The Decomposition of Silver Oxalate.

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In an attempt to resolve some of the apparent anomalies in previous work on the decomposition of silver oxalate, the ionic and photoconductance of this salt have been measured and the photolysis and thermal decomposition of several different preparations have been investigated. The kinetics of the photolysis are explained by an exciton mechanism similar to, but not identical with, that previously applied to the decomposition of barium and potassium azides. The theory, originally due to Macdonald, that the thermal decomposition of the freshly prepared salt proceeds by a branching-chain mechanism, has been successfully developed to account quantitatively for all features of the thermal decomposition. The role of dislocations in thermal decompositions of this type has been emphasized and some apparent discrepancies between the present and previous work have been reconciled.

THE several previous investigations of the thermal decomposition of silver oxalate have given markedly different results, and consequently different interpretations of the kinetics have been proposed. Benton and Cunningham (*J. Amer. Chem. Soc.*, 1935, **57**, 2227) and Tompkins (*Trans. Faraday Soc.*, 1948, **44**, 206) found the pressure of carbon dioxide evolved to vary as the third or fourth power of the time, a result consistent with three-dimensional growth of silver nuclei, whereas Macdonald (*J.*, 1936, 832, 839) concluded that the reaction starts from a fixed number of centres which grow two-dimensionally. Macdonald considered that the plates of silver so formed would branch, and thus accounted for the predominantly exponential character of his pressure–time plots. In later work, however, Macdonald and Sandison (*Trans. Faraday Soc.*, 1938, **34**, 589) showed that ionic conductance measurements favoured the concept of solid nuclei although the p–t plots were again exponential.

The rate of decomposition is sensitive to the method of preparation of the oxalate (Macdonald, *loc. cit.*), that obtained when using excess of oxalate ions during precipitation being of the " unstable accelerating " type, whereas that prepared with use of excess of silver ions is of the " stable, feebly accelerating " type. Consequently, in an attempt to resolve some of these differences, the ionic and photoconductance of silver oxalate, its decomposition at room temperature under ultra-violet radiation, and the thermal decomposition of irradiated and unirradiated salt have been investigated, different preparations being used.

EXPERIMENTAL

Preparation of Silver Oxalate.—Four different preparations were used, viz., (I) a " stoicheiometric " sample, prepared by Tompkins's procedure (*loc. cit.*); (II) an " excess of oxalate " sample prepared in the presence of excess of sodium oxalate; (III) as (II), but with use of oxalic acid; (IV) an " excess of silver " sample. The preparation of (II) and (IV) followed Macdonald's procedure and correspond to his samples C and E.

In the measurements of ionic and photoconductance the apparatus and procedure were similar to those used by Jacobs (*J. Sci. Instr.*, 1953, **30**, 204). The investigation of prolonged photolysis, pre-irradiation, and thermal decomposition followed closely the methods described by Thomas and Tompkins (*J. Chem. Phys.*, 1952, **20**, 662; *Proc. Roy. Soc.*, 1951, *A*, **209**, 550; **210**, 111).

RESULTS AND DISCUSSION

The specific ionic conductance κ of compressed pellets of (I) as a function of temperature was found to be well represented by the equation

$$\log \kappa = -6.00 - (10.7 \text{ kcal.}/2.3RT) \quad . \quad . \quad . \quad . \quad . \quad (1)$$

The reproducibility of conductance values was $\pm 2\%$ for different pellets of (I) while the values of κ obtained with samples (II), (III), (IV), and (I) after *slight* thermal decomposition at 320° K also obeyed formula (1) within the experimental error. The conductance

(10^{-12} ohm^{-1} cm.$^{-1}$ at 333° K) is thus of a similar order of magnitude to that of barium azide but differs markedly from that of silver chloride and bromide (10^{-7} ohm^{-1} cm.$^{-1}$ at the same temperature). Following Thomas and Tompkins (*Proc. Roy. Soc., loc. cit.*) it is concluded that the mechanism of growth of discrete silver nuclei, involving cationic transport, valid for the silver halides, cannot be applied to the oxalate, in which individual nuclei have never been observed; an interface reaction is, therefore, more probable.

