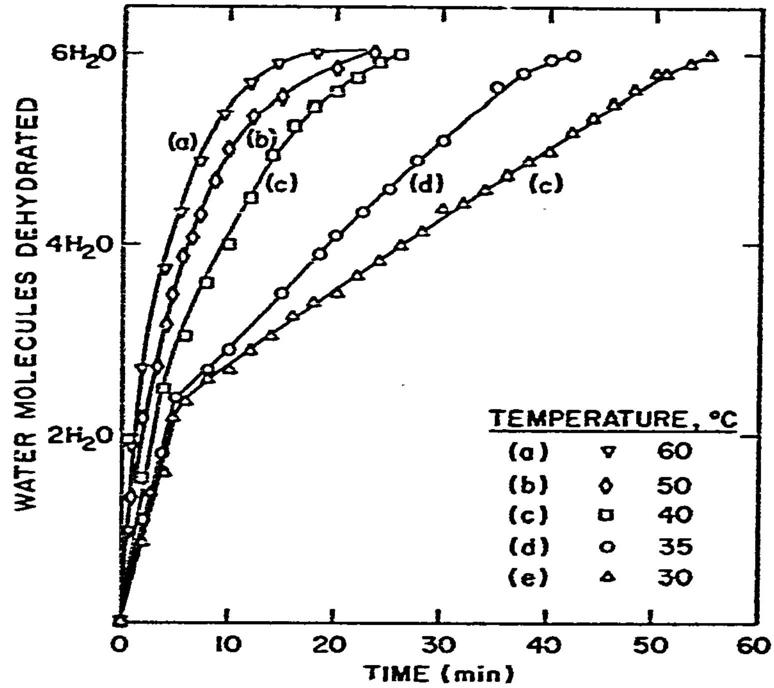

Fig. 10. Isothermal dehydration of powdered cadmium permanganate hexahydrate crystals between 30 and 60°C.

crystals decomposed at 120°C and 125°C, respectively, the effects of ^{60}Co gamma-ray irradiation are shown in Figs. 8 and 9, respectively, over the dose range of 1×10^4 to 1×10^6 rad. The principal result of the irradiation was to increase the rate of the acceleratory period and to shorten the decay period, i.e. to shorten the overall time for completion of the reaction. For example, the time required to complete the decomposition of ground crystals, pre-irradiated with 1.0×10^6 rad, was approximately half that for the unirradiated sample of the same temperature. Visual observation of a decomposing preirradiated crystal (dose 1.0×10^6 rad) shows that no fracture occurred during the acceleratory or decay periods.

Cadmium permanganate hexahydrate

The dehydration process in $Cd(MnO_4)_2 \cdot 6H_2O$ was examined kinetically between 30 and 60°C on powdered material only. Attempts to obtain results for whole crystals yielded markedly irreproducible results. The powder on dehydration exhibited no induction period. Two distinct dehydration processes appear to be operating at 30 and 35°C as shown in Fig. 10. The initial process was deceleratory in nature and appeared to encompass up to three hydrated water molecules from the weight loss measurements. The slower reaction, which is almost linear with time for later times, involves the evolution of the remaining three water molecules. The rates of the two reactions merge at the higher temperatures into one continuous curve (Fig. 10).

Since the dehydration curves were reproducible, attempts were made to fit

TABLE 4

DEHYDRATION KINETIC RATE CONSTANTS FOR CADMIUM PERMANGANATE HEXAHYDRATE, POWDERED CRYSTALS

Kinetic analysis	*Dehydration kinetic rate constant* (min^{-1})				
	30°C	*35°C*	*40°C*	*50°C*	*60°C*
ln α (initial stage)	0.0487	0.0743	0.117	0.141	0.283
	0.0466	0.0733	0.111	0.133	0.266
	0.0487	0.0744	0.115	0.145	0.282
ln (1-α) (final stage)	0.263	0.266	0.200	0.271	0.278
	0.263	0.266	0.200	0.266	0.279
	0.266	0.269	0.211	0.279	0.278

several kinetic equations over both periods. Neither the A–E equation, eqn. (3), nor the P–T equation, eqn. (2), provide a satisfactory fit over both periods. However, the exponential law, eqn. (11), and the unimolecular law, eqn. (12), were found to fit the data satisfactorily and were thus used to analyze the initial and final stages, respectively. Almost identical rate constants for several independent dehydration runs were obtained from the subsequent kinetic analyses. The resulting values of the respective rate constants are tabulated in Table 4. The respective activation energies were determined by plotting ln $k_{8,9}$ vs. $1/T$ K, yielding 1.3 ± 0.1 kcal/mole for the initial period and 11.9 ± 1.5 kcal/mole for the final period, respectively.

