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THE DEVELOPMENT AND THE FUNCTION OF THE INTERFACE PARTICIPATING IN THE NUCLEATION AND GROWTH REACTION BETWEEN CRYSTALLINE POTASSIUM BROMIDE AND CHLORINE GAS

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[Plates 1–10]

CONTENTS

A kinetic and microscopic study has been completed for the gas–solid reaction $KBr + Cl_2 \rightarrow KCl + BrCl$ to elucidate the mechanism of this nucleation and growth process. The work was concerned with reaction in two temperature intervals, under 400 K and over 450 K: reactivity was negligible in the intervening range (400–450 K).

The low temperature reaction (273–320 K in 25 kPa Cl_2) was characterized by long induction periods followed by a strongly acceleratory nucleation process yielding 'half-cube' shaped nuclei which grew at constant rate. Nucleation was catalysed by $SnCl_4$. Growth of nuclei ceased and required a second induction period for resumption of growth when reaction was interrupted by evacuation. The red-brown colouration of nuclei is attributed to liquid halogen (Br_2) retention; this was confirmed by titration. Product KCl crystallites were oriented in the KBr (111) directions, shapes of nuclei varied with reaction conditions. From kinetic measurements,

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and microscopic examinations of interface textures, it is concluded that reaction occurs within a thin zone (of around 10 μm) at the nucleus periphery, the chemical change proceeding between participants dissolved in liquid halogen. The probable reaction sequence is KBr dissolution in Br_2–BrCl–Cl_2,

$$Cl_2 + Br^- \leftrightharpoons [BrCl_2]^- \leftrightharpoons Cl^- + BrCl$$

and KCl precipitation.

Textural examinations of nuclei produced during the high temperature reaction (over 600 K) revealed the development of a subsurface pore system permeating unrecrystallized reactant. It is concluded that reaction in solid adjoining these pores yields product KCl that later recrystallizes, with (111) orientation relative to the reactant, in the form of irregularly shaped nuclei.

Introduction

The kinetic characteristics of solid state reactions are usually analysed by using rate equations derived through quantitative consideration of the geometry of the generation and development of product particle assemblages. For a selected rate process, the demonstration that isothermally measured yield–time data satisfactorily obey a rate equation of this form is accepted as evidence that the reaction proceeds through an identified pattern of progressive changes in geometry of the reactant–product interface. Such inferences are often confirmed by microscopic examination of the solid during progress of the chemical change or after a known extent of reaction. The reactant–product contact, the reaction interface, is therefore identified as the zone of chemical change, within which bond redistributions are preferentially effected.

The initiation of reaction at a new site, one that is not continguous with an existing nucleus, is termed *nucleation*. For many solid state decompositions it has been demonstrated (Thomas 1969, 1974) that this occurs at sites of crystal imperfection. Once established, a reaction interface advances into unchanged reactant and the consequent acquisition of reacted material, product, results in nucleus *growth*. Aspects of the growth of nuclei have been discussed by Clarke & Thomas (1969) and by Thomas & Renshaw (1969).

Microscopic measurements have identified various rate equations obeyed by the nucleation and the growth processes. Suitable combinations of these relations can then be integrated to yield kinetic expressions applicable to the overall reaction, based on progressive changes in geometry during interface development. When a second reactant participates and a solid product forms a barrier layer of constantly increasing thickness, the nucleus growth term requires modification by an appropriate diffusion limitation factor. The general review of this subject by Brown *et al.* (1980) describes the many successful applications of this approach to the kinetic analysis of numerous and diverse reactions involving solids.

The value of kinetic analysis of isothermal rate data in elucidating reaction geometry has been generally accepted. In contrast, the chemistry of the processes that participate in interfacial change are not so readily investigated. These specialized contact regions are of restricted thickness, often inaccessible to direct experimental study and probably unstable after reactant–product phase separation. Unlike homogeneous reactions, the kinetics of change do not give evidence of the molecularity or other controlling features of the bond redistribution step. Few surveys of interface chemistry are available but Galwey (1982) has proposed a classification scheme based on form and function of the reaction nucleus.