As with barium azide, no photocurrent greater than 10^{-13} A was obtained when the oxalate was illuminated either with a low-pressure argon-filled ultra-violet lamp or with a tungsten lamp. Calculations based on the light intensity (cf. Jacobs and Tompkins, *Proc. Roy. Soc.*, 1952, *A*, **215**, 254) show that any mechanism for photolysis involving conduction electrons cannot be applied and thus an exciton mechanism (cf. Thomas and Tompkins, *loc. cit.*) is probable.

On prolonged photolysis by ultra-violet light (about 90% $\lambda = 2537$ Å) silver oxalate decomposed stoicheiometrically into silver and carbon dioxide. At constant intensity and temperature, the rate of gas evolution was practically constant after an initial, more rapid rate during the first 15 min. when a fresh sample of oxalate was irradiated for the first time.
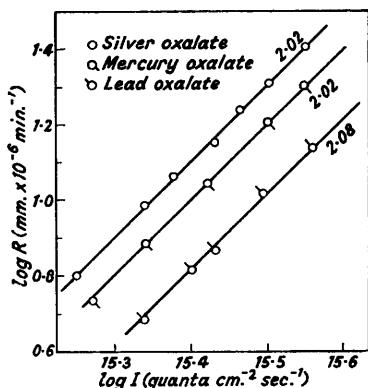

FIG. 1.
Variation of the rate of photolysis with intensity for oxalates of silver, lead, and mercury(II). Values on curve denote value of exponent in $R \propto I^n$.

Gas evolution commenced and ceased immediately on the light's being switched on and off. At constant intensity the linear rate increased slightly with temperature in the range 200—300° K with an activation energy E of 950 cal./mole, which was unaltered by a three-fold increase in the intensity (cf. Tompkins, *loc. cit.*, who found $E = 850$ cal./mole).
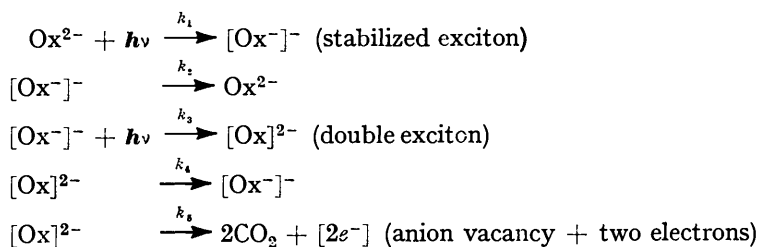
At constant temperature, the linear rate R varied as the square of the intensity I; this is shown in Fig. 1, where log R is plotted against log I. The same relation held for the oxalates of lead and mercury(II) (Fig. 1), and also, as found previously, for potassium and barium azides. Tompkins (*loc. cit.*), had obtained a dependence of rate on intensity of the form $R \propto I^{1.7}$; when these results are corrected for the outgassing rate, the square law is found to be obeyed, and particularly well at higher intensities.

The exciton theory, previously given for the photolysis of barium azide, may be applied to that of silver oxalate with little modification. The main difference is that a single oxalate " radical " may decompose to carbon dioxide, whereas with barium azide two excitons, or excited azide ions, are essential for the production of nitrogen according to the equation

$$2[N_3]^- \longrightarrow 3N_2 + 2F\text{-centres}$$
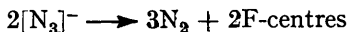
The process that we envisage for silver oxalate is the production of a singly excited oxalate ion (or exciton) by the ultra-violet radiation, such that the excited electron is still associated with the parent ion. The mobile exciton is trapped at an anion vacancy, a process that involves the capture of the excited electron by the vacancy which may accommodate two electrons. The complex formed is analogous to the coloration complex obtained with potassium azide (Jacobs and Tompkins, *loc. cit.*). This complex (i) may either be further excited by light absorption so that a second electron is captured by the anion vacancy, giving an oxalate radical associated with an anion vacancy containing two electrons; or (ii) it may be destroyed by the electron returning by tunnel effect from the anion vacancy

back to the singly-charged ion. Similarly, the oxalate radical formed by (i) may either (iii) decompose to give two molecules of carbon dioxide or (iv) revert to a singly-charged oxalate ion by regaining an electron from the anion vacancy. The possible processes are summarized by the reaction scheme :

$$Ox^{2-} + h\nu \xrightarrow{k_1} [Ox^-]^- \text{ (stabilized exciton)}$$

$$[Ox^-]^- \xrightarrow{k_2} Ox^{2-}$$

$$[Ox^-]^- + h\nu \xrightarrow{k_3} [Ox]^{2-} \text{ (double exciton)}$$

$$[Ox]^{2-} \xrightarrow{k_4} [Ox^-]^-$$

$$[Ox]^{2-} \xrightarrow{k_5} 2CO_2 + [2e^-] \text{ (anion vacancy + two electrons)}$$

