Reaction of Single Crystals of Potassium Bromide with Chlorine Gas*

By J. A. Morrison and K. Nakayama †

Division of Pure Chemistry, National Research Council, Ottawa, Canada

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The reaction of single crystals of potassium bromide with chlorine gas has been studied using several different experimental techniques. At room temperatures, kinetic measurements show that the initial step in the reaction is a nucleation process. From microscopic and other experiments, the conclusion reached is that the reaction is initiated at points on the crystal surfaces where local strain has been created by, e.g., mechanical damage or precipitation of impurities. No correlation has been found between nucleation sites and the points where dislocations or low-angle grain boundaries emerge at the crystal surfaces.

The nuclei grow at a rate which is orders of magnitude faster than can be accounted for by normal diffusion of ions in the crystals. Since, however, the reaction involves a large decrease in crystalline volume (~15 %), the unreacted crystal in the vicinity of a growing nucleus is subjected to a considerable stress, as seen from birefringence patterns, so that extensive slip bands are formed at large distances (as much as 0·5 mm) from the reaction interfaces. Therefore the high reaction rates should probably be ascribed to mechanical effects such as slip and/or to enhanced diffusion brought about by the applied stress.

Many reactions involving solids, such as thermal decomposition and dehydration, are interpreted in terms of models involving nucleus formation and growth [1] but the origin of the nuclei and the detailed growth mechanisms are not often specified.[2] The points at which gross imperfections such as dislocations cut surfaces are more reactive, because their locations may be found by etching of the surfaces. While dislocations may provide preferential sites for nucleation,[3, 4] examples have been found [5-7] where this does not appear to be so, and for one [6] it is concluded that impurities are more probable sources of nuclei.

In this paper we examine the reaction of potassium bromide crystals with chlorine gas. Much information about both gross and point imperfections in alkali halides has been accumulated,[8, 9] and therefore it provides a useful background for a study of chemical reactivity. For potassium bromide, cation and anion diffusion coefficients have been measured [10] over a wide temperature range; the solubilities of common impurities can be estimated from conductivity measurements; [11] suitable etches are available [12] for the determination of dislocation and grain boundary densities; defects in mixed crystals of potassium bromide and potassium chloride have been studied.[13] Finally, the single crystals are transparent so that the regions of the reaction interfaces can be examined microscopically.

RESULTS AND DISCUSSION

NATURE OF THE REACTION

The reaction of potassium bromide with chlorine may be written as

$$\mathrm{KBr}(s)+\tfrac{1}{2}\mathrm{Cl}_2(g)\rightarrow\mathrm{KCl}(s)+\tfrac{1}{2}\mathrm{Br}_2(g), \quad (1)$$

or

$$\mathrm{KBr}(s)+\mathrm{Cl}_2(g)\rightarrow\mathrm{KCl}(s)+\mathrm{BrCl}(g). \quad (2)$$

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† National Research Council Postdoctorate Fellow; present address: Electrotechnical Laboratory, Tokyo, Japan.

The changes in Gibbs energy at 298°K are estimated to be $-6{\cdot}6$ and $-7{\cdot}2$ kcal/mole for (1) and (2) respectively. The question remains as to which is the more probable. This was determined as follows.

An excess amount of potassium bromide was reacted with $3{\cdot}81\times10^{-4}$ mole of chlorine at room temperature. The change in weight of the crystal was 15·75 mg, which corresponds to the formation of $3{\cdot}54\times10^{-4}$ mole of potassium chloride. Hence one mole of chlorine produces close to one mole of potassium chloride, in agreement with eqn. (2). Also, by titration analysis (to an accuracy of about 2 %) of the product formed on the outside of the potassium bromide crystal, the reaction produced potassium chloride and not a mixed crystal of potassium chloride and potassium bromide.

Nominally pure crystals of potassium bromide made by the Kyoto Electronics Manufacturing Co. or by the Optovac Co. were used for most of the experiments. The crystals made by the former manufacturer contained a trace of thallium.[11]

REACTIONS AT OR NEAR ROOM TEMPERATURE

GRAVIMETRIC EXPERIMENTS

Kinetic measurements were made by following the change in weight of crystals (usually about 0·35 g) in a chlorine atmosphere as a function of time. The weight changes were measured with a quartz spring balance (maximum load ~0·5 g, sensitivity ~ ±10 μg). The specimens were hung from the balance at the end of a quartz fibre about 50 cm long, so that reactions could be carried out at different temperatures without affecting the quartz spring. A sealed glass (and in part quartz) system was used and it was thoroughly evacuated (~10^{-6} mm Hg) before the chlorine gas was admitted. The chlorine had been carefully purified by low-temperature distillation, and its pressure in the reaction system was measured (to ~ ±2 mm) with a glass bellows manometer. The chlorine was always present in a large excess.

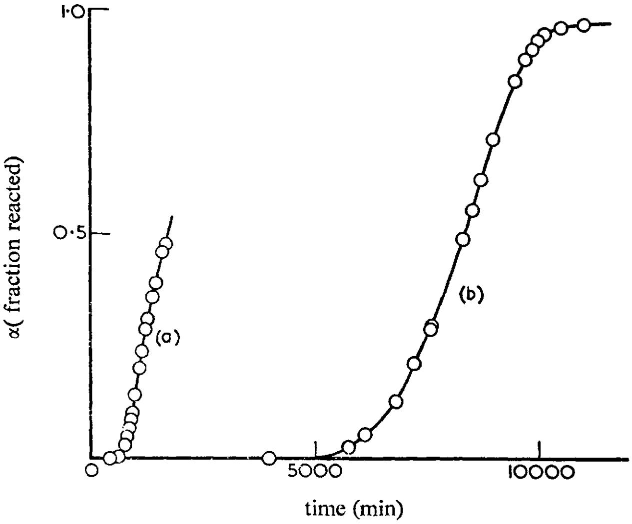

FIG. 1.—The reaction of two potassium bromide crystals (specimens (*a*) and (*b*), table 1) with chlorine gas (p = 210 mm Hg) at room temperature.

