820. *The Early Stages of the Thermal Decomposition of Potassium Permanganate–Potassium Perchlorate Solid Solutions.*

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The kinetics of the early stages of the isothermal decomposition of potassium permanganate–potassium perchlorate solid solutions have been investigated at temperatures between 187° and 237°, where only the permanganate component decomposes. In general, the reaction involved successively a sigmoid, constant-rate, and a t^2-power-law stage, with finally a main acceleration stage which was either of the exponential or the power-law type. The presence of the perchlorate was found to retard the first three stages more than the fourth. Activation energies for the stages have been determined and mechanisms are proposed. Influence on activation energies of the heat of formation of the solid solutions from the solid components, first considered by Hinshelwood and Bowen, has been shown to be insufficient to account for the observed inhibition by perchlorate.

Hinshelwood and Bowen [1] have shown that thermal decomposition of potassium permanganate–potassium perchlorate solid solutions is autocatalytic and that at *ca.* 200° only the permanganate decomposes. They explained the accelerating rate stage of the decomposition in terms of a progressive disintegration of the crystals with a consequent increase in the effective reaction interface. The slower rate of decomposition of the solid solutions than of the pure permanganate was attributed to increased stability of the permanganate ion when in presence of perchlorate, the increased stability being related to the heat of formation of the solid solutions from the pure components. It is now well established (see Hill and Welsh [2]) that the kinetics of the early stages of the solid-state decomposition of the pure permanganate are greatly affected by the method of preparation, the age of the crystals, and the presence of impurities. The following work on solid solutions was therefore carried out with crystals freshly prepared by a standardised procedure, and the extent of decomposition was limited to about 7% with respect to the permanganate content, in an attempt to establish in greater detail the influence of the perchlorate ion on the kinetics and mechanism of the early stages of the decomposition.

EXPERIMENTAL

Preparation of Crystals.—Potassium permanganate. A solution (500 c.c.) of " AnalaR " potassium permanganate saturated at 60°, after cooling to room temperature in the dark and filtering through a No. 4 porosity sintered-glass filter-funnel, was allowed to evaporate in air in the dark for 12 hr., and the supernatant liquid was then decanted. The crystals were dried as quickly as possible with filter paper, and those of linear dimensions 0·3—0·5 mm. were selected by gentle sieving. Two samples, A and B, were prepared. Crystals of approximate size 10 × 1 × 1 mm. (sample C) were obtained by prolonging the evaporation time and were selected by hand.

Potassium permanganate–potassium perchlorate solid solutions. Greenberg and Walden [3] have shown that potassium permanganate and potassium perchlorate form one continuous series of solid solutions, and by use of their solubility data saturated solutions were prepared such that on evaporation in a current of air in the dark at room temperature the solid phase deposited had the desired composition. We limited the total weight of crystals deposited from 2500 c.c. of saturated solution to not more than 1 g., and so the composition of the solution phase remained virtually constant and homogeneity of the solid solutions obtained was ensured. Separation, drying, and sieving of the crystals were carried out as for the pure permanganate, and standard volumetric analytical procedure was used to determine the permanganate content of the crystals. In this way, solid solutions containing 11, 30, and

[1] Hinshelwood and Bowen, *Proc. Roy. Soc.,* 1921, *A,* **99**, 203.
[2] Hill and Welsh, *Trans. Faraday Soc.,* 1960, **56**, 1059.
[3] Greenberg and Walden, *J. Chem. Phys.,* 1940, **8**, 645.

48 moles % of potassium perchlorate were prepared and are designated D, E, and F, respectively. Crystals of the required size containing 75 moles % of perchlorate (sample G) could not be obtained by the slow-evaporation procedure, but were obtained by cooling a saturated solution of the appropriate composition from 35° to room temperature.

All the above samples of crystals were stored in a desiccator in the dark and were used within a few days of their preparation. With the exceptions of sample G, which was markedly inferior, and sample A, which was a little inferior to B, all the crystals were well formed and free from all but minor surface imperfections.