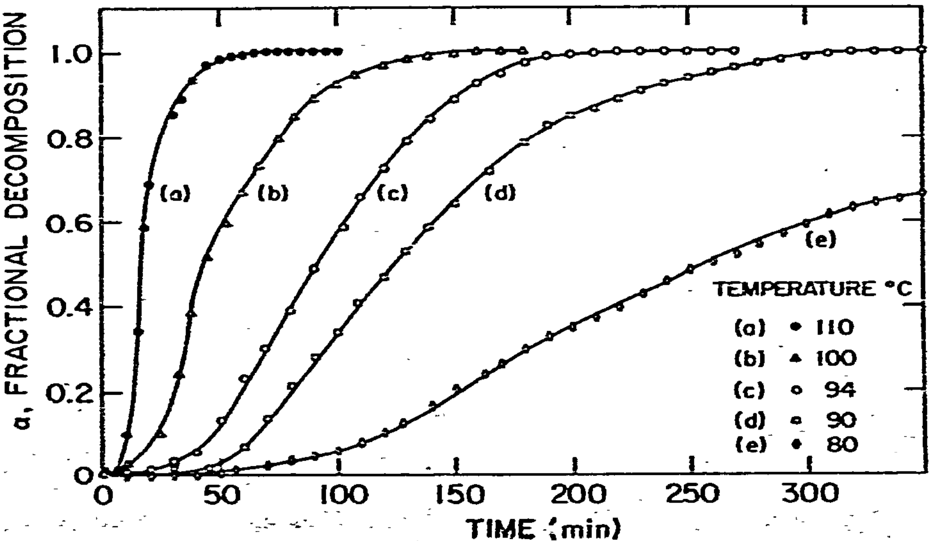

Fig. 11. Fractional decomposition, $\alpha = (W_i - W_t)/(W_i - W_f)$, versus time curves for whole crystals of dehydrated cadmium permanganate isothermally decomposed between 80 and 110°C.

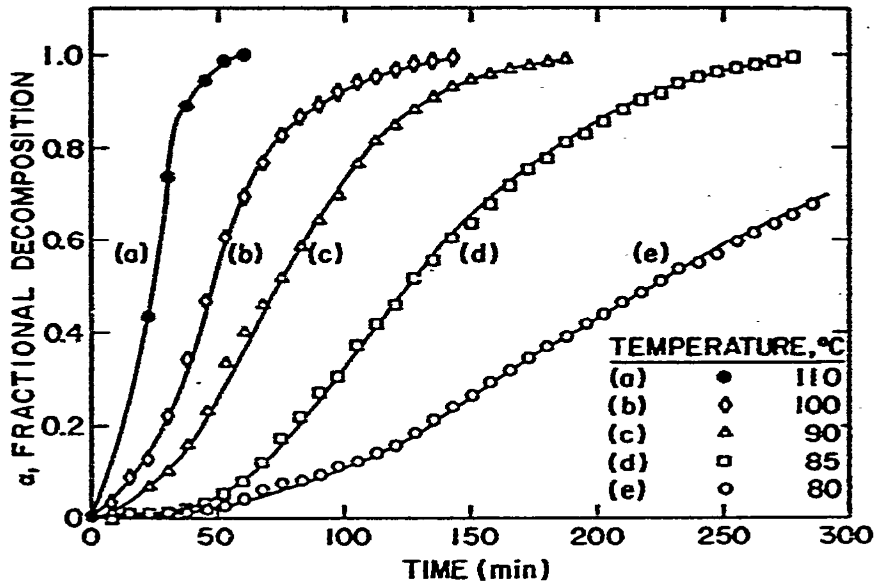

Fig. 12. Fractional decomposition, $\alpha = (W_i - W_t)/(W_i - W_f)$, versus time curves for powdered dehydrated cadmium permanganate crystals isothermally decomposed between 80 and 110°C.

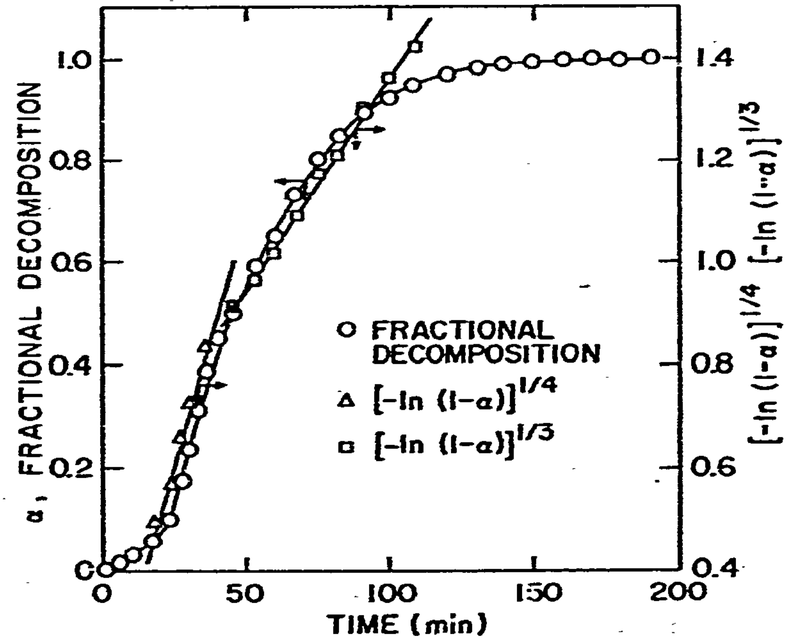

Fig. 13. Fractional decomposition, $\alpha = (W_i - W_t)/(W_i - W_f)$, versus time curve for whole crystals of dehydrated cadmium permanganate isothermally decomposed at 100°C. The figure also shows the Avrami–Erofeyev analysis of the data. This demonstrates the applicability of this equation to the experimental curve.

