669. *The Thermal Decomposition of Cæsium Permanganate.*

By P. J. Herley and E. G. Prout.

The thermal decomposition of whole and ground crystals of cæsium permanganate has been investigated in the range 240—285°, and the activation energies for the acceleratory and decay coefficients have been measured. The results are in agreement with the theory proposed for the decomposition of potassium permanganate. The effect of pre-irradiation by ^{60}Co γ-rays is similar to that found for pre-irradiated potassium and silver permanganate.

Both the acceleratory and decay periods of the decomposition of potassium permanganate [1] can be represented by Prout and Tompkins's equation:

$$\log_{10}[p/(p_f - p)] = k_2t + c \qquad \ldots\ldots \quad (1)$$

where p_f is the final pressure. The equation has been derived theoretically on the basis of a branching mechanism for the reaction. In the acceleratory period the surface array of product molecules produces lateral strains which are relieved by cracks along which nuclear formation is favoured. The reaction therefore spreads into the crystal down these crevices and covers the inner surfaces with product molecules. The cracking process is repeated on these surfaces and the reaction proceeds through the solid by a system of branching planes of decomposed material. These ultimately interfere, and after the time of maximum velocity the rate is controlled by the number of unchanged permanganate molecules which are contiguous to product molecules.

With silver permanganate [2] Prout and Tompkins's equation is applicable to the acceleratory period only up to $\alpha \approx 0{\cdot}10$. However, if the branching coefficient varies inversely as time, eqn. (1) is transformed into the modified equation:

$$\log_{10}[p/(p_f - p)] = k \log t + c \qquad \ldots\ldots \quad (2)$$

which describes the complete pressure–time curve.

The purpose was to examine the validity of the application of these equations to the decomposition of cæsium permanganate. As well, a knowledge of the kinetics of decomposition of unirradiated cæsium permanganate was necessary for work on the effects of pre-irradiation on permanganates.

Experimental and Results

Rhombic bipyramidal crystals of cæsium permanganate (0·5 mm. × 0·3 mm.) were obtained by adding the nitrate (B.D.H.; 5 g.) and potassium permanganate ("AnalaR"; 4 g.) to water (60 ml.) at 60° and then cooling to 0°. The crystals were twice recrystallized. Large single crystals could not be prepared and "whole" crystals refers to a mass of ~20 mg. of small crystals. The apparatus was similar to that previously described.[1]

The reproducibility of the pressure–time plots for whole crystals was good. For three consecutive runs at 250° the value of k_1 (eqn. 3) was 8·78, 8·76, 8·75 × 10^{-4}, and k_2 (eqn. 1) was 1·74, 1·75, 1·72 × 10^{-2} in the acceleratory periods. Over the decay period k_2 (eqn. 1) was 2·19, 2·17, 2·20 × 10^{-2}.

The pressure–time plots (Fig. 1) show an initial slow acceleration followed by a rapid increase. The decay stage takes the usual form. With ground crystals the slow acceleration is absent and the plots show only the rapid acceleration and decay (Fig. 2).

The pressure–time plots for whole and ground crystals are unaltered if the reaction is interrupted by sudden cooling and subsequent reheating to the original temperature after 3 hr. Likewise, the addition of end products did not affect the decomposition of whole or ground crystals. Exposure to ultraviolet light or bombardment with cathode rays (applied potential

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[1] Prout and Tompkins, *Trans. Faraday Soc.*, 1944, **40**, 488.

[2] Prout and Tompkins, *ibid.*, 1946, **42**, 482.

25 kv; residual oxygen pressure 1·5 × 10^{-3} cm.) at room temperature before decomposition had no effect. However, exposure to γ-rays from a ^{60}Co source (dose 3·3 Mrad) caused a pronounced change in the pressure–time plot of whole crystals (Fig. 3). A detailed study of the effects of pre-irradiation is in progress.

The percentage decomposition, in terms of the equation:

$$4CsMnO_4 \longrightarrow 2Cs_2O + 4MnO_2 + 3O_2$$

was 96·2% and 90·4% for whole and ground crystals, respectively. Variations of temperature or mass did not significantly affect these percentages.

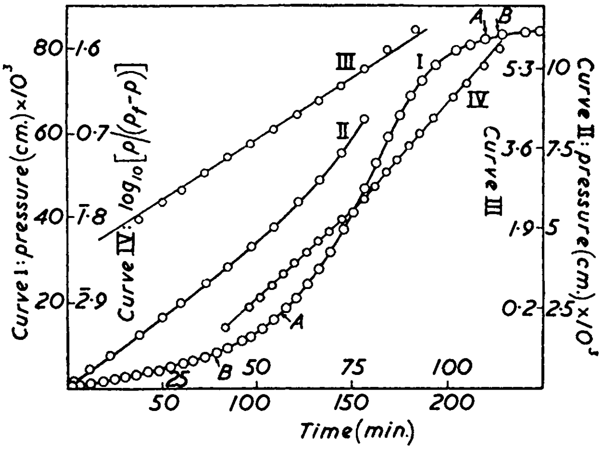

FIG. 1. *Curves* I *and* II: *Pressure–time plots for decomposition of whole crystals of* $CsMnO_4$ *at* 250°, *and the initial portion of* I *respectively. Curves* III *and* IV: *Plots of* $p^{\frac{1}{2}}$ *against t, and Prout and Tompkins's equation, respectively.*

Lower time scale refers to curves I and IV; upper time scale refers to curves II and III.