Thermal Decomposition Procedure.—The apparatus and experimental procedures were very similar to those already reported.[4] The quantities of solid used and the volume of the system were chosen so that the oxygen pressure after *ca.* 7% of the permanganate had decomposed was *ca.* 0·1 mm., which corresponded to 10 in. deflection on the recorder coupled to the Pirani gauge. Thus at any given time (t) during a decomposition, and by use of the equation $2KMnO_4 \longrightarrow K_2MnO_4 + MnO_2 + O_2$ to calculate the final oxygen pressure,[5] the fraction (α) of the permanganate decomposed could be determined to better than 0·0003. Experiment showed that, for temperatures not greater than 237° and with $\alpha \leqslant 0·1$, no decomposition of the perchlorate occurred, as judged from the absence of chloride in the solid decomposition products. Isothermal decompositions were carried out at temperatures in the range 187—237°.

Analysis of Oxygen Pressure–Time Curves.—The differential method of Hill and Welsh[2] was found to be the most accurate and sensitive, rates of decomposition being determined by drawing tangents directly to the continuous recorder traces. Plots of rate against time and of $(\text{rate})^{\frac{1}{2}}$ against α give straight lines for results which conform to the power-law equation $\alpha - \alpha_0 = k_n(t - t_0)^n$ with $n = 2$ and 3, respectively, while the graph of rate against α is the corresponding plot for the exponential equation $\alpha - \alpha_0 = \text{Const. exp } [k(t - t_0)]$. This method of plotting the results allows the rate constants k_n and k to be obtained independently of the values of the arbitrary parameters α_0 and t_0. All rates (including R and k_1, see below) were expressed in terms of α.

RESULTS AND DISCUSSION

The α–t curves could be divided into four sections on the basis of the kinetic analysis. In most cases, an initial sigmoid section (I) was followed by a constant-rate stage (II), then a power-law section (III) with $n = 2$, and finally the main acceleration stage (IV). Typical results are given in Figs. 1, 2, and 3, where the letters on the curves correspond to the sample designations.

Stage I is considered to be due to rapid decomposition at active sites involving subgrains at and near the surfaces of the crystals. For samples A and B, the stage terminated at $\alpha = ca.$ 0·006, and it is significant that for C (single crystal, low surface area) stage I was absent, being replaced by a gradually increasing rate up to $\alpha = ca.$ 0·006, while for the poorly formed crystals G stage I extended to $\alpha = ca.$ 0·01. Through the series B to F, where all the crystals were well-formed, the extent of stage I progressively decreased to $\alpha = ca.$ 0·0015 as the concentration of perchlorate increased, indicating a gradual decrease in the number of active sites. Owing to the relatively small extent of stage I for the majority of the samples, the kinetics could not be examined in detail, and only the maximum rates R were calculated and are discussed below.

Stage II corresponds to the linear progression into the crystals of a constant-area reaction interface, which was most probably developed during the previous stage of the decomposition. In terms of α, the extent of stage II was approximately equal to that of stage I for all samples except C and G. For C, the constant rate occurred over the range $\alpha = ca.$ 0·006—0·036, while for G no constant rate was found. Values of the constant rates are designated below by k_1.

If the reaction, in addition to penetrating into the crystallite bulk, begins to spread rapidly down previously undecomposed subgrain boundaries, so nucleating the subgrain surfaces, the reaction interface area could increase linearly with time, giving rise to the

[4] Taylor, *J.*, 1955, 1033; 1958, 2378, 3323; 1962, 1047.
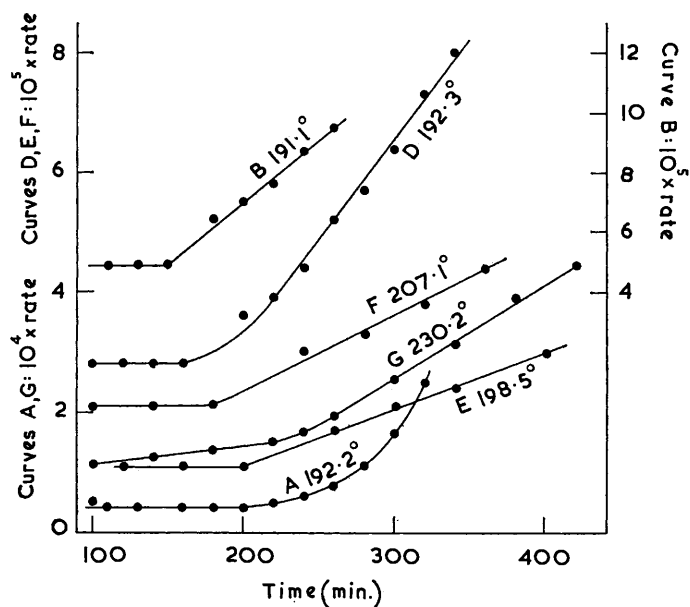[5] Prout and Tompkins, *Trans. Faraday Soc.*, 1944, **40**, 488.