Fig. 1 shows the results of kinetic measurements on two nominally pure crystals of potassium bromide. Their reactivities are evidently much different: e.g., the apparent induction periods differ by about a factor of ten. The reaction with specimen (*b*) was followed for a longer time and the plot of the fraction reacted against time has a typical sigmoid shape (cf. fig. 1(*a*) of ref. (1)).

A logarithmic plot of the same data is given in fig. 2. For small amounts of reaction (fraction reacted <0·05) the results can be described by

$$\alpha = At^n, \tag{3}$$

where α is the fraction reacted, and A and n are constants. However, the values of A and n derived from the results of different experiments vary enormously, as

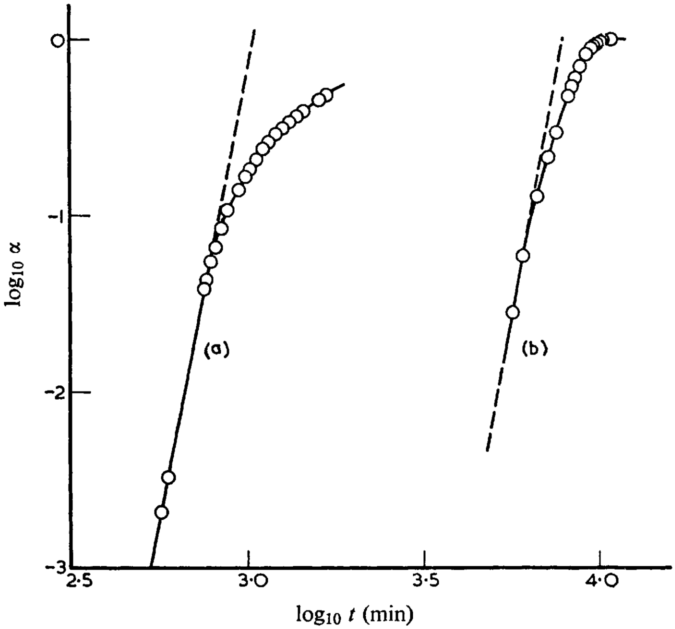

FIG. 2.—The reaction of specimens (*a*) and (*b*) expressed as the logarithm of the fraction reacted against the logarithm of the time.

is shown in table 1. There is no consistency amongst the values of A and n for the different specimens, and a physical inspection, show no consistency with regard to the number and location of reaction zones on the crystal surfaces. In the early stages of reaction, many zones appeared on all surfaces of specimens (*a*) and (*b*), while for

TABLE 1.—PARAMETERS OF EQUATION (3) FOR SEVERAL REACTIONS

(chlorine pressure = 210 mm Hg)

specimen	T(°C)	A (sec.$^{-n}$)	n
(a) pure (KEM)	25	$1{\cdot}37\times10^{-30}$	9·9
(b) pure (Opt.)	21	$8{\cdot}20\times10^{-45}$	11·3
(c) pure (KEM)	25	$1{\cdot}83\times10^{-17}$	5·3
(d) calcium doped (30 ppm. Ca^{2+})	25	$1{\cdot}94\times10^{-11}$	3·3
(e) calcium doped (30 ppm. Ca^{2+})	23	$4{\cdot}05\times10^{-31}$	8·7

KEM, Kyoto Electronics Manufacturing Co. Opt., Optovac Co.

specimen (*c*) reaction occurred mostly along the edges. For specimen (*d*), reaction took place at not more than about 10 locations on the surface.

A particularly wide variability was found with calcium-doped crystals. This is seen in part by the entries under (*d*) and (*e*) in table 1. A third specimen containing 30 p.p.m. Ca^{2+} did not react at room temperature in 2 days, nor in 7 days at 200°C. However, when it was then cooled to room temperature it started to react within 5 h. A fourth crystal, which did not previously react at room temperature, began to react immediately after it had been cooled to 0°C for 4 h.

These observations indicate that initiation of reaction cannot be ascribed to thermal fluctuations otherwise the reactivity should increase consistently with increasing temperature. For the calcium-doped crystals, it seems more probable that the nucleation step is connected with the solubility of the impurity which varies greatly[11] in the temperature range $T<200°C$. More generally, it would appear that reaction is structure sensitive.

RATES OF NUCLEATION

For several single crystals, the number N of nuclei or reaction zones occurring on one crystal face, was determined as a function of time using a low-power microscope (×10). The rate of nucleation so obtained only refers to the initial formation of nuclei if it is assumed that the rate of growth is a constant (as is shown later).

