1069. *Thermal Decomposition of Potassium Metaperiodate.*

By B. R. Phillips and Duncan Taylor.

The isothermal decomposition of potassium metaperiodate has been investigated at 256—288°, the decomposition being accurately given by $2KIO_4 \longrightarrow 2KIO_3 + O_2$. With 0·25—0·3 mm. crystals, an initial small decay process followed by a prolonged slow constant-rate stage preceded the main autocatalytic and decay stages. The last two stages were best represented by the Prout and Tompkins and the contracting-sphere kinetic equation, respectively. Very small crystals (0·04 mm.) behaved similarly except that the initial decay and constant-rate stages were replaced by a t^2 power-law process. For most of the stages, ageing of the crystals or ultraviolet pre-irradiation increased the rate of decomposition, but, within the limits of experimental error, did not change the activation energies. The kinetic measurements have been supplemented by visual observations of the decomposition, by infrared absorption and electrical conductivity measurements, and by *X*-ray and electron-diffraction experiments. Mechanisms for the various stages are proposed. It is suggested that the primary chemical act in the decomposition is $KIO_4 \longrightarrow KIO_3 + O$ ($\Delta H \sim 50$ kcal. mole^{-1}), and that Hill's diffusion-chain theory could not apply in the autocatalytic stage.

Although a great deal of work has been carried out on the thermal decomposition of permanganates [1,2] and perchlorates,[3] no detailed work appears to have been published for periodates. Potassium metaperiodate was chosen for study since it has the advantage that the chemistry of the reaction near 270° is comparatively simple and involves only the release of oxygen with the formation of the iodate.[4] Further, since preliminary experiments showed that potassium metaperiodate crystals disintegrate on decomposition in much the same way as potassium permanganate, it was important to see if the kinetics of the metaperiodate reaction could be interpreted in terms of the chain mechanisms [1,5] applied to the permanganate reaction.

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[1] Prout and Tompkins, *Trans. Faraday Soc.*, 1944, **40**, 488; Hill and Welsh, *ibid.*, 1960, **56**, 1059.

[2] Herley and Prout, *Nature*, 1960, **188**, 717; Herley and Prout, *J. Phys. Chem.*, 1960, **64**, 675; Phillips and Taylor, *J.*, 1962, 4242.

[3] Bircumshaw and Newman, *Proc. Roy. Soc.*, 1954, *A*, **227**, 115; 1955, *A*, **227**, 228; Bircumshaw and Phillips, *J.*, 1957, 4741; Galwey and Jacobs, *J.*, 1959, 837; Solymosi and Révész, *Nature*, 1961, **192**, 64.

[4] Mellor, " Comprehensive Treatise on Inorganic and Theoretical Chemistry," Longmans, Green and Co., London, 1922, Vol. II, p. 406.

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

EXPERIMENTAL AND RESULTS

Preparation of Crystals.—A saturated solution of " AnalaR " potassium metaperiodate in distilled water was prepared at 60° and allowed to come to equilibrium at room temperature. The mother-liquor was then decanted into large crystallising dishes and allowed to evaporate in a slow current of air over a period of weeks, the solution in the dishes being replenished periodically with fresh mother-liquor. The resulting crystals (tetragonal bipyramids [6]) were dried with filter paper and those of linear dimensions 0·25—0·3 mm. selected by gentle sieving. The crystals were free from all but minor surface imperfections, and are referred to below as " large " crystals. Samples of well-formed crystals of dimensions about 0·04 mm. were obtained by sieving crystals prepared by rapid cooling to room temperature of a solution saturated at 90°; these are referred to as " small " crystals. Both types of crystals were stored in the dark in a vacuum-desiccator over calcium chloride. The water content of the crystals, determined by drying in air at 110° for one week, was shown to be less than 0·01%. For some experiments, the crystals were stored before use for periods of between one and two years, in which cases the crystals are referred to as " aged."

Thermal-decomposition Procedure.—The apparatus and procedure were essentially those described previously.[7] Samples of crystals (10—20 mg.) were decomposed isothermally at temperatures in the range 256—288°, the pressure of oxygen evolved being measured at known times with a Macleod gauge of range 10^{-6}—0·16 mm. Hg. In order to obtain adequate sensitivity during the first 10% of the reaction, the volume of the system was limited initially to 984 c.c., and when the oxygen pressure approached the limit of the gauge, the volume was increased to 6722 c.c. at a known time. The volumes and temperatures of the various sections of the apparatus being known, all gauge readings were converted into pressures (p) at 0° for a volume of 6722 c.c. The final oxygen pressure (p_0) measured about 1 hr. after the end of the decomposition showed no tendency to increase when the time of heating was prolonged. The fraction of the sample decomposed at a given time (t) after the start of the reaction was given by $\alpha = p/p_0$.