Fig. 1. Rate–time curves illustrating the constant-rate and t^2-stages. A, B = pure permanganate; D, E, F, G = solid solutions containing 11, 30, 48, 75 moles % of perchlorate, respectively.
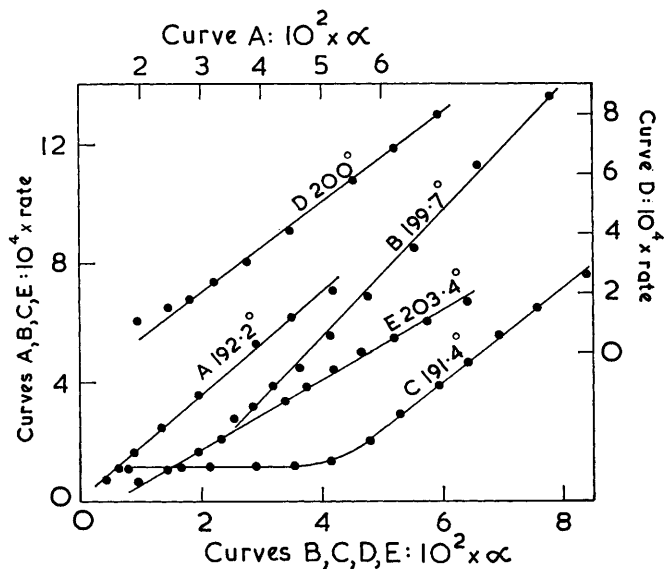

Fig. 2. Rate–α curves illustrating the exponential-law stage. The constant-rate stage for sample C is also shown.

observed power-law kinetics with $n = 2$ for stage III. The rate constant k_2 thus contains the product of the rate constants for movement of the interface into the subgrains and for propagation of the reaction along subgrain boundaries. Such a mechanism is similar to
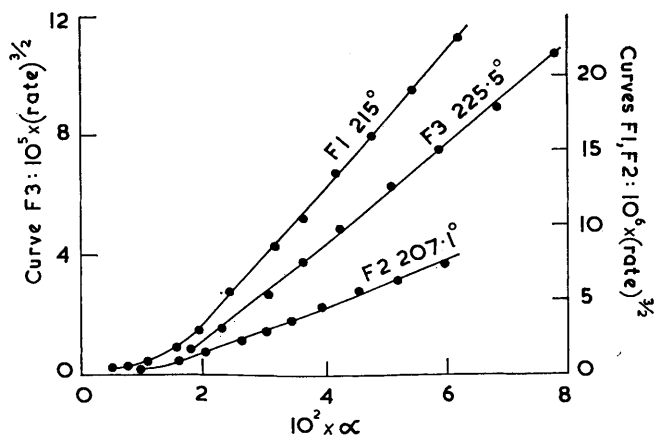

FIG. 3. (Rate)$^{\frac{2}{3}}$–α curves illustrating the power-law ($n = 3$) stage for sample F.

that envisaged by Tompkins and Young [6] for the dehydration of small crystals of barium styphnate monohydrate. The fraction of the permanganate decomposed during this third stage varied between two and four times that involved in the sum of stages I and II, so that the first three stages were completed when α was *ca.* 0·025 for B and G, which value
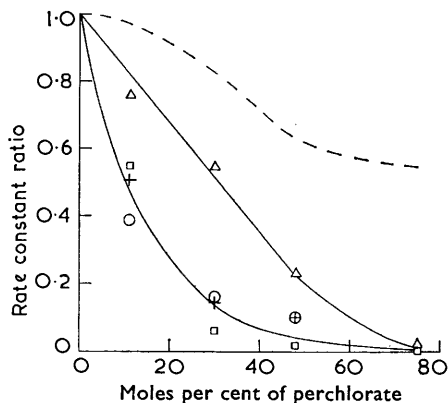

FIG. 4. Plot of rate-constant ratios against per-
chlorate concentration.