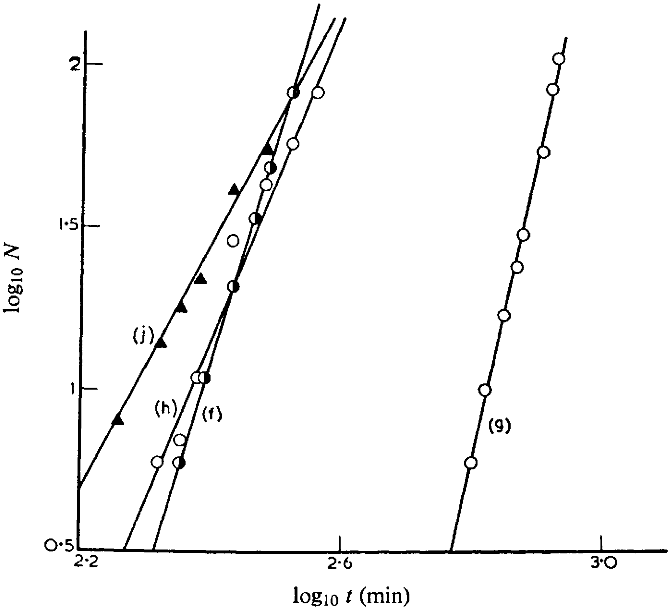

FIG. 3.—The number of reaction zones formed on different specimens of pure potassium bromide as a function of time at room temperature.

The results of four experiments are given in fig. 3 where log N is plotted against log time; counting was stopped when a significant fraction (~1/10) of the reaction zones had overlapped. Within the probable uncertainties, the data given in fig. 3 are well represented by straight lines, showing that the nucleation process is obeying a power law

$$N = Bt^m; \tag{4}$$

the numerical values of B and m obtained are given in table 2. Nucleation processes often obey a power law,[1] but such large and variable values of m seem not to be found usually. For example, $m = 2$ for the dehydration of nickel sulphate heptahydrate [14] and $m = 3$ for the thermal decomposition of barium azide.[15] These small and integral values of m are ascribed [1] either to the successive decomposition of m molecules or to the combination of m active intermediates to form a stable nucleus. An extension of either of these interpretations to an example such as $m = 8{\cdot}4$ is not reasonable physically.

TABLE 2.—KINETIC PARAMETERS FOR NUCLEATION REACTIONS

specimen	T(°C)	chlorine pressure (mm Hg)	B (sec^{-m})	m	k (sec^{-1})
(e) calcium doped (30 ppm Ca^{2+})	23	210	$6{\cdot}90\times10^{-18}$	5·4	0·0038
(f) pure (KEM)	25	210	$4{\cdot}00\times10^{-16}$	6·9	0·040
(g) pure (KEM)	24·5	195	$2{\cdot}59\times10^{-23}$	8·4	0·017
(h) pure (KEM)	25	490	$1{\cdot}16\times10^{-11}$	5·0	0·034
(j) pure (KEM)	25	490	$1{\cdot}76\times10^{-8}$	3·8	0·037

The coefficient B is not a satisfactory " constant " for use in investigating the temperature or pressure dependences of the rate of nucleation. Eqn. (4) can, however, be transformed to a more suitable form. The rate of nucleation is given by

$$\mathrm{d}N/\mathrm{d}t = mBt^{m-1}. \tag{5}$$

Substitution for t from eqn. (4) leads to

$$\frac{\mathrm{d}N}{\mathrm{d}t} = mB^{\frac{1}{m}}N^{\frac{m-1}{m}}. \tag{6}$$

This equation is of the form

$$\mathrm{d}N/\mathrm{d}t = kN^{x} \tag{7}$$

with $k = mB^{1/m}$ and $x = (m-1)/m$. The quantity k may be described as a rate constant; its values given in table 2 show variations within about a factor of ten which suggests that k is affected by a parameter of the reaction which is so far unspecified. This parameter is probably concerned with the crystal because there is no obvious correlation between k and the pressure of chlorine gas. (The variations in temperature from one reaction to another are negligibly small.) Some substantiation for this view is provided by the following observation: specimens (*f*), (*g*), (*h*) and (*j*), for which the variation in k is smaller, had been freshly cleaved, whereas specimen (*e*), for which k is an order of magnitude less, had been stored in air for several months. It has been demonstrated e.g., (ref. (16)) that the mechanical properties of alkali halide crystals are strongly dependent upon the condition of their surfaces.

GROWTH OF NUCLEI

Photographs of reaction zones showed that, in general shape, the zones were rectangular parallelopipeds. Since also the reaction product formed an opaque mass of small crystals, the reaction interface was always well defined and its motion through the single crystal could be followed with a microscope. The rates of growth of a number of nuclei were therefore determined by measuring the change in linear dimensions with time, at three temperatures (0°, 25° and 50°C) and at several chlorine pressures between 60 and 500 mm Hg. At any temperature the results could be described by

$$\mathrm{d}L/\mathrm{d}t = k'p^{\frac{1}{2}}, \tag{8}$$

where L is a linear dimension and k' is a rate constant. The square root dependence is easily explained if the reaction involves chlorine atoms. The apparent activation energy for the growth process, estimated from the temperature dependence of k' at p = 210 mm Hg, was $0{\cdot}5 \pm 0{\cdot}1$ eV, which is of the magnitude of the activation energy for motion of the cation in potassium bromide (~0·7 eV).[11]

In examples where both the width and depth of the growing nuclei could be measured, the depth was always close to half of the width, i.e., the nuclei grew from a single point at an equal rate in three perpendicular directions. Therefore, the transfer of gaseous products through the solid product cannot be rate determining.