Chemistry of the Reaction.—Standard chemical tests, taken in conjunction with the decrease in weight of the sample and the quantity of oxygen evolved, showed that the equation $2KIO_4 \longrightarrow 2KIO_3 + O_2$ accurately represented the decomposition reaction for both the fresh and the aged crystals. Further, the *X*-ray powder photograph of the solid decomposition product was identical with that of recrystallised " AnalaR " potassium iodate. The photograph supported Smith's report [8] that the iodate is monoclinic in structure. In a search for intermediate products, infrared absorption measurements (Nujol mull technique. Hilger H 800 spectrophotometer) were carried out on the metaperiodate and on samples which had been separately decomposed to the extent of 0·3, 25, 50, 75, and 100%. No absorption peaks were observed other than those corresponding to the metaperiodate and iodate ions. The intensity of the metaperiodate absorption [9] at 848 cm.$^{-1}$ decreased linearly with the percentage decomposition, while the iodate absorption at 738 cm.$^{-1}$ correspondingly increased.

Microscopic and Visual Observation of the Decomposition.—The large crystals of metaperiodate, when heated in air at about 290° on a hot-stage microscope, first became white and opaque, and then began to break up in a random manner unrelated to the directions of the crystal axes. The rate of disintegration rose to a maximum and then fell sharply to zero. The small crystals, on similar heating, also became opaque but showed no signs of decrepitation. By use of a vapour-bath in place of the electric furnace to heat the reaction vessel and with the sample in a glass bucket, otherwise normal decomposition runs were carried out to correlate the disintegration behaviour of the large crystals with the percentage decomposition. At 280°, only very slight break-up of the crystals occurred up to the end of the constant-rate stage at about 0·6% decomposition (Fig. 1) by which time the crystals were opaque. Rapid disintegration occurred during the acceleration stage over the decomposition range 1—30%, and thereafter ceased. At 270°, with crystals which had been pre-irradiated with ultraviolet light for 18·5 hr. (see below), the same behaviour was found except that the onset of disintegration occurred later at about 3% decomposition. By use of standard sieves, it was shown that at

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[6] Hylleraas, *Z. Physik*, 1936, **39**, 308.
[7] Taylor, *J.*, 1955, 1033; 1958, 2387, 3323; 1962, 1047.
[8] Smith, *Nature*, 1925, **115**, 334.
[9] Millar and Wilkins, *Analyt. Chem.*, 1952, **24**, 1253.

the end of a decomposition the crystal fragments ranged in size from 0·15 mm. to less than 0·05 mm., about 60% of the fragments being between 2 and 3 times larger than the untreated small crystals.

Irradiation of Crystals with Ultraviolet Light.—For several series of the thermal-decomposition experiments, crystals were pre-irradiated *in vacuo* with ultraviolet light for periods up to 18·5 hr. at a distance of 8 cm. from a 300-w Hanovia mercury lamp. The vitreous-silica tube containing the crystals was shaken every half-hour in order to expose fresh crystal surfaces to the radiation. Dilute copper sulphate solution contained in a silica vessel was used as a heat-filter, so that the temperature of the crystals did not rise above 35°. It was found, by measurement with the Macleod gauge of the oxygen released during irradiation, that after 18·5 hr. 0·005% of decomposition had occurred with the large crystals, and 0·035% with the small crystals. The difference in the rates of photodecomposition was accounted for by the difference in the surface areas of the large and small crystals exposed to the radiation. After irradiation, the crystals appeared unchanged under the microscope, apart from the development of a very slight yellow colour. Since this colour was completely bleached by heating the crystals for 30 seconds at about 280°, the colour and its causes are unlikely to have a significant effect on runs with pre-irradiated crystals.