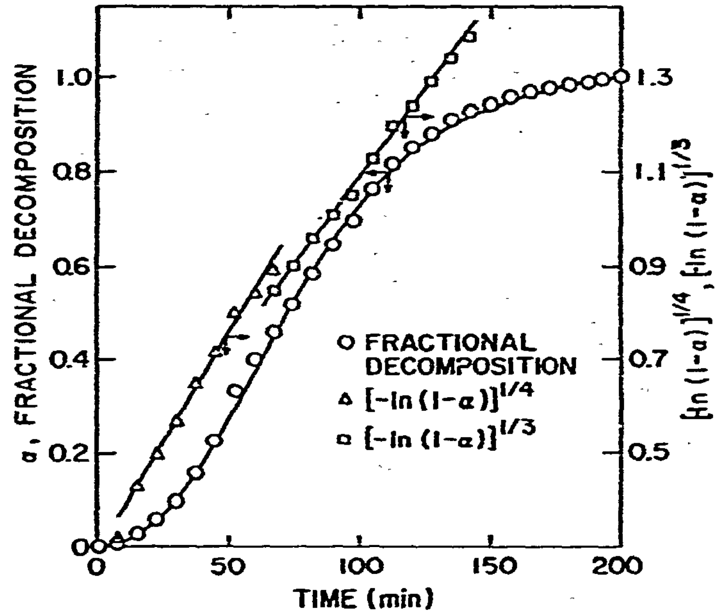

Fig. 14. Fractional decomposition, $\alpha = (W_i - W_t)/(W_i - W_f)$, versus time curve for powdered dehydrated cadmium permanganate crystals isothermally decomposed at 90°C. The figure also demonstrates the applicability of the Avrami–Erofeyev analysis to the experimental curve.

TABLE 5

THERMAL DECOMPOSITION KINETIC RATE CONSTANTS FOR CADMIUM PERMANGANATE, WHOLE AND POWDERED CRYSTALS

	Period	*Thermal decomposition kinetic rate constant (10^{-2} min^{-1})*				
		85°C	*90°C*	*94°C*	*100°C*	*110°C*
Whole crystals	Induction		0.444	0.710	1.08	2.66
			0.460	0.770	1.08	2.59
			0.400	0.700	1.20	2.69
	Acceleratory		0.683	0.970	1.72	4.36
			0.783	0.980	1.75	4.00
			0.689	0.977	1.72	4.37
	Decay		0.320	0.440	0.616	1.60
			0.333	0.450	0.639	1.61
			0.333	0.450	0.600	1.60
Ground crystals	Induction	0.781	1.29		2.81	6.01
		0.769	1.31		2.90	5.92
		0.816	1.33		2.80	5.93
	Acceleratory	0.271	0.561		1.60	4.43
		0.233	0.556		1.55	4.43
		0.264	0.579		1.59	4.33
	Decay	0.156	0.300		0.687	1.57
		0.172	0.315		0.675	1.50
		0.181	0.308		0.689	1.57