Since a steady state is set up, the rate of decomposition R is given by

$$R = k_1 k_3 k_5 N I^2 / (k_2 + k_3 I)(k_4 + k_5) \quad \cdots \cdots \quad (2)$$

Here N is the number of anion vacancies per cm.^{2} of surface; k_1, k_3 are the probabilities that the absorption of a quantum will lead to excitation of an oxalate ion adjacent to an anion vacancy; k_2 and k_4 are tunnelling probabilities; and k_5 is the rate constant for the decomposition of complexes. The latter is given by $sve^{-E/RT}$, where s is a steric factor and v the lattice frequency ($\sim 10^{13}$ sec.$^{-1}$); E, the activation energy for the decomposition of complexes, has the measured value of 950 cal./mole, provided k_2 and k_4 are temperature-independent. Since $R \propto I^2$, it follows that $k_2 > k_3 I$, and since there is a single experimental activation energy, $k_4 > k_5$. Equation (2) may, therefore, be put in the approximate form

$$R = k_1 k_3 k_5 N I^2 / k_2 k_4 \quad \cdots \cdots \quad (3)$$
$$= 2 \cdot 9 \times 10^{13} e^{-950/RT}$$

Following Jacobs and Tompkins (*loc. cit.*), we put $k_1 I \simeq k_3 I \simeq 6 \times 10^8$ sec.$^{-1}$, $k_2 \simeq k_4$, and calculate N from the conductance equation as $1 \cdot 5 \times 10^5$ cm.$^{-2}$. Substitution of these values in equation (3) gives

$$k_2 \simeq k_4 = 1 \cdot 4 \times 10^{11} s^{\frac{1}{2}}$$

But since $k_2 > k_3 I$ and $k_4 > k_5$,

$$0 \cdot 043 < s^{\frac{1}{2}} < 0 \cdot 07$$

and therefore

$$s \simeq 3 \times 10^{-4}$$

and

$$k_2 \simeq k_4 \simeq 2 \cdot 5 \times 10^9$$

This value is in fair agreement with that calculated by Jacobs and Tompkins (*Proc. Roy. Soc.*, 1952, *A*, **215**, 265) for the rate of decay of colour centres in potassium azide (5×10^{10}). Thus the theory allows a self-consistent set of the constants appearing in equation (3) to be calculated.

The main objection is that such a low value for s would not be expected for a " unimolecular radical " decomposition at a solid surface. However, this may be accounted for in the following way. Griffith's X-ray work (*J. Chem. Phys.*, 1946, **14**, 403) has shown that silver oxalate possesses a layer lattice, the silver and the oxalate ions occurring in alternate layers with the oxygen atoms in successive oxalate ions co-ordinately bound to one another. It is thus necessary to break more than a single C–C bond to free two molecules of carbon dioxide from the lattice. Nevertheless, the activation energy to do this (~ 1 kcal.) is small and we would not expect any considerable steric factor to be associated with a disruption requiring so little energy. More probably, k_2 and k_4 are temperature-dependent, *i.e.*, tunnelling only takes place from a thermally excited state within the vacancy. This seems likely from the work of Schneider ("Photographic Sensitivity," Butterworths London, 1951) on the bleaching of coloration complexes in potassium chloride and of Groocock and Tompkins (*Proc. Roy. Soc.*, 1954, *A*, in the press) on the decomposition of barium and sodium azides after electron bombardment. Writing $k_2 \simeq k_4 = \kappa v e^{-E'/RT}$ we find that $E \simeq 4 \cdot 5$ kcal. if the transmission coefficient κ is unity. The true activation energy for the decomposition of complexes is thus about 10 kcal. and the low steric factor found is thus reasonable.