◯ $R/R(B)$; + $k_1/k_1(B)$; ☐ $k_2/k_2(B)$; △ $k/k(B)$.
Broken curve: rate ratios calculated from heats
of formation.

gradually decreased to *ca.* 0·01 through the series B—F. For sample G stage III followed after I, while for A stage III did not occur.

The main acceleration stage of the decomposition occurred after stage III with all samples except A, where it followed immediately after stage II. The kinetics agreed well with the exponential law for samples A—E, but for F a power-law with $n = 3$ was more satisfactory, while for G a power-law with $n = 2$ was best and with a larger value of k_2 than that found for G in stage III. For samples A—E, the kinetics are consistent with the Prout and Tompkins branching mechanism,[5,7] since the corresponding kinetic equation reduces to an exponential law for small values of α. With increasing perchlorate

[6] Tompkins and Young, *Trans. Faraday Soc.*, 1956, **52**, 1245.
[7] Finch, Jacobs, and Tompkins, *J.*, 1954, 2053.

concentration, however, the situation could arise where the probability of branching is no longer rate-controlling, and the three-dimensional growth of individual nuclei, as with sample F, becomes more important. When each permanganate ion is surrounded by a still higher proportion of perchlorate ions, as in sample G, the coherent reaction interface of three-dimensional growth evidently cannot be maintained, so that two-dimensional growth applies with the reaction spreading probably in a zig-zag manner through the lattice. For crystals A, in contrast to B, the inferior form of the crystals and the absence of a t^2-stage indicate a higher density of dislocations leading to a higher rate of branching which can now begin directly after the constant-rate process. In fact, for A the values of k were about twice those for B at corresponding temperatures.

The inhibiting effect of potassium perchlorate on all stages of the decomposition at 217° is illustrated in Fig. 4, where respectively the ratios of the rate constants R, k_1, k_2, and k for solid solutions to the corresponding constants for pure permanganate B are plotted as a function of the perchlorate concentration. Sample B was chosen as the standard of reference rather than A in view of B's superior crystal form. For sample G, the point for R/R(B) is omitted from the figure owing to the unusually large stage I for this sample. The ratio k/k(B) is available only for D and E, since with F and G the main acceleration stage did not follow the exponential law. However, approximate values of this ratio for F and G were obtained by drawing the rate–α curves and measuring the tangent gradients at the point $\alpha = 0.05$. Fig. 4 shows that the inhibiting effect of perchlorate follows the same general pattern for the first three stages of the decomposition, and is less pronounced in the exponential law stage where the mechanism differs significantly from those of the earlier stages. The sharp decreases in R, k_1, and k_2 with increasing perchlorate concentration may be related to a preferential concentration of perchlorate ions at the dislocation networks which constitute the subgrain boundaries. The corresponding (but smaller) decrease in the branching coefficient k could be due partly to the presence in the solid solution lattices of fewer potential branching sites, and partly to the development, at these sites during the decomposition, of stresses which are smaller the higher the perchlorate concentration. Unfortunately, the activation energy associated with k (see below) could not be determined with sufficient accuracy to test the suggestion that the stress required for branching may increase with increase in the perchlorate concentration.

Hinshelwood and Bowen [1] have suggested that the decrease in rate for any given solid solution is caused by an increase in activation energy equal to the heat of formation of the solid solution from its component solids. From the data given by Sommerfeld,[8] heats of formation for samples D—G have been calculated, and thus values of the ratio (solid solution rate)/(permanganate rate) were obtained from the Arrhenius equation, the pre-exponential factors being assumed to be constant. The broken line in Fig. 4 shows how this ratio varied with perchlorate concentration. Clearly, the heat of formation effect is insufficient to account for the observed perchlorate inhibition.