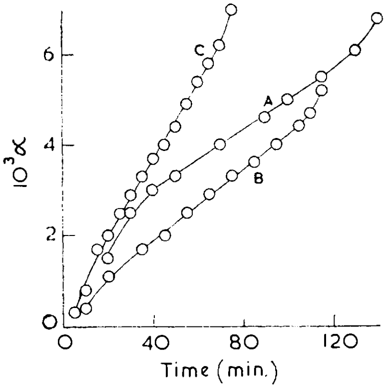

FIG. 1.

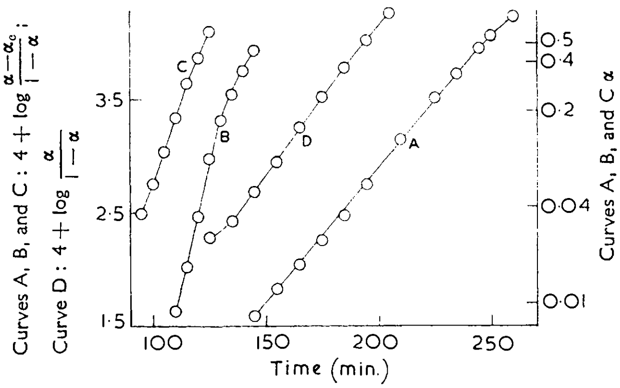

FIG. 2.

FIG. 1. Initial decay and constant-rate stage for fresh (A), aged (B), and pre-irradiated (C) large crystals. Decomposition temperatures: A, 267·5°; B, 266·6°; C, 265·5°.

FIG. 2. Plots of Prout and Tompkins equation. Crystal type and decomposition temperature: A, large fresh, 269·1°; B, large aged, 269·5°; C, large pre-irradiated, 268·8°; D, small pre-irradiated, 260·4°.

Electrical Conductivity Measurements.—By use of a conductivity cell, similar to that described by Jacobs,[10] and a Vibron electrometer, it was found that the specific resistance of potassium metaperiodate pellets, prepared by compression at 2—3 tons per sq. in., was of a similar order of magnitude at 270° (10^{12} ohm cm., obtained by extrapolation from measurements over the range 150—210°) to those of barium azide [11] and silver oxalate [12] at their respective decomposition temperatures. Similarly, the specific resistance of a potassium iodate pellet at 270° was found to be 10^{10} ohm cm.

Electron-microscope Experiments.—Electron-diffraction photographs of metaperiodate crystals (size about 0·001 mm.) were taken with a Metro-Vickers No. 6 microscope. The crystals were grown on a collodion film, supported on a copper grid, by the slow evaporation of an aqueous solution. The photographs showed that the metaperiodate rapidly decomposed in the electron beam (undoubtedly partly thermally), to give iodate crystallites which showed no sign of preferred orientation.

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[10] Jacobs, *J. Sci. Instr.*, 1953, **30**, 204.

[11] Thomas and Tompkins, *J. Chem. Phys.*, 1952, **20**, 662.

[12] Finch, Jacobs, and Tompkins, *J.*, 1954, 2053.

Kinetics of the Thermal Decomposition.—For fresh and for aged large crystals, the oxygen pressure–time curves (Fig. 1) showed an initial small decay stage terminating at $\alpha = 0{\cdot}002$—$0{\cdot}003$, followed by a prolonged slow constant-rate stage (rate constant k_1) up to $\alpha = 0{\cdot}005$—$0{\cdot}006$. These processes occupied as much as 30—50% of the total reaction time. The accelerating-rate stage (Fig. 2) could best be represented up to the maximum rate point (co-ordinates α_i, t_i) by the Prout and Tompkins equation $\log_{10}[(\alpha - \alpha_c)/(1 - \alpha)] = kt +$ Constant, where α_c is the value of α at the end of the previous constant-rate process. The acceleration terminated at $\alpha_i = 0{\cdot}5$ for fresh crystals, and at $\alpha_i = 0{\cdot}2$ for aged crystals. The decay stage of the reaction agreed well with the contracting-sphere equation $\alpha = 1 - [\text{Constant} - k_3(t - t_i)]^3$ up to $\alpha = 0{\cdot}8$—$0{\cdot}9$ (Fig. 3). Ageing of the crystals increased the respective rate constants.