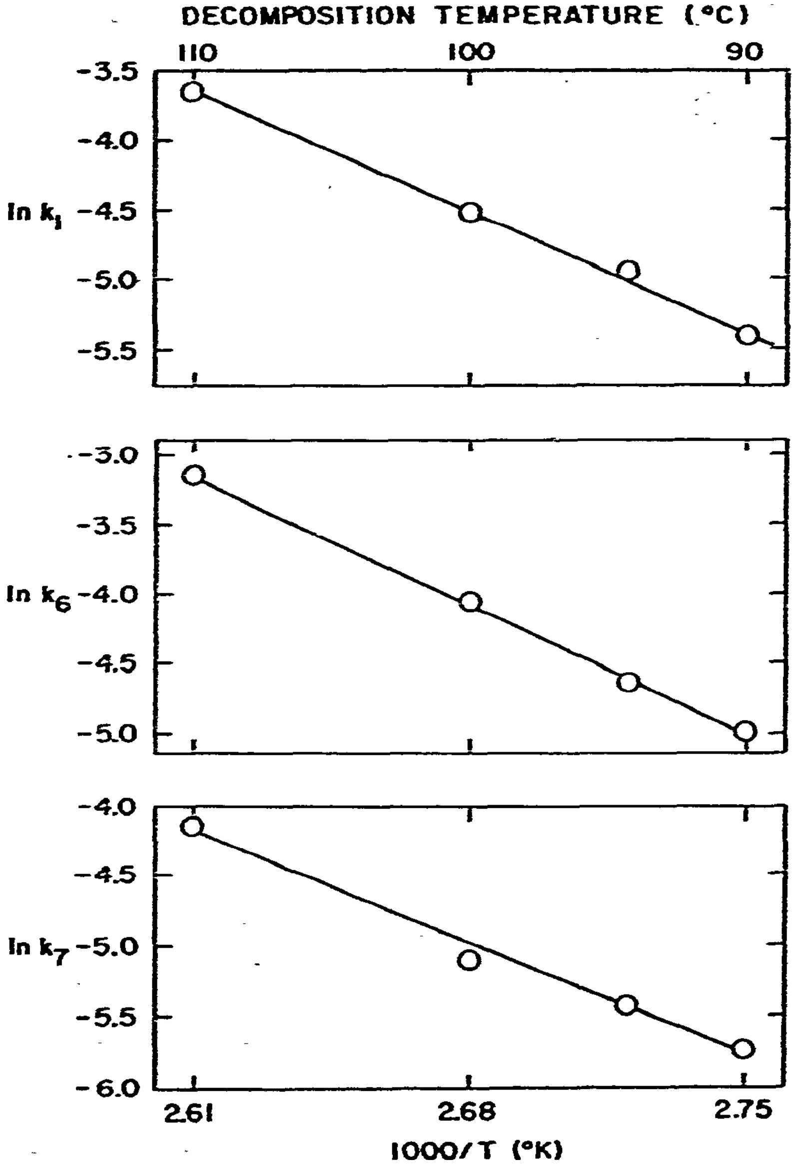

Fig. 15. Plots of ln (rate constant) versus $1/T$ K for the induction (k_1), acceleratory (k_6) and decay (k_7) periods of the thermal decomposition of whole crystals of dehydrated cadmium permanganate.

Cadmium permanganate

The isothermal decomposition of cadmium permanganate, whole crystals and powdered material, was investigated over the temperature range 80–110°C (Figs. 11 and 12, respectively). The curves were sigmoid in shape with an inflexion point between an α values of 0.3 and 0.4 over the whole temperature range. All the curves exhibited an initial linear induction stage followed by acceleratory and decay periods. Since the exponential equation, eqn. (10), fitted only to a limited extent, the A–E

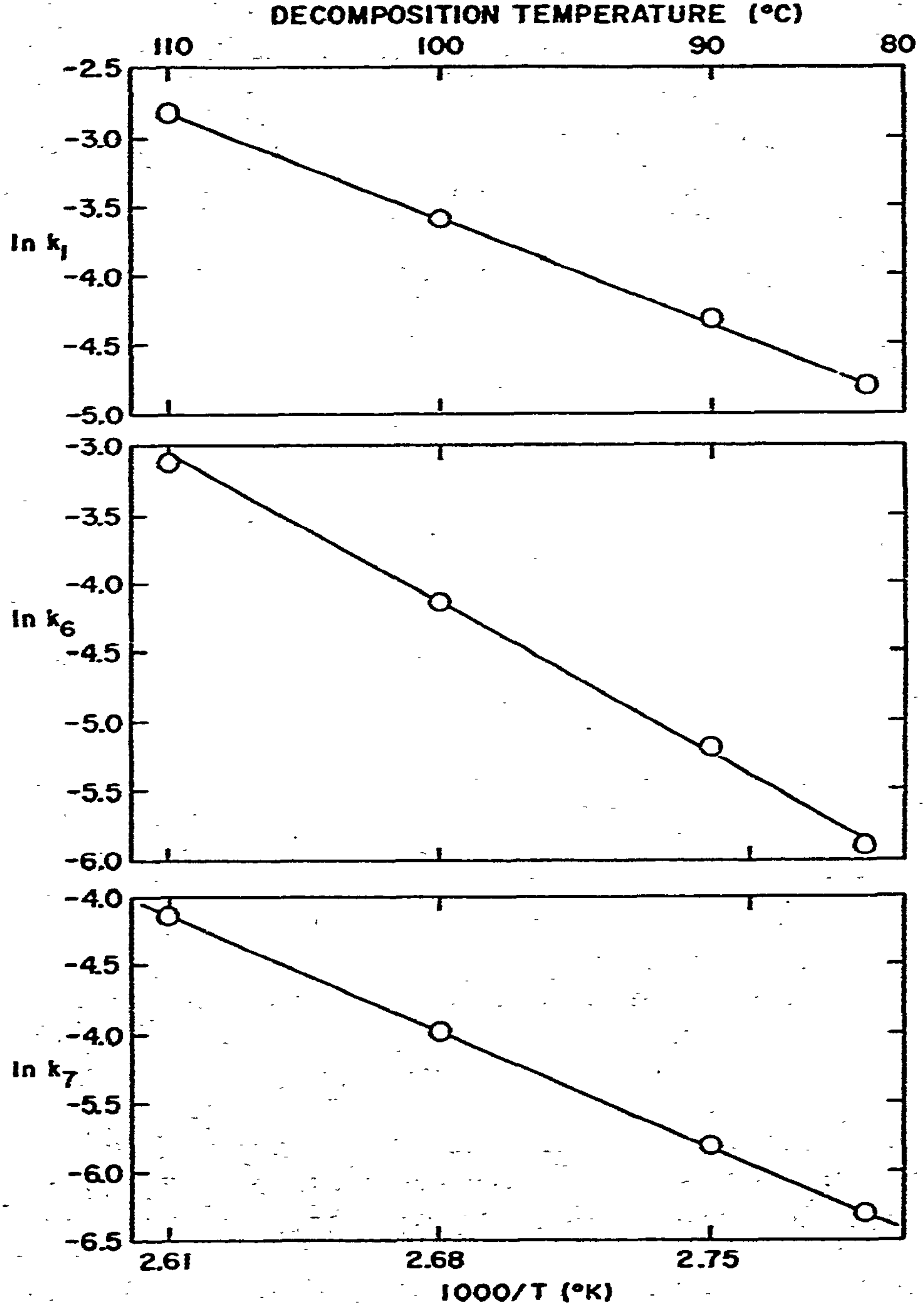

Fig. 16. Plots of ln (rate constant) versus $1/T$ K for the induction (k_1), acceleratory (k_6) and decay (k_7) periods of the thermal decomposition of powdered dehydrated cadmium permanganate crystals.

equation, eq. (3), in the form of eqns. (4) and (5) was used to analyze the data of the acceleratory and decay periods (see Figs. 13 and 14, respectively).