Against this state of current development of the subject, we report here a kinetic and mechanistic study of the gas–solid reaction

$$KBr(s) + Cl_2(g) \rightarrow KCl(s) + BrCl. \quad (1)$$

It has already been established that this is a nucleation and growth process (Morrison & Nakayama 1963; Morrison & Tuzi 1966). Boldyrev & Ivanov (1976) conclude that dislocation proliferation promotes the interfacial chemical change. Our original motivation, in further re-examining this reaction, was to investigate the reaction interface microscopically at higher magnifications than hitherto (Galwey *et al.* 1980, 1981), to establish more precisely the suggested role of imperfections in promoting the chemical change. We were also mindful of the advantages (Morrison & Nakayama 1963) of working with a reactant solid of simple and well-characterized structure, that contains imperfections of known properties.

During the early stages of the work, however, it became apparent that our observations were not consistent with previous mechanistic conclusions for reaction (1). Accordingly, we extended our objectives to reappraise generally the reaction mechanism by investigating the form and function of the nuclei. We also reinvestigated the previously reported irreproducibility of kinetic behaviour (Morrison & Nakayama 1963; Morrison & Tuzi 1966). From our rate and microscopic observations we conclude that this reaction is more satisfactorily represented by a mechanism that involves the active participation of *liquid* halogen present at the interface, retained within the fine channels and pores between product crystallites. This has been described as a fluid–flux nucleus (Galwey 1982).

Reaction models that involve the participation of an intranuclear liquid phase have not often found favour in recent mechanistic discussions concerned with nucleation and growth processes. Indeed, it has been maintained that for some solids, e.g. alum dehydrations (Garner 1955), the residual solid offers negligible impedance to volatile product escape: see also, however, Galwey *et al.* (1981). For the present low temperature reaction (under 400 K), we consider that it is reasonable to expect volatile product (BrCl and Br_2) condensation and temporary retention within the narrow intranuclear channels. This liquid halogen, in providing a solvent medium for reaction, offers an attractive explanation of the enhancement of reactivity associated with the reaction interface. Crystal components may undergo chemical change more readily on removal of the stabilizing lattice forces, as occurs, for example, on melting (Bawn 1955) or on dissolution (Galwey & Hood 1982). It was pointed out in a preliminary report of the present study (Galwey & Pöppl 1981) that the intervention of dissolved intermediates can provide an alternative and preferred reaction pathway, not available in the absence of the solvent.

Experimental

Kinetic measurements

Vacuum apparatus

Rates of nucleation and of growth were measured by microscopic observations, with a vacuum apparatus identical with that described previously (see figure 1 in Galwey *et al.* 1981). The reactant KBr crystal was supported on a thermostatted (± 0.1 K) plane surface within a glass envelope which could be evacuated under 10^{-3} Pa. This crystal was observed through an optical flat glass by a Reichert Zetopan microscope, used either in the transmission mode or in the reflection mode with interference contrast by the Nomarski technique. Chlorine gas could

be admitted to the reaction vessel and pressures measured to ± 0.5 kPa by a calibrated glass spiral gauge.

In each experiment, one or two KBr crystals (some 5–10 mm square $\times$ 0.3–0.7 mm thick) were placed on the thermostatted support, *immediately* after the reactant faces had been exposed by cleavage. Samples were evacuated under 10^{-2} Pa for 10–30 min during thermal equilibration at reaction temperature (± 0.1 K). Reaction was then commenced by the admission of the required pressure of chlorine gas, usually 25 ± 0.5 kPa Cl_2 but kinetic studies included observations throughout the interval 7–70 kPa Cl_2. Rates of interface advance were determined microscopically by using a calibrated eyepiece graticule to measure distances between the parallel opposite edges of the approximately square nuclei. Normally 15–40 length measurements were made for each nucleus, at appropriate time intervals. It was our usual practice to measure rates for the concurrent growth of several nuclei on the same or on neighbouring KBr reactant surfaces.

Tube reactions

This alternative and complementary technique, referred to subsequently as *tube reactions*, was found convenient for studies at temperatures greater than 320 K or when induction periods were unduly prolonged.