The average size of $(\mathrm{d}L/\mathrm{d}t)$ was 5×10^{-3} mm/min. An estimate of the diffusion coefficient of the cation (the more mobile species) at room temperature, based on higher temperature measurements [10] and on a general knowledge of diffusion in the alkali halides,[8] is 10^{-20} cm^2/sec. This corresponds to an average linear displacement of 6×10^{-8} mm/min. The observed motion of the reaction interface is therefore some 10^5 times faster than can be accounted for by diffusion of the cation. The uncertainties in the estimate of the diffusion coefficient are not large enough to vitiate this result.

MICROSCOPIC INVESTIGATIONS

(i) REACTION PRODUCTS AT ROOM TEMPERATURE.—Two photographs illustrating the shape of reaction products formed at room temperature are shown in fig. 4(*a*) and (*b*). In 4(*a*), one should note the generally square cross-section of the product, the cracking due to the decrease in volume and the serrated profile of the reaction interface. The cube or ⟨100⟩ directions are essentially parallel to the edges of the photograph and so the serrations or ridges lie in the ⟨110⟩ direction which is the direction of easy glide (or slip) in crystals of NaCl structure. The extent of coherence of the product to the parent crystal is difficult to judge from the photograph. However, the cracks clearly extend to the reaction interfaces and so it is not surprising that transport of gases through the product is not rate-determining.

(ii) NUCLEATION SITES.—Most of the reaction products shown in fig. 4(*b*) lie along cleavage steps which suggests that the steps are preferred nucleation sites. However, not all steps are effective. This is also evident in fig. 4(*a*) where cleavage steps run continuously across unreacted crystal and reaction product. Furthermore, with crystals whose surfaces had been purposely damaged by scratching or scoring, the initial reaction with the chlorine gas occurred in the vicinity of the scratches without exception.

Fig. 5 shows a " before " and " after " sequence of a reaction with a freshly cleaved crystal containing calcium as an impurity. The irregular rows of dots are precipitates, probably of calcium bromide. The ones most clearly visible in fig. 5(*a*) are in the surface and were exposed by cleavage. As fig. 5(*b*) shows, it is these spots where the initial reaction with chlorine occurs; in fact, the correlation is nearly perfect.

On the average, the number of nuclei or reaction zones formed at room temperature is small compared with dislocation densities which usually amount to 10^4-10^8/cm^2 in the alkali halides (cf. fig. 6). Here a crystal was cleaved in two; one-half was reacted with chlorine and the other was etched using a recipe of Lubenets and Kostin.[12] A comparison of fig. 6(*a*) and 6(*b*) shows that the number of reaction zones is orders of magnitude less than the number of etch pits. There is, therefore, to be no correlation between nucleation sites and the points where dislocations or sub-grain boundaries emerge at the surface.

To summarize: there seem to be several sources of nucleation sites such as cleavage steps, scratches, precipitates and perhaps other irregularities. Some steps, etc., produce reaction and others do not. An examination of a number of unreacted reacting and reacted crystals with polarized light suggests that the general cause of nucleation is a local strain at the surface of the crystal.

(iii) THE USE OF BIREFRINGENCE.—Cubic crystals become double refracting when deformed anisotropically. The effect has been used to study internal strains in crystals of the alkali halides [17] and silver halides.[18] Two examples of its use in the present experiments are given in fig. 7.* In both, the directions of polarization are parallel to the edges of the photographs. The crystal used for fig. 7(*a*) and fig. 5 is the same. The precipitates now stand out as bright spots and the largest are in or near the surface. There is in addition a more diffuse strained volume around the rows of precipitate particles. A different strain pattern is displayed in fig. 7(*b*). Extensive slip bands in $\langle 110 \rangle$ directions are clearly visible; intense but largely structureless bands occur off the corners of the reaction zones.

Fig. 8 contains two views of the same reaction zone taken with different polarizer angles; these show unambiguously that it is slip bands which are seen in the $\langle 110 \rangle$ directions. Also on comparing fig. 8(*a*) with fig. 4(*a*), which shows the structure of the reaction zone profile, we might suggest that the growth of the nuclei involves a repetitive sequence of the steps: strain, slip, reaction.

Finally, fig, 9 shows a series of three photographs of portions of two crystals, taken at different times during the course of a reaction. They show that the strain patterns in the host crystals change in a complex way as the reaction zones increase in size and interfere with one another, and that nucleation does not occur uniformly over the surfaces of the crystals. Fresh nuclei seem to form preferentially in the vicinity of existing reaction zones. This suggests that the autocatalytic nature of nucleation might be ascribed to the building-up of local strains at the crystal surfaces.

REACTIONS AT HIGHER TEMPERATURES

Only a few results will be given to show that as the temperature is increased, the character of the reaction and its kinetics gradually change. No attempt was made to vary systematically the temperature, pressure or other parameters.

1. MICROSCOPIC OBSERVATIONS

Fig. 10 illustrates some physical features of the initial reaction at a temperature of about 300°C. These are: (i) many more nuclei are formed than at room temperature; (ii) the reaction zones no longer have the general rectangular profile of zones formed at room temperature—they have long " tongues " extending along $\langle 110 \rangle$ directions. This is also seen in fig. 11. In this example, reaction was allowed to take place for a limited time at 300°C. The crystal was then removed from the chlorine atmosphere, cleaved and the cleaved surface etched. Fig. 11 shows a part of the etched surface; the reacted portion of the crystal appears black and extends in from the original surface whose position is marked by the arrows; the reaction has clearly proceeded in the diagonal directions. A few of the " tongues "