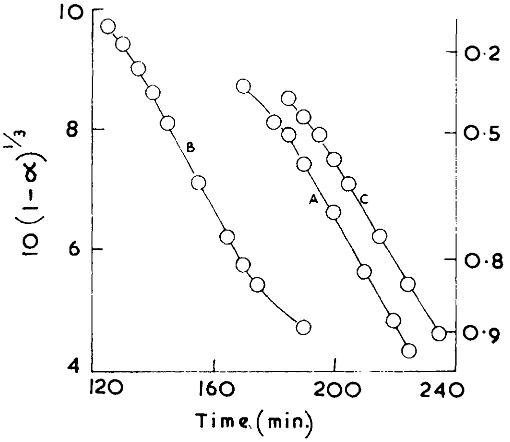

FIG. 3. Plots of contracting-sphere equation. Crystal type and decomposition temperature: A, large fresh, 272·5°; B, large aged, 269·5°; C, small pre-irradiated, 260·4°.

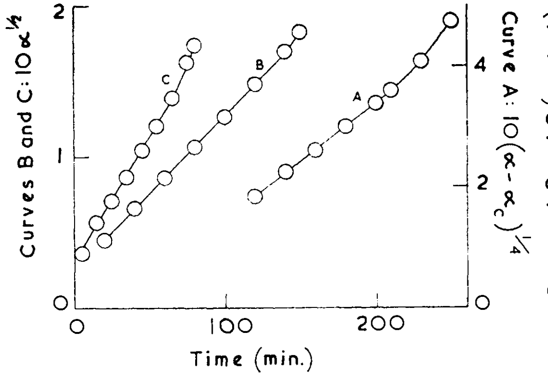

FIG. 4.

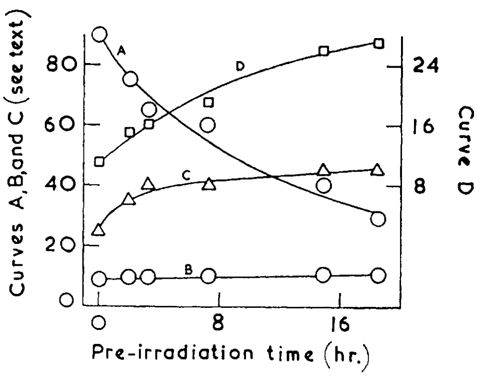

FIG. 5.

FIG. 4. Curve A: plot of t^4 power-law equation for large pre-irradiated crystals. Curves B and C: plots of t^2 power-law equation for small fresh and small pre-irradiated crystals, respectively. Decomposition temperatures: A, 256°; B, 267·9°; C, 267·5°.

FIG. 5. Large crystals, pre-irradiated subsequent to ageing: influence of pre-irradiation time on rate of decomposition at 272·3°. (A) Time required for α to reach $\alpha_c = 0{\cdot}006$. (B) $10^2 k$. (C) $10^2 \alpha_i$. (D) $10^3 k_3$.

Large, fresh crystals, pre-irradiated for 18·5 hr., showed the same kinetic stages as above, but with rate constants increased in comparison with those for unirradiated material, and with one additional feature, namely, a power-law stage (Fig. 4) given by $\alpha - \alpha_c = k_4{}^4(t - t_0)^4$ occurring over the α-range 0·005—0·04 between the end of the constant-rate stage and the beginning of the Prout and Tompkins stage. The significance of t_0, the value of t at the start of the power-law stage, is discussed below. Pre-irradiation tended to reduce the value of α_i from 0·5 to about 0·4. The effect of pre-irradiation on large crystals which had been previously aged for 12 months is shown in Fig. 5. The rate constants for the various stages, with the exception of k, progressively increased with increasing irradiation time, and the value of α_i correspondingly increased from 0·25 to 0·45. Also, with long-pre-irradiation a t^4 power-law stage was again observed.

The decomposition curves for small crystals, irrespective of ageing or pre-irradiation for 18·5 hr., showed first (Fig. 4) a power-law stage given by $\alpha = k_2^2(t - t_0)^2$ terminating at $\alpha = 0{\cdot}03$, followed by a Prout and Tompkins stage (Fig. 2) given by $\log_{10} [\alpha/(1 - \alpha)] = kt +$ Constant, up to $\alpha_i = 0{\cdot}5$, and finally a contracting-sphere process over the α-range 0·5—0·85 (Fig. 3). Pre-irradiation increased the values of k, k_2, and k_3; ageing increased k and k_3, but k_2 was unaffected. The values of t_0 in the power-law equation are discussed below.