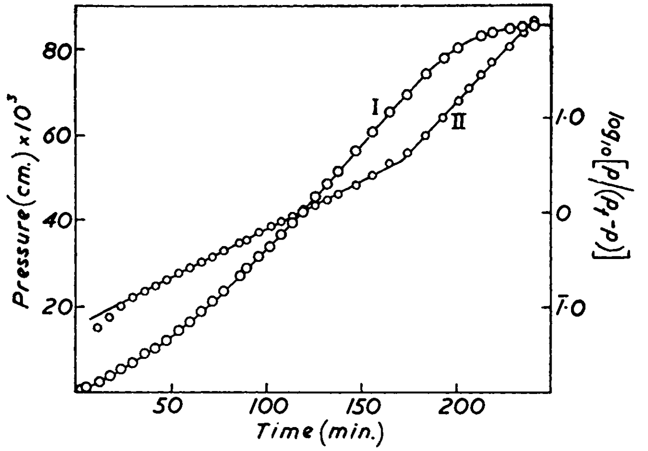

FIG. 2. *Curve* I: *Pressure–time plot for decomposition of ground crystals of* $CsMnO_4$ *at* 250°. *Curve* II: *Plot for Prout and Tompkins's equation.*

Because of the small size of the crystals it was not possible to follow the decomposition visually, but specimens were removed at various times during the reaction and examined microscopically. It was concluded that no significant fracturing of the crystals occurred from the start of the decomposition until just before the onset of decay. At this point (~150 min. for curve I, Fig. 1) disintegration occurred. The particles were of various sizes but the approximate average was 0·07 mm. × 0·05 mm. No further disintegration took place during the decay period.

The power law

$$p^{1/n} = k_1t + c \quad . \; . \; . \; . \; . \; . \; . \; . \; . \quad (3)$$

applied to whole-crystal decompositions during the slow acceleration, for $n = 2$. The plot of $p^{\frac{1}{2}}$ against t and an enlarged plot of p against t for this period are shown in Fig. 1. For both whole- and ground-crystal decompositions Prout and Tompkins's eqn. (1) was valid for the main acceleratory and decay periods (Figs. 1 and 2, respectively). The extent of applicability

(*AA*) in the case of whole crystals was improved (*BB*) if the origin was transferred to the pressure and time values corresponding to the end of the period of slow acceleration. This point corresponds to the point of departure from linearity of the plot of $p^{\frac{1}{2}}$ against t. This was done for the analyses of all pressure–time curves.

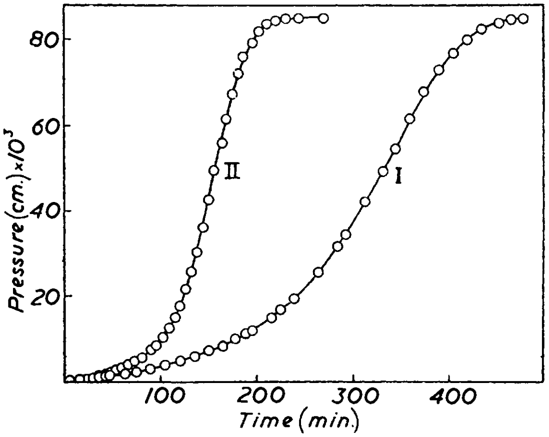

FIG. 3. *Effect of pre-irradiating whole crystals of* $CsMnO_4$ *with* ^{60}Co γ*-rays (dose 3·3 Mrad). Curve* I, *unirradiated; and curve* II, *irradiated crystals decomposed at 240°.*

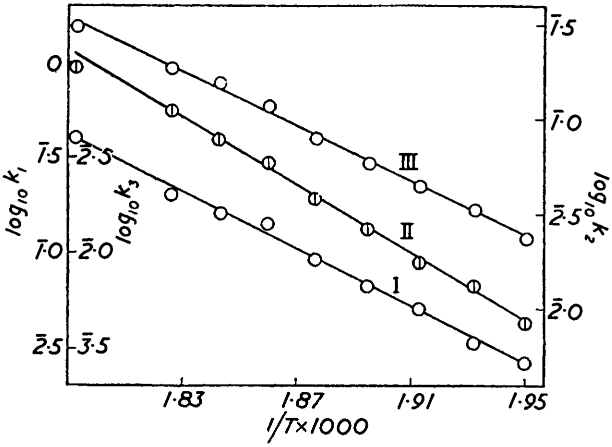

FIG. 4. *Activation energy plots for whole crystals of* $CsMnO_4$. I, *log* k_1; II, *log* k_2; III, *log* k_3; *against* $1/T$ (°K).