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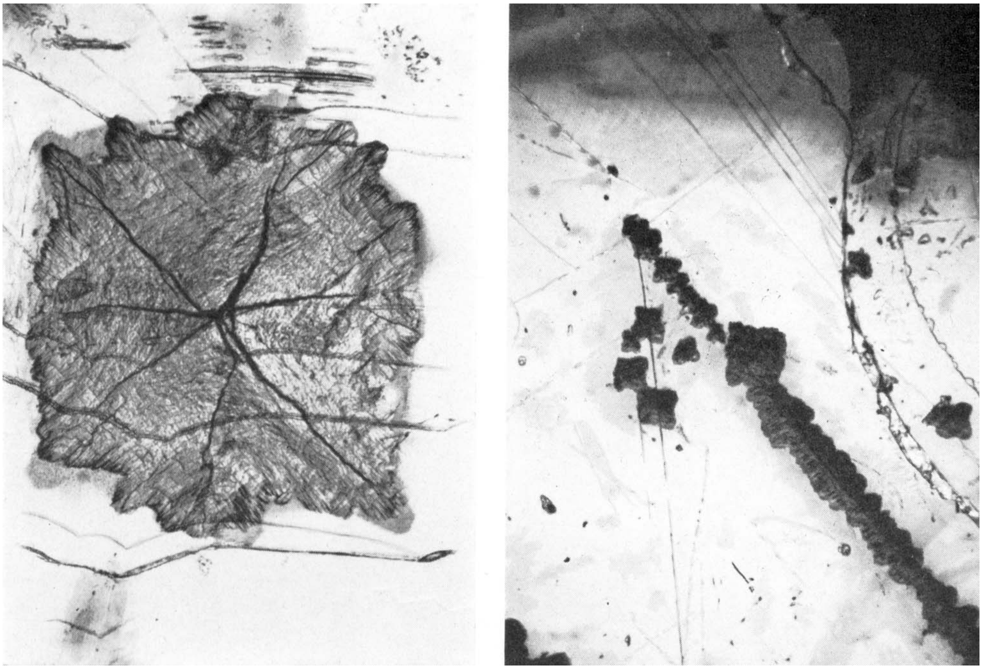
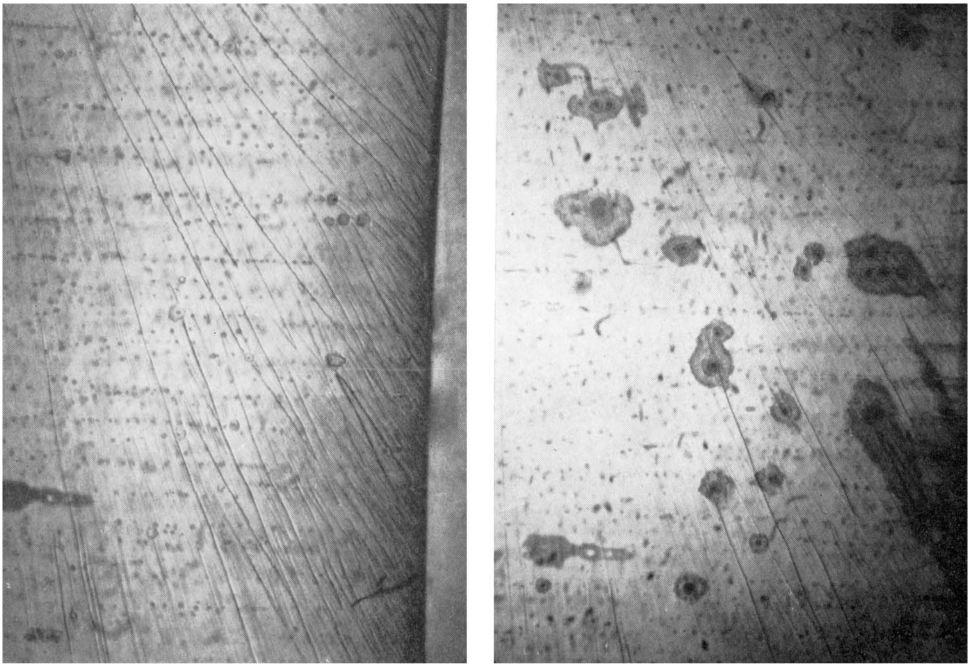
* Thin crystals (~0·2 mm) were used. Roughly, therefore, the patterns displayed may be taken as those of two-dimensional structures. All photographs of birefringence were taken with green light.



(*a*) (× 47) (*b*) (× 47)

FIG. 4.—Some reaction zones formed at room temperature.



(*a*) (× 47) (*b*) (× 47)

FIG. 5.—A potassium bromide crystal containing calcium impurity, (*a*) before reaction and (*b*) shortly after being exposed to chlorine.