As before, the reproducibility of the results was highly satisfactory (see Table 5). The activation energies were determined for these periods from plots of the ln(rate

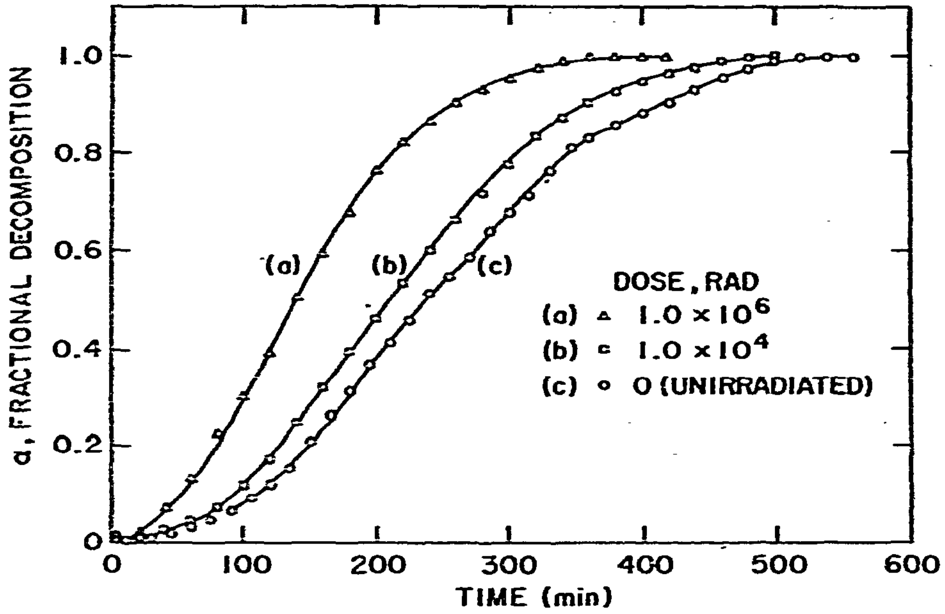

Fig. 17. The effect of 1 × 10^6 and 1 × 10^4 rad gamma-ray doses on the subsequent thermal decomposition of powdered dehydrated cadmium permanganate crystals. The plot shows the fractional decomposition, $\alpha = (W_i - W_t)/(W_i - W_f)$, versus time for ground crystals decomposed at 80°C.

constant) vs. $1/T$ K and are shown in Figs. 15 and 16, respectively. From these plots, activation energies of 21.4 ± 2.9, 25.6 ± 2.2 and 23.2 ± 2.6 kcal/mole were obtained for the induction, acceleratory and decay stages, respectively, for whole crystals and 20.3 ± 3.1, 28.9 ± 2.4 and 28.7 ± 3.2 kcal/mole for the same periods for powder.

The crystals remained intact throughout the decomposition although the color changed from purple-violet to steel-blue.

A preliminary study of irradiation effects was carried out on the isothermal decomposition. Samples were exposed to ^{60}Co gamma-ray doses of 1.0 × 10^6 and 1.0 × 10^4 rad prior to decomposition at 80°C and the results are shown in Fig. 17. The main effect of the irradiation was to reduce the time of the overall reaction, i.e. the induction period was reduced and the rate constants for the acceleratory and decay periods increased. A study of the variation of the rate constants with temperature is presently under way and the results will be reported elsewhere.

Calcium permanganate hexahydrate

A preliminary study was carried out on the isothermal dehydration and decomposition of calcium permanganate. Dehydration studies were attempted at 100°C; however, the results were found to be highly irreproducible. Dehydration time for the removal of the five hydrated water molecules varied from 25 to 95 min, with some indication that the dehydration process occurs in two stages: the first corresponds to the initial removal of two water molecules and the second to the removal of the remainder. However, no quantitative kinetic data could be obtained.