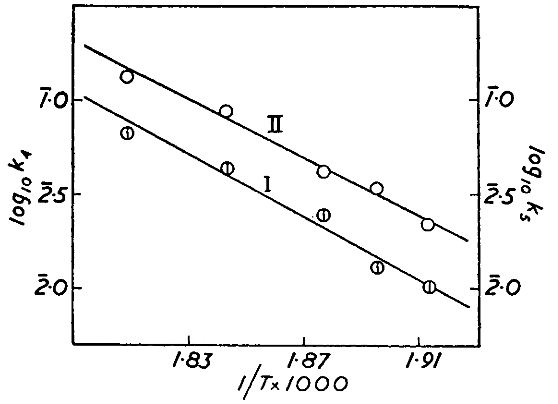

FIG. 5. *Activation energy plots for ground crystals of* $CsMnO_4$. I, *log* k_4; II, *log* k_5; *against* $1/T$ (°K).

The plots of the $\log_{10}$ values of k_1, k_2, k_3, k_4 and k_5 against $1/T$(°K) are well-defined straight lines (Figs. 4 and 5). The activation energies calculated from these plots for whole crystals are 33·7 kcal./mole for the slow acceleration, 40·0 kcal./mole for the rapid acceleration, and

33·6 kcal./mole for the decay. The values for the acceleratory and decay periods for ground crystals are 40·8 kcal./mole and 35·1 kcal./mole, respectively.

DISCUSSION

The decomposition of cæsium permanganate resembles that of potassium and silver permanganate in that, (i) a molecular chain theory involving degenerate branching is improbable, (ii) since irradiation with ultraviolet light and bombardment with cathode rays have no effect on the subsequent decomposition a mechanism of photochemical reduction, as with barium azide, is unlikely, (iii) Prout and Tompkins's theory of branching reaction planes is feasible, and (iv) the thermal decomposition is altered in a similar way by pre-irradiation with 1·3 Mev γ-rays.[3] The kinetics, however, resemble those of potassium permanganate rather than silver permanganate since eqn. (1) describes the characteristics of the pressure–time curves.

The initial slow acceleration of the reaction is of interest. The fit of the square-root plot in this region indicates the growth of two-dimensional nuclei, probably on the crystal surfaces. The negative intercept on the abscissa of the plot of $p^{\frac{1}{2}}$ against t shows that initially the growth of the two-dimensional nuclei is abnormally fast. At the end of the period of slow acceleration, if the crystal faces are covered with a layer of product, strain will be produced in the surface of the reactant. This strain, it is suggested, is relieved by the formation of cracks down which the reaction spreads into the crystal. Thereafter, the reaction proceeds as suggested by Prout and Tompkins.

The non-appearance of the slow acceleration with ground crystals is due to the creation during grinding of a large number of centres from which nuclei grow. These cover the surface very shortly after the commencement of heating. The failure of Prout and Tompkins's equation over a small portion of the curve in the early stages of the decomposition of ground crystals is probably due to the evolution of the gas resulting from this rapid surface coverage.

The improved fit of Prout and Tompkins's equation on transferring the origin is expected, since their mechanism operates after the surface is covered by product.

The difference in the activation energies of the acceleratory and the decay period is possibly associated with the diffusion of the oxygen through the network of cracks formed in the crystal during the main acceleratory period. Reaction during that period comprises the liberation of oxygen at the reactant–product interface and its diffusion through the solid and along the cracks. If the crystal collapses along these cracks just before the onset of the decay stage then during this final stage diffusion along cracks will be absent, since the reaction proceeds by a non-branching mechanism. The measured activation energy will be that for the liberation of oxygen and its diffusion through the solid. It is to be noted that the activation energy over the slow acceleratory period, when the reaction is possibly confined to the growth of two-dimensional nuclei on the external surface, corresponds to the activation energy for the decay period.

Roginsky *et al.*[4] measured the temperature (potassium permanganate, 255°, and cæsium permanganate, 260°) at which the maximum velocity was reached in the same time (120 min.). By using the value 38·6 kcal./mole for whole crystals of potassium permanganate the calculated heat of activation for whole crystals of cæsium permanganate is 39·0 kcal./mole, which is in good agreement with the value found here.

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RHODES UNIVERSITY, GRAHAMSTOWN, SOUTH AFRICA. [*Received, March* 20*th*, 1959.]

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[3] Prout, *J. Inorg. Nuclear Chem.*, 1958, **7**, 368.
[4] Roginsky, Elovich, and Shmuk, *Izvest. Akad. Nauk S.S.S.R., Otdel. khim. Nauk*, 1950, 469.