From the temperature coefficients of the rate constants, activation energies for the corresponding stages of the decomposition were calculated. All the values given below are in kcal./mole and have a probable error of $\pm 10\%$. For stage I, the activation energy increased gradually from 35 to 46 through the series B to F. The value for stage II was 39 and was independent of the perchlorate concentration; this value is significantly greater than Herley and Prout's figure [9] of 25.5 for the same stage for large permanganate crystals. Irrespective of whether the kinetics followed an exponential or a power-law equation and independently of the perchlorate concentration, the value for stage IV was 39, compared with 38.5 given by Prout and Tompkins [5] for large permanganate crystals. On the basis of the mechanism proposed for stage III, the activation energy, found to be 78, is equal to the sum of those for (a) penetration of the interface into the subgrain bulk and

[8] Sommerfeld, " Neues Jahrbuch für Mineralogie," Beilage Band XIII, Schweizerbart'sche, Stuttgart, 1900, p. 443.
[9] Herley and Prout, *J. Phys. Chem.*, 1960, **64**, 675.

(b) propagation of the reaction along subgrain boundaries. The value for (a) from stage II being 39, the activation energies for (a) and (b) are equal, which indicates a common rate-determining process.

An alternative explanation of the kinetics can be derived on the basis of Hill's diffusion chain mechanism,[10] in which the creation of growth nuclei is a consequence of the diffusion of a product species into the unchanged lattice *via* grain boundaries and dislocations. The diffusion process is considered to be relatively rapid, so that the rate of nucleation involves dependence on both the number of diffused species and their ability to convert potential nuclei into growth nuclei, but not on the diffusion coefficients of the species. In the present work, diffusion coefficients would not be expected to vary much with solid solution composition in view of the closely similar structures of the permanganate and the perchlorate lattice. Hill has shown that this mechanism leads to an exponential law when t is large. This is in agreement with the results in Fig. 2. From Fig. 4, it is seen that as the lattice is diluted with perchlorate the percentage reduction in the rate constants $[= 100(1 - \text{rate constant ratio})]$ is always greater than the mole % of perchlorate present, and thus the inhibiting effect of perchlorate is greater than corresponds to a simple dilution effect. On the basis of the diffusion-chain theory, this means that as permanganate is replaced by perchlorate, not only does the number of diffused species decrease (in proportion to the dilution), but also their ability to fertilise potential nuclei. It can be argued therefore that a diffused species must be near several permanganate ions to have optimum effect upon them, and if a species has, and can affect, say, six neighbouring ions, it would be expected that the replacement of two or three of these neighbours by perchlorate ions would seriously affect the rate. In fact, with 30 moles % of perchlorate in the lattice, the value of k is reduced by *ca.* 50%, the corresponding figure for the other rate constants being *ca.* 90%. Furthermore, near 50 moles % of perchlorate, the exponential process ceases to occur.

The simplest kinetic equation obtained by Hill, based on random nucleation followed by one-dimensional growth, is

$$\alpha - \alpha_0 = P[\cosh Q (t - t_0) - 1],$$

which by suitable choice of the parameters P and Q could reduce to a power law with $n = 2$ for low values of α and to an exponential law for higher values of α. The equation is thus qualitatively in agreement with the observed kinetics. The equation can be recast into the form

$$(\text{Rate})^2/Q^2(\alpha - \alpha_0) = \alpha - \alpha_0 + 2P,$$

so that the plot of $(\text{Rate})^2/(\alpha - \alpha_0)$ against α should be linear for the range of α values included in both the power law and the exponential stage. Tests showed that linearity was in fact found for the exponential stage, but pronounced curvature for the power-law stage, curvature which persisted with all values of α_0 from zero up to the value at the end of the constant-rate stage. Whether this failure reflects over-simplification of the model to give the above equation, or a fundamental flaw in the diffusion chain mechanism, is not known.

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[10] Hill, *Trans. Faraday Soc.,* 1958, **54**, 685.