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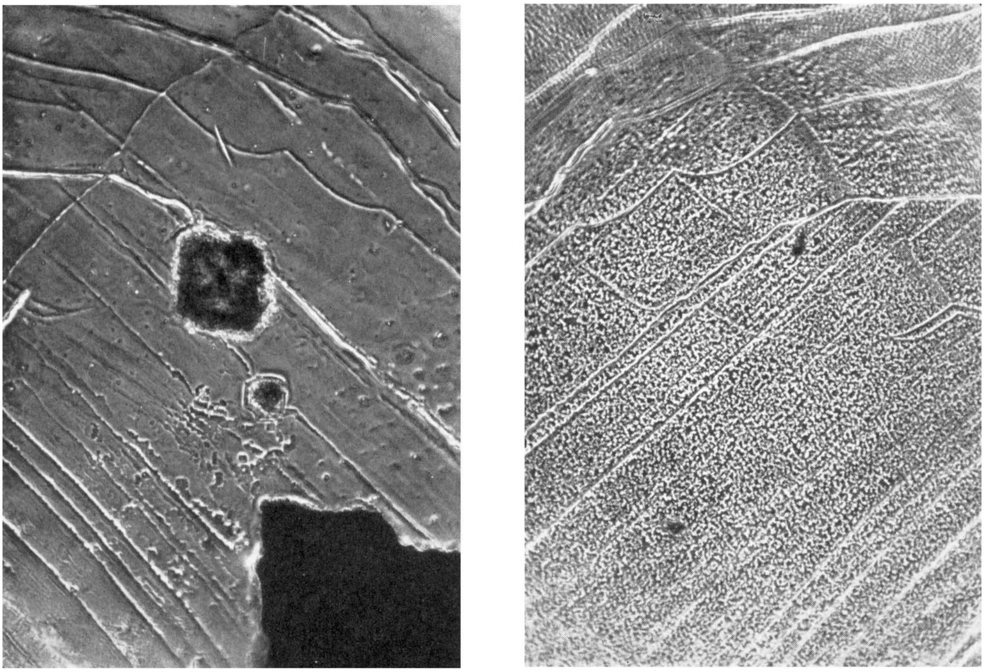
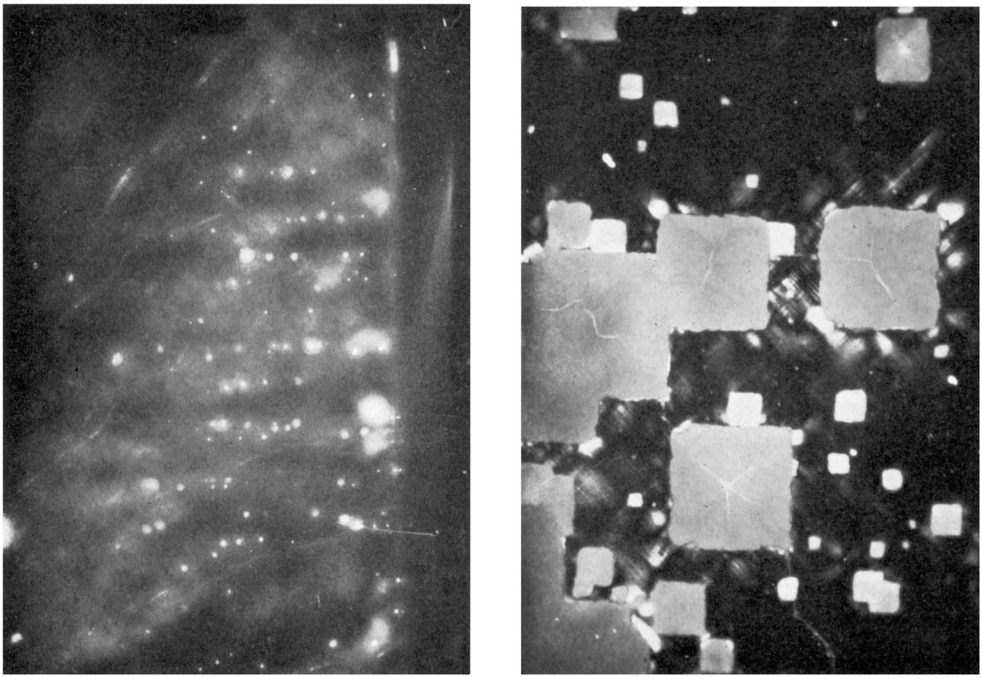


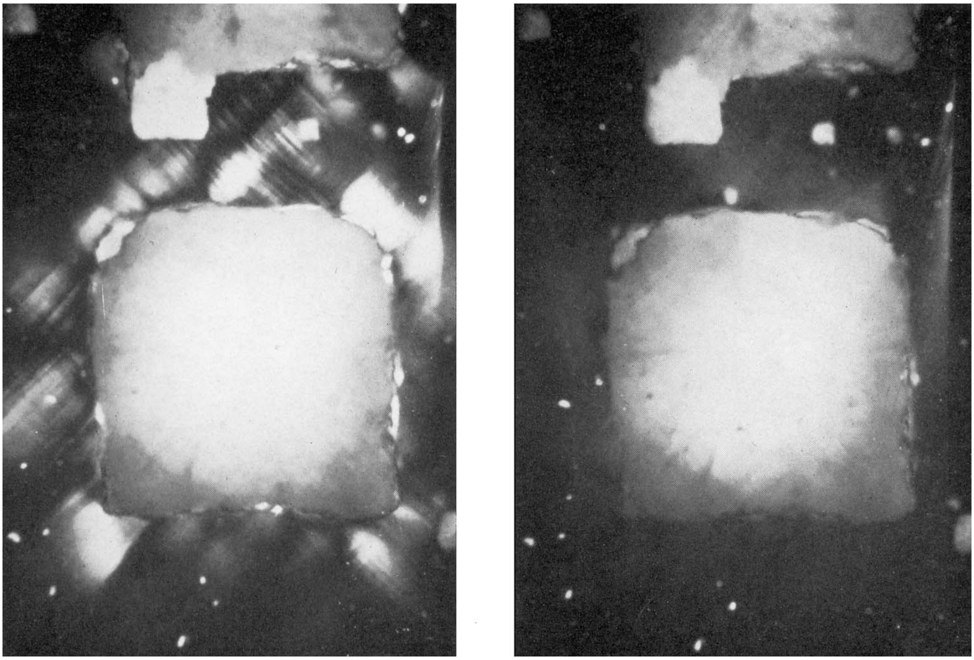
(*a*) (×87) (*b*) (×87)

FIG. 6.—A comparison of matching halves of a cleaved crystal.
(*a*) Reacted in chlorine; (*b*) Etched.