The Thermal Decomposition.—The thermal decomposition of all four preparations was investigated between 105° and 120° c, in which temperature range self-heating is negligible (Macdonald, *loc. cit.*). All the pressure–time curves obtained were well represented from α = 0·05% decomposition to at least 30% by the equation

$$p = Ce^{kt}. \qquad \qquad (5)$$

where C and k are constants. Typical plots of log p against t are given in Fig. 2, and plots of log k against $1/T$ for various preparations are shown in Fig. 3. Values of k were consistently reproducible to ±2% for any one preparation; C was independent of temperature and of the method of preparation, but k increased when excess of oxalate, and decreased when excess of silver ions, was used in the preparation. The activation energy (Fig. 3) was 27 kcal./mole for all preparations (Macdonald, *loc. cit.*, found 32 kcal./mole).

Pre-irradiation accelerated the subsequent thermal decomposition at 110°, according to the equation

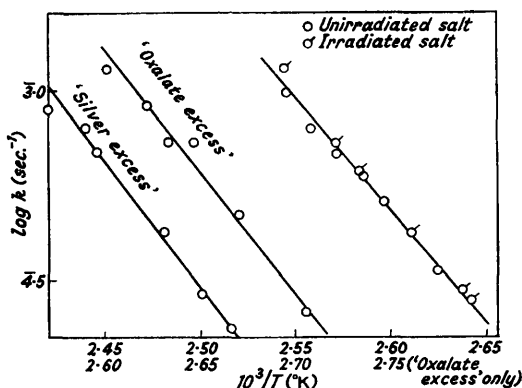$$C_i - C_u = \text{const.} \times I^2 t_i$$

where t_i is the time of irradiation and C_i and C_u are the value of C [in equation (5)] for the irradiated and the unirradiated salt, respectively. Pre-irradiation, therefore, increases the

FIG. 2.
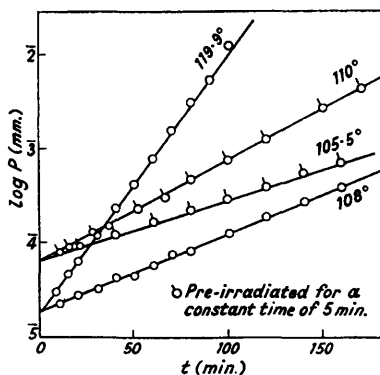
FIG. 3.

Thermal decomposition of silver ox-alate, showing conformity with $p = C \exp (kt)$ for a few plots for unirradiated and irradiated salt at various temperatures.

Variation of the rate of thermal decomposition of silver oxalate with temperature for different preparations.

value of C, although equation (5) is still obeyed and the activation energy is unchanged (Fig. 3). Previously Tompkins found $C_i - C_u \propto I^{3\cdot3}t_i^{2\cdot8}$, but this result may be discounted since pre-irradiation was there performed in air when the silver nuclei react with oxygen and not *in vacuo* as in the present work.

All these results may be explained by a mechanism similar to that suggested by Macdonald (*loc. cit.*), but our additional data allow a more detailed and specific treatment. We assume that the activation energy for the formation of nuclei is high except at special surface lattice defects where it is low. These are later identified as slip lines. Consequently, nucleation at these special sites is rapid and, therefore, after the first few minutes, the reaction consists effectively of growth from a fixed number of reaction centres (N_0). The exponential law [equation (5)] is consistent with a branching mechanism, and there are good reasons (Macdonald, *loc. cit.*) for assuming branching of two-dimensional plate-like nuclei rather than linear branching chains. If the total number of all nuclei present at time t is N, and k_b is the branching coefficient, then the rate of formation of new nuclei is

$$dN/dt = k_b N \qquad \qquad (6)$$

so that $$N = N_0 \exp (k_b t) \qquad \qquad (7)$$

Cubic particles being assumed, the size of a plate-like nucleus formed at $t = \tau$, after time t is

$$x = wk_g (t - \tau) \qquad \qquad \qquad \text{(8)}$$

where k_g is the rate of growth of the nuclei into the interior of the crystal and w is their (constant) width, taken to be the linear dimension of the cubic particles. In other words, it is assumed that the N_0 surface nuclei consist of rows of decomposed oxalate ions extending the whole width of the particle, and that these penetrate into the crystal by the decomposition of successive rows beneath the first.