For both small and large crystals, the activation energies calculated from the temperature coefficients of the rate constants were 46 ± 4 kcal. mole^{-1} for all the stages except the t^2 power-law stage for small crystals and the constant-rate process for large crystals, where the respective values were 41 ± 4 and 50 ± 5 kcal. mole^{-1}. The activation energies were not significantly influenced by the ageing or pre-irradiation of the crystals.

In the following Table, values of the rate constants at 267° are given, together with the rate (R_i) and the value of α_i at the maximum rate point. The Table also shows that the constants were reasonably reproducible for different preparations of the crystals.

Rate constants (267°).

Large crystals		10^5k_1	10^4k_2	10^2k	10^3k_3	α_i	10^3R_i
1st Preparation:	fresh	3·3	—	1·7	6·0	0·5	8·3
	aged	4·5	—	7·0	7·8	0·2	16
2nd Preparation:	fresh	3·3	—	2·2	7·8	0·5	10
	pre-irradiated	9·6	—	5·5	13	0·4	21
Small crystals							
1st Preparation:	fresh	—	10	2·4	8·9	0·5	13
	aged	—	10	3·9	11	0·5	18
2nd Preparation:	fresh	—	7·9	2·4	8·9	0·5	13
	pre-irradiated	—	14	5·5	13	0·5	22

DISCUSSION

In view of the very low electrical conductivity of the metaperiodate near its decomposition temperature and the absence of any preferred orientation of the crystallites of the iodate product, a mechanism for the decomposition involving significant ionic transport evidently cannot apply (cf. barium azide [11] and silver oxalate [12]). Satisfactory mechanisms can be derived for the several stages if the kinetics are discussed in three sections: (1) those occurring before the main acceleration process; (2) the Prout and Tompkins stage; and (3) the contracting-sphere decay stage.

Large Crystals.—Section (1). The small initial decay process up to $\alpha = 0{\cdot}002$ is regarded as decomposition at active sites involving crystal surfaces and some of the subgrain boundaries. From the initial rates of the process, the activation energy was found to be about 45 kcal. mole^{-1}, so that the process is chemical in nature and not merely the desorption of physically adsorbed oxygen. Its effect is the creation of a constant-area reaction interface which progresses into the subgrains, thus accounting for the slow constant-rate process which occurred over the α-range 0·002—0·005. Ageing of the crystals had little effect on α_c and increased k_1 by about 35%; on the other hand, pre-irradiation raised k_1 by a factor of about three, but with still little change in α_c. The first effect of pre-irradiation is thus to cause nucleation of subgrain boundaries such that a higher proportion of them can participate in the constant-rate stage leading to an increase in k_1. On this basis, an increase in α_c would also be expected, but this is not realised owing to the second effect of pre-irradiation, namely, the introduction of a t^4 power-law stage, apparently holding from $\alpha = 0{\cdot}005$ to $\alpha = 0{\cdot}04$, which effectively swamps the constant-rate stage at $\alpha = 0{\cdot}005$ but is sufficiently slow when α is less than 0·005 for the constant-rate process to be observed. The value of t_0 in the t^4 power-law equation was found to be small and positive, showing that in fact the corresponding stage began virtually at zero time; furthermore, calculation showed that the contribution to α from the power-law process could not be more than about 10% of the observed total during the greater part of the constant-rate stage. It was also found adequate when plotting the results for the power-law process to use a constant value for α_c instead of the more accurate value calculated from $\alpha = k_1t + 0{\cdot}002$. In terms of the Avrami theory,[13] the t^4 power-law process corresponds to the three-dimensional growth of nuclei with a constant rate of production of growth nuclei from germ nuclei. The suggested second effect of pre-irradiation is thus the production of germ nuclei near subgrain boundaries as a result of the very slight photolytic decomposition; the germ nuclei, when heated, are then converted into growth nuclei at a constant rate. The latter rate corresponds to the limiting case of the exponential law [14] of conversion when the probability of conversion is low.