(*a*) (×55) (*b*) (×21)

FIG. 7.—Two different crystals photographed under polarized light.
(*a*) Crystal containing calcium impurity. (*b*) Partially reacted pure crystal.



(*a*) (×47) (*b*) (×47)

FIG 8.—A reaction zone photographed with the polarizers at different angles to the crystal axes.
(*a*) Polarization direction parallel to the sides of the photograph.
(*b*) Polarization direction at angle 45° to the sides of the photograph.

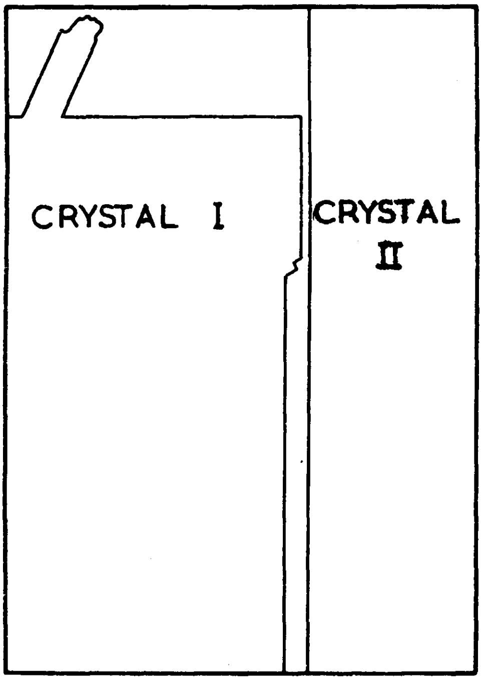


FIG. 9 (*a*)

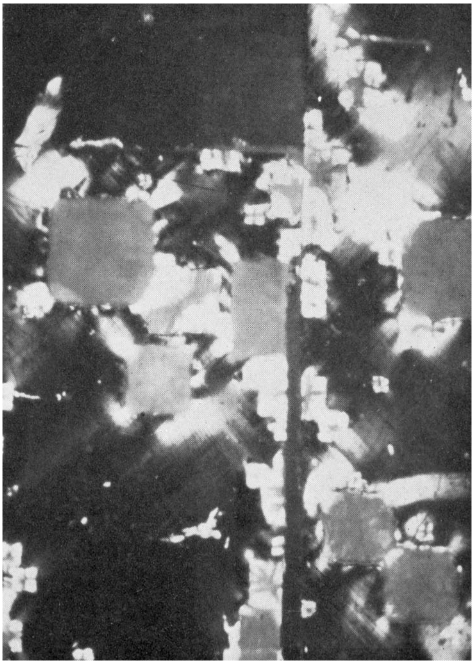
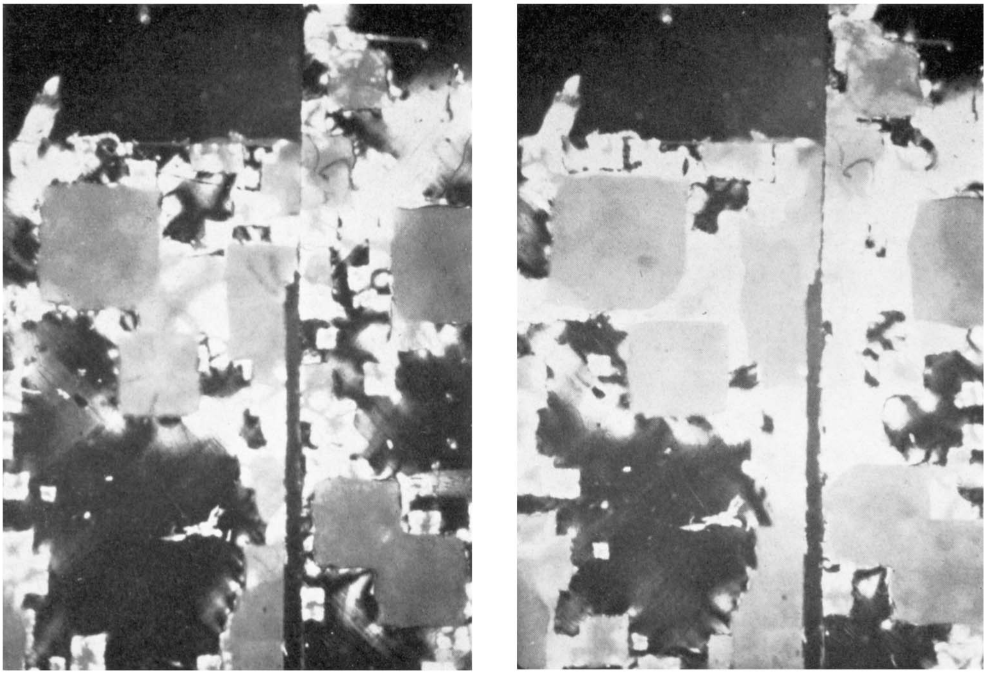
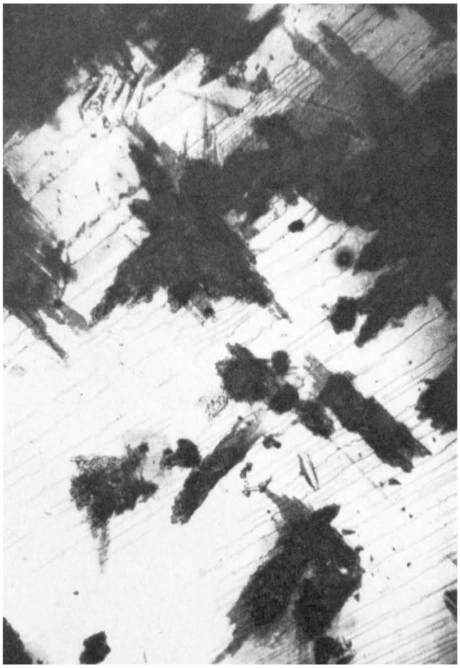