The total size of all nuclei at time t is

$$X = \int_{\tau = 0}^{\tau = t} x \mathrm{d}N + N_0 k_g t \qquad \qquad \text{(9)}$$

$$= (N_0 k_g w)/k_b)\{e^{k_b t} - 1\}. \qquad \qquad \text{(10)}$$

Since $k \simeq 10^{-3}$ sec.$^{-1}$, for $t > 20$ min. (*i.e.*, $\alpha > 0.04\%$ decomposition), equation (10) becomes

$$X = (N_0 k_g w / k_b) \exp (k_b t)$$

The pressure of carbon dioxide developed is, therefore,

$$p = (FN_0 k_g w / k_b) \exp (k_b t) \qquad \qquad \text{(11)}$$

where F is a factor converting the number of radicals decomposed into our practical pressure units (mm. $\times 10^{-4}$). In fact, the experimental results fit this equation over a slightly wider range than predicted, *i.e.*, from $t \simeq 10$—15 min., or $\alpha = 0.03\%$, up to at least $\alpha = 30\%$, the limit to which the thermal decompositions were followed.

Since $\qquad \qquad k_b = \beta\nu \exp (-E_b/\boldsymbol{R}T) \qquad \qquad \text{(12)}$

and $\qquad \qquad k_g = \nu \exp (-E_g/\boldsymbol{R}T) \qquad \qquad \text{(13)}$

where ν is the lattice frequency, E_b and E_g are the activation energies for branching and growth respectively, and β is a probability factor, equation (11) becomes

$$p = \frac{FN_0 w\nu \exp (-E_g/\boldsymbol{R}T)}{\beta\nu \exp (-E_b/\boldsymbol{R}T)} \exp (k_b t) \qquad \qquad \text{(14)}$$

Macdonald (*loc. cit.*) has shown experimentally that $E_b \simeq E_g$, hence,

$$p = (FN_0 w/\beta) \exp (k_b t) = C \exp (k_b t) \qquad \qquad \text{(15)}$$

where $\qquad \qquad C = FN_0 w/\beta \qquad \qquad \text{(16)}$

We note that (i) C is independent of temperature, as found experimentally; (ii) pre-irradiation increases the value of C by increasing the number of surface nuclei N_0, whereas β, being governed by crystallographic considerations in the interior of the crystal, is unaffected by radiation; (iii) the method of preparation affects k_b, but not E_b; this effect must, therefore, be confined to β, the probability factor. But since C is unaltered, it follows that $N_0 w$ and β must vary in such a way that their ratio remains constant. This criterion can be satisfied if nucleation and branching are both caused by the same type of lattice defect. Two such possibilities are illustrated in Fig. 4, where branching is considered to be facilitated either by a cation–anion vacancy pair or by a dislocation. Branching is then determined by the presence of a crystallographic imperfection and is not a consequence of the creation of an alternative reaction path requiring a lower activation energy. In view of the ease with which reaction could spread to a whole row simultaneously, the dislocation mechanism is to be preferred.

We have shown that, in prolonged photolysis, reaction proceeds at anion vacancies. If the same mechanism is retained for the thermal process, the activation energy for nucleation represents the energy required to transfer an electron from an oxalate ion into an anion vacancy. Since pre-irradiation certainly produces additional anion vacancies (N_v in number), the increase in the number of sites at which nucleation can occur (ΔN_0) should be related to N_v. For $I = 10^{15}$ quanta cm.$^{-2}$ sec.$^{-1}$, $N_v = 6 \times 10^{14}$ cm.$^{-2}$ at $t_i = 3.2$ sec. The

area of salt exposed is approximately 0.3 cm.^{2}, and therefore $N_v = 2 \times 10^{14}$. From equation (16), we have

$$\Delta C/F = 2 \times 10^{14}\, Aw/\beta \qquad . \qquad . \qquad . \qquad . \qquad . \qquad . \qquad (17)$$