Section (2). At the end of the section (1) processes, the great majority of the large crystals will still be intact and will have iodate product sandwiched between many of the subgrains. Continued decomposition now leads to a branching chain process of the Prout and Tompkins type and to disintegration of the crystals. In the main acceleration stage, ageing of the crystals increased the value of k by a factor of about 4 and brought forward α_i from 0·5 to 0·2. Since the crystals, after ageing, appeared unchanged under the microscope and contained no iodate, the ageing process is regarded as a physical change involving the dislocation networks such that the branching process of the Prout and Tompkins mechanism is facilitated. Since at the same time the maximum-rate point is brought forward, a smaller degree of decomposition is required before the crystals are subdivided into the " spherical " particles completely nucleated on the surface as required for the decay process. It is suggested, therefore, that ageing increases the effective number of branch points by reducing the stresses (and thus the degree of decomposition) necessary to produce branching at potential sites in the dislocation network. Pre-irradiation also considerably increased k but changed α_i only from 0·5 to 0·4; it thus has the bulk-effect on the crystals of increasing the number of branch points and of slightly reducing the stresses required for branching. For pre-irradiated crystals in the α-range 0·04—0·4, better Prout and Tompkins plots were obtained when the correction factor α_c was used rather than a factor equal to the α-value at the end of the t^4 power-law stage. This suggests that the branching-chain process in fact began at the end of the constant-rate stage (cf. unirradiated crystals) but was masked by the power-law process when α was less than 0·04.

Section (3). Ageing and pre-irradiation of the crystals increased the values of k_3 in the decay stage by factors of 1·3 and 1·7, respectively (the former figure probably represents a just significant increase in rate). For a contracting-sphere process which begins when $\alpha = \alpha_i$ and $t = t_i$,

$$(\alpha - \alpha_i)/(1 - \alpha_i) = 1 - [1 - m(t - t_i)/a]^3,$$

where m is the linear rate of growth of the interface into the spherical particles whose radii are a at time t_i. Also, $4\pi a^3/3 = (1 - \alpha_i)V/n$, where n is the total number of the particles and V is the volume of the undecomposed crystals at time zero. It can thus be shown that the experimental k_3 is given by $(4\pi/3V)^{\frac{1}{3}}mn^{\frac{1}{3}}$. For the experiments under discussion, the initial weight (and thus V) of the crystals was constant within a few percent, and hence k_3 is dependent only on $n^{\frac{1}{3}}$. On the assumption that the degree of branching in the Prout and Tompkins stage determines the value of n at time t_i, increases in k due to ageing or pre-irradiation should be paralleled by smaller increases in k_3, as was in fact observed. Furthermore, since R_i is equal to the (initial) rate of the contracting-sphere process at time t_i, R_i is directly proportional to a^2n and therefore to $(1 - \alpha_i)^{\frac{2}{3}}n^{\frac{1}{3}}$. Thus

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[13] Avrami, *J. Chem. Phys.*, 1939, **7**, 1103; 1940, **8**, 212; 1941, **9**, 177.

[14] Garner, " Chemistry of the Solid State," Butterworths, London, 1955, p. 188.

the ratio $R_i(A)/R_i(B)$ for two materials A and B can be calculated if $n^{\frac{1}{3}}$ is put directly proportional to k_3. The observed and calculated ratios were as follows:

Materials, A/B	Ratio of maximum rates Calc.	 Observed
1st Preparation: aged/fresh	1·8	1·9
2nd Preparation: pre-irradiated/fresh	1·9	2·1

The agreement between the calculated and the observed ratios is considered satisfactory, especially in view of the assumption that the particles at t_i are true spheres all of equal radius.

Large Crystals, Pre-irradiated Subsequent to Ageing.—The results shown in Fig. 5 are reasonably consistent with the mechanisms proposed above. An unexpected feature was the increase in α_i from 0·25 to 0·45 with increasing time of pre-irradiation. The increase in α_i suggests that irradiation gradually neutralised the effect of the previous ageing, and that at the same time (since the time required for α to reach α_c decreased and k_3 increased) the effects characteristic of the pre-irradiation of fresh crystals were superimposed. Compensation for the loss of the ageing effect by the gain of the irradiation effect explains qualitatively why k did not change significantly with increasing time of irradiation. The calculated and the experimental values of the ratio R_i(aged + irradiated)/R_i(aged) were again in good agreement for each time of pre-irradiation.

Small Crystals.—Since the small crystals are only about four times greater than average subgrains in dimensions,[15] a smaller number of subgrain boundaries will be present than in the large crystals. It is to be expected therefore that the greatest difference in behaviour between the two types on decomposition will be found in section (1), where for large crystals the decomposition is mainly concerned with subgrain surfaces and boundaries.