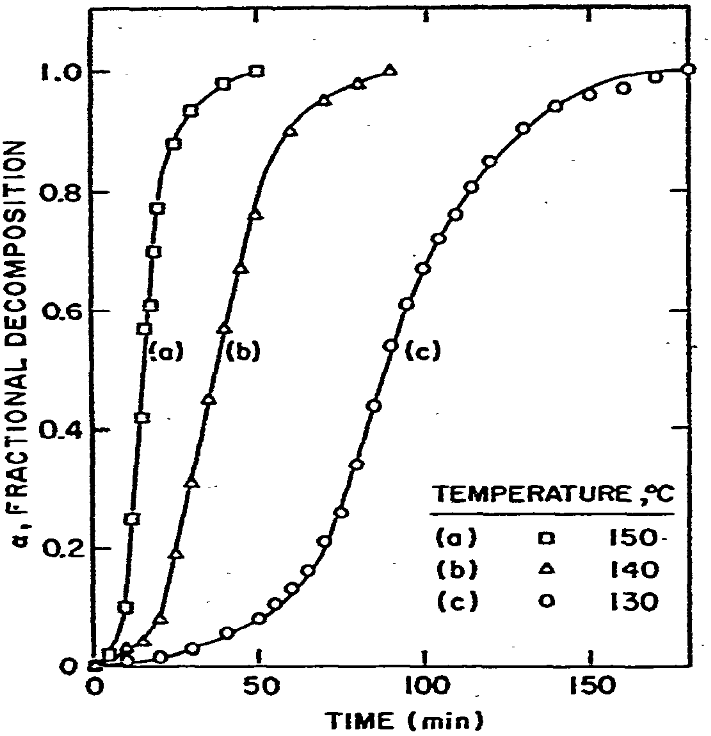

Fig. 18. Effect of temperature on the isothermal decomposition of powdered dehydrated calcium permanganate crystals. This plot shows the fractional decomposition, $\alpha = (W_i - W_t)/(W_i - W_f)$, versus time plots for crystals decomposed between 130 and 150°C.

TABLE 6

THERMAL DECOMPOSITION KINETIC RATE CONSTANTS CALCIUM PERMANGANATE, POWDERED CRYSTALS

Kinetic analysis	*Thermal decomposition kinetic rate constant (10^{-2} min^{-1})*		
	150°C	*140°C*	*130°C*
Linear fit (induction period)	0.710	0.275	0.169
	0.650	0.275	0.152
	0.659	0.276	0.148
P–T (acceleratory period)	3.50	1.90	0.00666
	4.00	1.60	0.00666
	4.00	1.60	0.00600
P–T (decay period)	2.00	1.05	0.450
	1.80	0.983	0.390
	1.66	1.00	0.333

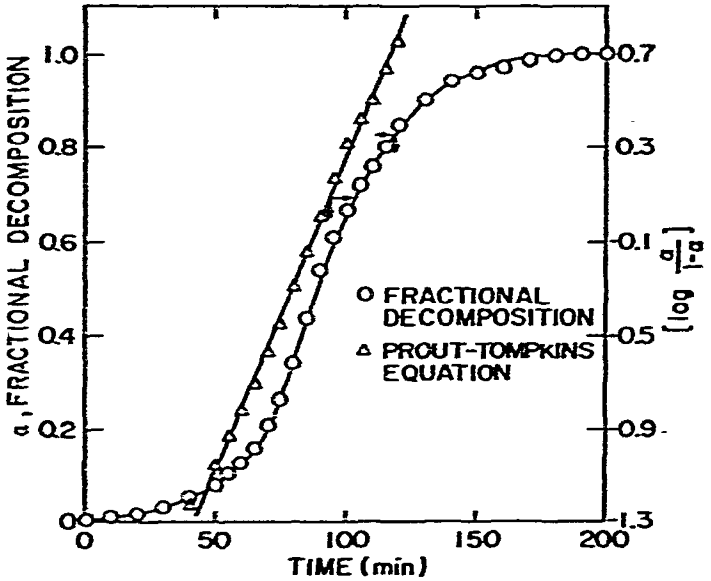

Fig. 19. Fractional decomposition, $\alpha = (W_i - W_t)/(W_i - W_f)$, versus time for powdered dehydrated cadmium permanganate crystals decomposed at 130°C. Also shown in this figure is the Prout–Tompkins analysis of the data demonstrating the applicability of this equation to the experimental curve.

Calcium permanganate

The isothermal decomposition of dehydrated material was investigated on ground crystals over the temperature range 130–150°C (see Fig. 18). The resulting α vs. t curves were sigmoidal in shape with an induction period which was more pronounced than that found for either strontium or cadmium permanganates. The reproducibility of these curves was again found to be satisfactory by comparing their rate constants from three runs at the same temperature (see Table 6).

The Prout–Tompkins equation was found to fit the data best, a typical fit at 140°C being given in Fig. 19, where the extent-of-fit was found to be $0.02 < \alpha > 0.98$. The resulting activation energies for the induction, acceleratory and decay periods were determined to be 29.9 ± 2.6, 30.3 ± 1.3 and 26.1 ± 2.9 kcal/mole, respectively.

DISCUSSION

The chemical purity of all the permanganates discussed in this paper was found to be below 97%. Several reasons may be suggested for these low values. Firstly, the observed impurity levels could have resulted from samples which were easily reduced under normal atmospheric conditions. Secondly, the strontium, calcium, and cadmium permanganate crystals are very hygroscopic. During the weighing procedure, even under carefully controlled environmental conditions, the crystals could have absorbed additional water. The recorded weight would be proportionally higher and the resulting purity of the materials thus lowered. Thirdly, even after several recrystallization steps, some chemical impurities remain in the crystals. On many occasions during recrystallization, a surface scum was observed to form. Attempts were made repeatedly to remove the surface layer but some oxidized material could have adhered to the crystallites as impurities. (The thin scum-like layers were assumed to be oxidized material.) It is important to note that the thermal dehydration and decomposition kinetics have been examined under the described limitations.

The thermal dehydrations

The dehydration of strontium trihydrate and cadmium hexahydrate occurs as a sequential series of dehydration steps. No induction period is observed in either material for the process of removal of water molecules. Both compounds appear to lose two water molecules initially with a very small required activation energy.