FIG. 9 (*b*) (×21)



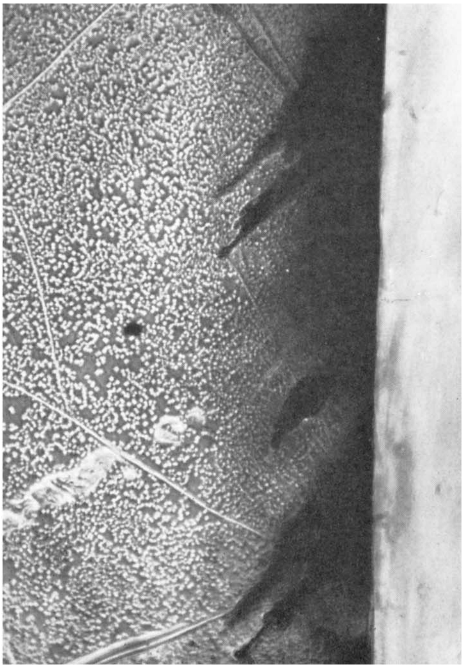
(*c*) (× 21) (*d*) (× 21)

FIG. 9.—Two pure crystals reacting at room temperature.
(*b*) Time t min; (*c*) time = t + 30 min; (*d*) time = t + 60 min.



(× 47)

FIG. 10.—The early stages of a reaction at 300 C.



(× 87)

FIG. 11.—The cleaved and etched surface of a crystal partially reacted at 300°C.

are far in advance of others but it is difficult to tell whether or not there is an increase of dislocation density in their immediate vicinity. It may be definitely concluded, however, that the " tongues " are not in any way connected with low angle boundaries.

KINETIC MEASUREMENTS

A number of measurements of weight change as a function of time were made for annealed pure crystals between 300° and 550°C. No induction periods were observed, and in every example the initial part of the reaction ($\alpha < 0{\cdot}05$) was well described by eqn. (1) with n close to unity. In particular, n was $1{\cdot}4 \pm 0{\cdot}1$ at 300° and $1{\cdot}0 \pm 0{\cdot}1$ at all of the other temperatures. A possible interpretation is that, at higher temperatures, nucleation is instantaneous and the initial growth is one-dimensional. The latter conclusion is in agreement with the microscopic observations.

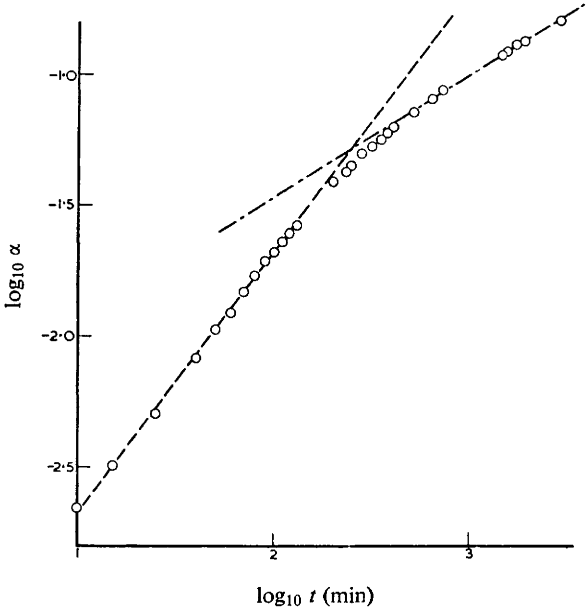


Fig. 12.—The fraction reacted as a function of time at 500°C.
— — — line of slope 1·0 ; —.—.— line of slope 0·5.

Fig. 12 illustrates the results obtained at 500°C. The dashed line of unit slope is a satisfactory limiting line for representing the initial reaction. The later stages are better represented by the dot-dash line of slope 0·5. This indicates that when the reaction has proceeded to the extent of 10 % or more it becomes diffusion-controlled.

Finally, although the initial reactions at higher temperatures show no induction periods, their rates increase with temperature only up to about $T = 350$°C, and even then the maximum rate ($d\alpha/dt$) is much less than that found at room temperature. Beyond 350°C the rates decrease steadily with increasing temperature. Consequently, the reaction goes to completion at room temperature much faster than at higher temperatures. This substantiates our arguments that lattice strain is an essential factor in promoting the reaction because strain cannot be sustained at higher temperatures. Practically, the conversion of potassium bromide crystals quantitatively to potassium chloride by reacting them with chlorine can be done most efficiently at room temperature.

We thank Mr. V. Paetkau for his assistance with some of the experiments, Dr. J. Rolfe for providing a number of the crystal specimens and some unpublished experimental results and Dr. Z. S. Basinski for helpful discussion.

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