Section (1). The t^2 power-law, which accurately represents the decomposition up to $\alpha = 0·03$ (Fig. 4) corresponds to the two-dimensional growth of nuclei on the crystal surfaces. In view of the relatively small number of subgrain boundaries available, it is considered less likely that the t^2 law corresponds to one-dimensional growth coupled with a linear increase with time of the number of growth points. The ageing process did not affect the surfaces since k_2 was unchanged, but pre-irradiation increased k_2 by a factor of 1·8 and therefore increased the number of growth nuclei. The values of k_2 varied by about 20% with different preparations of the small crystals, suggesting that the initial state of the surfaces was reasonably reproducible. The values of t_0 in the equation $\alpha = k_2^2(t - t_0)^2$ were relatively large and negative and were temperature-dependent, but, for a given temperature, t_0 was constant for all the crystals, whether fresh, aged, or pre-irradiated On the other hand, the values of α at zero time, given by $\alpha_0 = k_2^2t_0^2$, were independent of temperature and were unchanged by ageing. The values varied between 0·00035 and 0·0005 for different preparations, and by pre-irradiation were increased by an amount equal to the extent of the decomposition caused by the irradiation. Thus the negative values of t_0 indicate very rapid initial growth of nuclei which were originally present on the crystal surfaces and whose number is proportional to α_0, a number which varies from one preparation to another and is increased by pre-irradiation. The duration of rapid growth, however, is independent of the number of nuclei present. As demanded by the temperature-independence of α_0, the activation energy obtained from the temperature coefficient of t_0 was the same (41 kcal. mole^{-1}) as that obtained from k_2.

Sections (2) and (3). In the Prout and Tompkins and the contracting-sphere stages of the decomposition (Figs. 2 and 3) the results for small crystals were similar to those for large crystals in that ageing and pre-irradiation increased k and k_3, but differed in that the value of α_i remained constant at 0·5. The pre-treatments thus increased the number of effective branching points and hence increased the value of n at the start of the decay process. The calculated and experimental values of the ratio R_i(aged)/R_i(fresh) and also

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[15] Tompkins and Young, *Discuss. Faraday Soc.*, 1957, **23**, 202.

of R_i(pre-irrad.)/R_i(fresh) were again in good agreement. The fact that the small crystals did not disintegrate during the Prout and Tompkins process has a parallel in the case of ammonium dichromate crystals.[7]

The values of k for the large and the small fresh crystals (see Table of rate constants) differ by less than a factor of two; the same applies when the pre-treated crystals are compared and also when corresponding values of k_3 are compared. This suggests that at the end of the section (1) processes, the large and the small crystals are in roughly the same state as far as the later decomposition is concerned; the only difference is that, whereas for large crystals the iodate product is sandwiched between subgrains, with small crystals the product exists as an external layer on individual particles of very approximately subgrain dimensions. It is suggested that, by the time the maximum-rate point has been reached, the crystal fragments from the large crystals and the (unbroken) small crystals are internally subdivided by the iodate product into randomly oriented particles of approximately mozaic-block size. This view is consistent both with the electron-microscope observations and with the fact that an X-ray powder photograph of uncrushed small crystals showed only diffraction spots, while the same sample after decomposition and again without crushing gave rings typical of ground material. Furthermore, calculations, based on the Polanyi–Wigner equation and on reasonable dimensions[15] for the subgrain and mozaic blocks in order to obtain the respective reaction interface areas, have shown that the observed value of 200—300 for the ratio R_i/k_1 can be accounted for within a factor of ten.

Diffusion-chain Theory.—It has been shown[16] that the approximate value of ΔH for the reaction $KIO_4 \longrightarrow KIO_3 + O$ is 50 kcal. mole^{-1}. Since this value is comparable with the observed activation energies, it is suggested that the above equation represents the primary chemical act in the thermal decomposition. For the purposes of a mechanism based on Hill's diffusion-chain theory,[5] the only feasible diffusing species would therefore be the oxygen atom. Since, in order to effect further nucleation of the crystal, the oxygen atom would presumably react according to $KIO_4 + O \longrightarrow KIO_3 + O_2$, in which case the diffusion-chain is broken, it is considered unlikely that the theory could be here applied.

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CHEMISTRY DEPARTMENT, UNIVERSITY OF EDINBURGH. [*Received, March 27th,* **1963.**]

[16] Phillips, Thesis, " Thermal Decomposition of Inorganic Solids," Edinburgh, 1961.