For ground crystals of strontium permanganate trihydrate, the dehydration was examined using a linear weight loss vs. time relation for the initial stage, and the Avrami–Erofeyev decay equation for the later period. The initial weight loss in the sample probably corresponds to nuclei generation on the external crystal surfaces. Presumably the nuclei can form initially only at a select number of sites on the surface, since the whole process involves only two water molecules. At first, it would seem that only certain sites are involved also within the bulk. The kinetic results indicate that during the stage of initial nucleation the number of nuclei were directly proportional to time. This could occur if a single dehydration nucleus were formed in one step by the loss of a certain configuration (e.g. a pair) of water molecules at specific type sites. Experimentally, the second dehydration stage would appear to involve additional energy. At this time, it would be reasonable to question why two water molecules were easier to remove than the third. A possible explanation can be proposed using the X-ray data of Ferrari et al.[16]. One water molecule is found to be located near the strontium cation at a distance to 2.573 Å, and other two water molecules are located nearest to an oxygen atom with the same distance, 3.097 Å, between them and the oxygen atom. Both of these water molecules are on the same (211) plane. Thus it would appear that the two molecules located near the oxygen are probably less tightly bonded than the one closer to the cation, suggesting that these two water molecules are easier to extract than the third.

For whole crystals, the x vs. t dehydration curves contain no well-defined point for partial removal of the water molecules. In these crystals, the dehydration nuclei presumably form by the same process as for the powder but grow at such a rate as to be indistinguishable from each other kinetically.

The dehydration results for powdered cadmium permanganate were analyzed using the exponential equation for the initial and the unimolecular decay equation for the final stages. Presumably the dehydration nuclei form and grow at a surface in a successive, non-overlapping progression. The activation energies were determined to be 1.3 ± 1.0, and 11.9 ± 1.5 kcal/mole for the initial and the final stages, respectively.

Although a preliminary study of the dehydration kinetics was attempted for calcium permanganate pentahydrate, no analysis was possible due to the irreproducibility of the results. However, there is some evidence that a partial dehydration occurs involving two water molecules.

The thermal decomposition processes

The nucleation process occurring during the thermal decomposition of whole and ground crystals of dehydrated strontium permanganate can be explained since the acceleratory and decay periods fit the Prout–Tompkins equation. This indicates that, after an initial induction period corresponding to formation of the nuclei on the external surfaces, the acceleratory period begins with the growth of these nuclei on the surface and the decomposition progresses uniformly into the bulk of the material. This is evidenced by the smooth transition from the induction period into the acceleratory stage. Subsequently, the reaction spreads into the crystal by a system of branching chains.

The decomposition process might occur in several ways. For example, a number of molecules of reactant, whose decomposition was highly favored, could decompose and form product nuclei on the surface. These product nuclei would produce localized strains in the crystal, which are ultimately relieved, for example by the formation of Smekal cracks[13]. Nuclei formation would be favored at or near the strain zones associated with these cracks. The reaction could therefore spread into the crystal down the cracks. The newly cracked and reacted surface array would set up, in turn, lattice strains leading to further cracking. Thus the reaction would penetrate still further into the crystal as the phenomenon is repeated, producing a series of branching nuclei. However, the branching would not be determined solely by the crystal or the size of the ultimate Smekal blocks[14]. Inherent impurities could also influence the decomposition path. Eventually the crystal would consist of small unreacted blocks or grains of material. These small grains would decompose by a contracting interface mechanism. For the crystals in the present study, probably because of the large adherent grains formed during dehydration, the composite particles were sufficiently resilient to the onset of the induced volume of product formation to remain intact throughout the decomposition.

Comparing the various materials used in this decomposition study, it will be noted that the values of the activation energies for both the acceleratory and decay stages of each decomposition are, within experimental error, the same for the same material. However, the induction period activation energies tend to be lower. These lower values are presumably associated with the formation of nuclei at surface sites which require a lower energy for formation than in the bulk.

The preliminary studies on the effects of ^{60}Co gamma-ray radiation on the thermal decomposition of both whole and ground crystals produced several interesting results. Firstly, decomposition was accelerated by the irradiation. Secondly, the radiation did not appear to have influenced the quantity of material which was decomposed. For $Sr(MnO_4)_2$ whole crystals (1×10^6 rad), the percentage decomposition was 93.2 ± 1%, and for ground crystals (1×10^6 rad), it was 93.0 ± 1%. For $Cd(MnO_4)_2$, the percentage decomposition for ground crystals (1×10^6 rad) was

97.9 ± 1%. The same kinetic expressions fit the pre-irradiated α vs. t data as for the case of the unirradiated crystals. The resulting rate constants exhibit an increase over the unirradiated equivalent, and, in general, increase monotonically. Presumably increasing the dose of ionizing radiation produces, in turn, additional electronic species (electrons and holes) which are available for conversion into additional thermal nuclei, e.g. at sites where dislocations intersect the surface, or they can form aggregates, or these species might migrate to previously unreactive centers, such as benign impurities and form nuclei.