where A is a proportionality factor given by $\Delta N_0/N_v$. From the increase in C found experimentally, $\Delta C/F = 1.8 \times 10^{13}$, so that $Aw/\beta = 0.1$. From the experimental values of k_b and E_b, we find $\beta = 5 \times 10^{-2}$ for $\nu = 10^{13}$ sec.$^{-1}$; w is the number of ions per row in an average particle, and we consider that a value $w = 5 \times 10^3$ (corresponding to a cubic particle size of 10^{-4} cm.) is a reasonable estimate. This means that $A \simeq 10^{-6}$ and, therefore, that single anion vacancies are not highly effective in forming centres where nucleation can occur thermally. We interpret this as meaning that the activation energy for formation of nuclei is less at imperfections consisting of a group of anion vacancies than at single vacancies. Consequently, the reaction starts first at those places where pre-irradiation has decomposed a whole patch of oxalate ions. Now since nucleation and branching are both caused by the same (macro) imperfection and since the results of pre-irradiation indicate

FIG. 4.
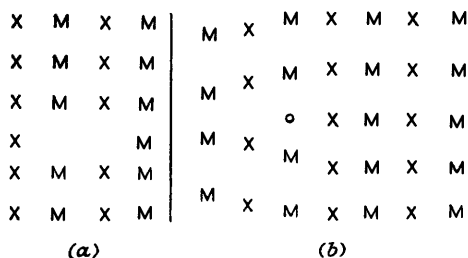
FIG. 5.

Branching of reaction " chains " facilitated by (*a*) a cation–anion vacancy pair and (*b*) a dislocation. M = two Ag^+; X = oxalate ion; point o is referred to as an incipient vacancy.
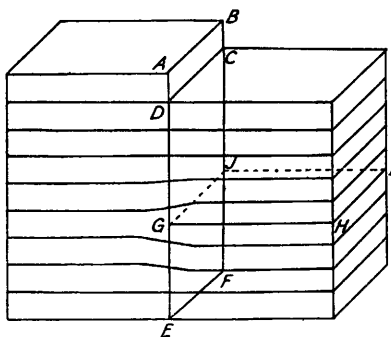
Taylor–Orowan edge dislocation with slip line. Slip line *ABCD*; slip plane *AEFB*; additional " half-plane," *GHIJ*. Alternate planes parallel to *ABEF* contain silver or oxalate ions only. Fig. 4(*b*) represents a plane at right angles to the line *GJ*.

that single vacancies do not easily facilitate nucleation, we conclude that in the thermal decomposition of the unirradiated salt, nucleation starts at " steps " in the surface. For simplicity, we first consider a linear step provided by the slip line (*AD* in Fig. 5) of a Taylor–Orowan dislocation. Branching will occur when the decomposing row of anions meets the additional half-plane *GJHI*. Since branching occurs every time the advancing nucleus meets an extra half plane, the probability of branching will be given by

$$\beta = b/w \qquad . \qquad . \qquad . \qquad . \qquad . \qquad . \qquad . \qquad . \qquad (18)$$

where b is the width of the slip line and w, as before, the total number of planes in the particle. Therefore

$$C/F = N_0 w/\beta = N_0 w^2/b \qquad . \qquad . \qquad . \qquad . \qquad . \qquad . \qquad (19)$$

Substituting the experimental values $C/F = 3.2 \times 10^{12}$, $\beta = 0.05$ as before, and our estimate of w, 5×10^3, we find $N_0 = 3 \times 10^7$; $b = 250$. Though no measurements on dislocations in silver oxalate are available, all the numerical values are of a reasonable order of magnitude, a dislocation density of 10^8 per cm.^{2} being quite normal even in a well-annealed crystal.

The real crystal, however, is more likely to contain general dislocation rings than simple Taylor–Orowan dislocations, but these also lead to slip lines in the surface (as indicated below) and, as far as surface nucleation is concerned, introduce no new features. However, the advantage gained is that the presence of dislocation rings leads naturally to an explan-

ation of the constant magnitude of C with various preparations, whereas we are unable to reach this conclusion using Taylor–Orowan dislocations unless a further assumption (for which we can find no justification) is made, *viz.*, that the width b of the slip line increases linearly with the number N_0 of slip lines in the surface.