For the case of cadmium permanganate, the thermal decomposition kinetics of both whole and ground crystals were analyzed with Avrami–Erofeyev kinetics. The main failure of the Prout–Tompkins equation was due to the fact that the inflexion point did not rigorously occur at $\alpha \simeq 1/2$. Again, as for strontium permanganate, the

TABLE 7

ACTIVATION ENERGIES OF THE THERMAL DECOMPOSITION PROCESSES IN ALKALI AND ALKALINE EARTH PERMANGANATES

		Activation energy (kcal/mole)		
		Induction period	*Acceleratory period*	*Decay period*
*$LiMnO_4$ (dehydrated)	Whole	22.8	32.4	31.6
	Powdered	22.6	33.3	30.4
*$NaMnO_4$ (dehydrated)	Whole		28.6	31.9
	Powdered		31.3	30.5
*$KMnO_4$	Whole	25.5	38.5	38.8
	Powdered		38.5	33.1
$Ca(MnO_4)_2$ (dehydrated)	Whole			
	Powdered	29.9	30.3	26.1
*$RbMnO_4$	Whole	31.4	39.5	40.2
	Powdered		38.3	39.3
$Sr(MnO_4)_2$ (dehydrated)	Whole	25.9	34.9	32.2
	Powdered	29.5	33.7	32.6
*$AgMnO_4$	Whole	21.4	25.6	23.2
	Powdered	20.3	28.9	28.7
$Cd(MnO_4)_2$ (dehydrated)	Whole	21.4	25.6	23.2
	Powdered	20.3	28.9	28.7
*$CsMnO_4$	Whole	33.7	40.0	33.6
	Powdered		40.8	35.1
*$Ba(MnO_4)_2$	Whole		36.1	29.6
	Powdered		36.9	34.2

* See ref. 1.

induction period is linear, i.e. the rate of nuclei formation is constant. Presumably the lower activation energies for this period are associated with the formation of *surface* nuclei.

For the pre-irradiated studies on cadmium permanganate, the doses used were 1×10^4 and 1×10^6 rad. Even after a 1×10^6 rad irradiation, the reaction rate was only slightly faster than for the unirradiated material. It was not obvious why this material should be more "resistant" to irradiation. Factors which might be influential in affecting this stability include the ion co-volumes, the stability of electron traps, as well as others. Another possible explanation of this effect might be that many of the electron–hole pairs formed during the irradiation are unstable at room temperature and are thermally annealed and thus do not contribute to nucleation.

For calcium permanganate, the thermal decomposition kinetics of ground crystals are well fitted by the Prout–Tompkins equation over the acceleratory and decay stages. The inflection point occurs at $\alpha \simeq 1/2$, and the extent-of-fit of the equations showed that the curves fit over a wide range (e.g. from $\alpha = 0.07 \sim 0.98$) at all temperatures. The activation energies of the linear induction period, the acceleration and decay stages were all found, within experimental error, to be the same, suggesting that the same chemical process was operative over each stage.

It is thus concluded that strontium, cadmium, and calcium permanganates are similar in behavior to all of the alkali-earth permanganates so far investigated. As found previously, the resulting α vs. time decomposition curves are sigmoidal in shape, all containing an induction, acceleratory and decay stage. These stages are shortened by exposure to ionizing radiation prior to decomposition. Furthermore, the kinetic data can be described by equations similar to those fitted previously to lithium[1], sodium[1], potassium[2, 3], caesium[4], barium[5] and silver[6] permanganates. The activation energies for the induction, acceleratory and decay periods are not markedly different from the other permanganates (see Table 7). Detailed studies of the effects of preirradiation are underway and will be reported elsewhere.

REFERENCES

1 E. G. Prout and P. J. Herley, *J. Phys. Chem.*, 66 (1962) 961.
2 E. G. Prout and F. C. Tompkins, *Trans. Faraday Soc.*, 40 (1944) 488.
3 P. J. Herley and E. G. Prout, *J. Phys. Chem.*, 64 (1960) 675.
4 P. J. Herley and E. G. Prout, *J. Chem. Soc. A*, (1959) 3300.
5 E. G. Prout and P. J. Herley, *J. Phys. Chem.*, 65 (1961) 208.
6 E. G. Prout and M. J. Sole, *J. Inorg. Nucl. Chem.*, 9 (1959) 232.
7 P. J. Herley, P. W. M. Jacobs and P. W. Levy, *J. Chem. Soc. A*, (1971) 434.
8 P. J. Herley, P. W. M. Jacobs and P. W. Levy, *Proc. Roy. Soc. London, Ser. A*, 318 (1970) 197.
9 P. J. Herley and P. W. Levy, in *Reactivity of Solids*, 8th Int. Symp., Plenum Press, London, 1977, p. 355.
10 P. W. M. Jacobs and H. M. Whitehead, *Chem. Rev.*, 69 (1969) 551.
11 P. J. Herley and P. W. Levy, *J. Chem. Phys.*, 49 (1968) 1493, 1500.
12 D. A. Young, *Decomposition of Solids*, Pergamon Press, London, 1966.
13 A. Smekal, *Phys. Z.*, 26 (1925) 707.
14 W. E. Garner and H. R. Hailes, *Proc. Roy. Soc. London, Ser. A*, 139 (1933) 576.
15 F. H. Herbstein, G. Ron and A. Weissman, *J. Chem. Soc. A*, (1971) 1821.
16 A. Ferrari, A. Braibante, G. Bigliardi and A. M. Lanfredi, *Acta Cryst.*, 21 (1966) 681.