Now the presence of excess of sodium oxalate during precipitation increases the probability of the incorporation of foreign cations. The presence of several of these at the edge of a growing plane is likely to cause cessation of growth resulting in a disc of vacancies (Seitz, *Phys. Review*, 1950, **79**, 239). When the opposite faces of the disc collapse, the general dislocation ring so formed will in general not lie in the principal slip plane and consequently act as a Frank–Read source (*ibid.*, *p.* 722) which generates slip lines in the surface of the crystal. Increased incorporation of foreign cations, therefore, increases the number of slip lines in the surface. These lines need only attain a thickness of several atomic layers since the stress set up by the Frank–Read source may be relieved by the anchoring effect of foreign ions (Koehler, " Imperfections in Nearly Perfect Crystals," Wiley and Sons Inc., New York, 1952, p. 200). Here b now represents the frequency of anchoring and is, therefore, proportional to the concentration of foreign ions, so that N_0/b, and therefore C, is independent of preparation as found experimentally.

Increase in silver nitrate in the mother-liquor reduces the probability of incorporation of foreign cations and hence the number of dislocations. Evidently the incorporation of foreign anions does not lead to sites where nucleation can occur.

Our picture of the freshly prepared salt is, therefore, that it consists of fine particles, each with the characteristic silver oxalate layer-lattice but containing a large number of ring dislocations with associated slip lines in the surface, and dislocation lines anchored in the interior of the crystal. Only prolonged pre-irradiation leading to large groups of surface anion vacancies is effective in increasing the normal thermal rate of decomposition. Many of these groups that facilitate nucleation will be situated above the randomly distributed closed dislocation rings which are operative in the branching process described above, and consequently such groups act as normal branching nuclei. The branching probability β is thus clearly a property of the crystal, and the only service rendered by pre-irradiation is to facilitate nucleus formation at sites where nuclei would not normally be formed in the unirradiated salt.

In a highly disorganized salt, where the branching coefficient is high (*i.e.*, β large), branching will predominate, leading to the exponential law

$$p = C \exp (k_b t)$$

This equation will be expected to hold only for a sample of silver oxalate in which the dislocation density is high. This will certainly be so for a salt freshly prepared by rapid precipitation, but with ageing, a process akin to annealing will occur at a slow rate, resulting in a decrease in both N_0 and β. If the number of rapidly formed nuclei at " steps " is small, those formed more slowly at single anion vacancies will be the controlling factor so that equation (6) must be reformulated as

$$dN/dt = k_f(N_0 - N)$$

or

$$N = N_0\{1 - \exp(- k_f t)\} \quad . \quad . \quad . \quad . \quad . \quad (20)$$

where k_f is the rate of formation of nuclei, N_0 being the number of potential centres. Previously, with N_0 large and branching rapid, the contribution of nuclei additionally created during decomposition was small, but with aged salt in which little branching can occur and normal growth predominates, this term cannot be neglected and, in the limit, controls the kinetics. For two-dimensional growth, we have, therefore,

$$p = \text{const.} \times \int_0^t k_g(t - \tau)^2 k_f N_0 \exp (- k_f \tau) d\tau$$

or

$$p \simeq Dt^3, \text{ for } k_f \text{ small} \quad . \quad . \quad . \quad . \quad . \quad . \quad (21)$$

Although with rapid branching the slow rate of growth perpendicular to the plate is negligible, yet in the well-aged salt this may not be so, in which case exponents between 3

and **4** may be expected in equation (21). Thus the power law found previously should be obtained when well-aged crystals are used, as when Tompkins, for example, used a preparation which had been preserved in the dark in a desiccator for over 6 months. To test this conclusion, Mr. D. A. Young, of this Department, has studied the thermal decomposition of the same sample of oxalate (I) which, when freshly prepared, had given an exponential p–t curve (measurements by A. F.) after ageing in the dark at room temperature for 6 months. The exponential law could be fitted only over the first 2—3% of decomposition, whereas a power law with exponents varying between 3·2 and 3·5 fitted the p–t plots over the range 3—35% of decomposition. It is thus possible, by using the present mechanism, to give a detailed picture of the decomposition of silver oxalate and to reconcile the views of various investigators.