A freshly cleaved KBr crystal, identical with those used in vacuum apparatus studies, was placed at the sealed end of a glass tube (8 mm diameter) and a constriction pulled some 100 mm above the closed end. After evacuation, the required pressure of chlorine was admitted and the tube rapidly sealed at the constriction. Tube reactions were invariably prepared in batches and treated concurrently, usually in groups of six. This permitted the recognition of the occasional instances of anomalous behaviour, attributable either to the presence of water vapour or to air admitted to the tube by imperfect sealing.

After an appropriate time at reaction temperature, reacted crystals were withdrawn from the tubes for microscopic examination. Optical measurements through the cylindrical glass walls of these tubes were subject to distortion and had qualitative value only. Some quantitative measurements were made with a re-usable tube having an optical flat sealed into a glass envelope, some 3 mm above a planar glass surface and with a side-arm for reactant admission.

Other experimental methods are mentioned at appropriate places in the text below.

Electron microscopy

A Stereoscan S180 (Cambridge Instruments) scanning electron microscope (s.e.m.) was used to examine the surfaces of representative samples (precoated with gold–palladium). This technique is capable of studying surfaces only, and specimens examined included the pristine reactant (freshly cleaved KBr) together with similar surfaces after exposure to bromine or chlorine. The internal structures of developed nuclei were characterized from examinations of cleavage surfaces traversing the features of interest and exposed after partial reaction. Whenever practicable, information obtained by the s.e.m. was supplemented by comparisons from optical microscopy.

Preliminary work showed that KBr surfaces were sensitive to textural modification promoted by water vapour, particularly for surfaces previously exposed to chlorine. Accordingly it was necessary to store specimens for the minimum time possible in a dry environment between preparation and microscopic examination: all doubtful specimens were discarded.

No surface replication technique (Galwey *et al.* 1980) was found that could be reliably applied to the examination of KBr surface textures. KBr was sufficiently soluble in all solvents tested to result in obvious changes in the textural features of interest.

Reactants

Potassium bromide

Kinetic measurements for reactions in KBr crystals were concerned exclusively with freshly cleaved fragments from a single large block of potassium bromide ($20 \times 20 \times 100$ mm) supplied by Specac. Impurities detected by spectrographic analysis and subsequently measured by atomic absorption were (in micrograms per gram): Na (580); Ca (3.2); Mg (0.2); Fe (5.3) and Cu (2.1) with trace amounts of Al (under 0.2). Analar KBr, used to prepare reactant pellets and analysed in the same way, contained Na (190), Ca (0.9), Mg (0.3), Fe (5.4) and Cu (1.8). Reactant pellets were prepared by 2 min compression at approximately 1 GN m^{-2} of KBr (Analar), after crushing and preignition at about 1000 K.

Chlorine

Chlorine gas, specified as being over 99.5 % pure, was obtained from a cylinder supplied by B.O.C. This was bubbled through concentrated sulphuric acid and stored in a previously outgassed bulb. Storage for periods longer than five days was avoided because thereafter the silicone tap grease deteriorated, with adverse effects on the reproducibility of the apparent kinetic characteristics of the reaction.

Results and discussion

Preliminary and background observations

Retention of halogen within growth nuclei

The most obvious feature identified with the onset of reaction was the appearance of the strongly coloured red-brown nuclei. Since the retention of either *liquid* bromine or BrCl (or both) at the interface could have important implications for the reaction mechanism, by providing an alternative reaction path that involves dissolved ionic intermediates, this possibility was investigated.

The free halogen retained in KBr crystals, after reaction to known extents, was measured by titration (standard $Na_2S_2O_3$) of the iodine released on dissolving the solid in acidic KI solution. From 15 such determinations, for samples after reaction in 25 or in 50 kPa Cl_2, between 283 and 325 K, the mean halogen content corresponded to 3.0 % Br_2, though values ranged between 1.0–5.4 % Br_2. Theoretically, pseudomorphic replacement of KBr by KCl yields some 13 % void space and the amounts of bromine required to fill this volume are 0.04 % Br_2 vapour or 15 % Br_2 liquid. Our measurements confirm, therefore, that usually more than 10 % and sometimes more than 30 % of the pore space within nuclei is occupied by condensed halogen.

This rather wide variation in halogen retention (1.0–5.4 % Br_2) is due, at least in part, to its facile release on evacuation or as a brown pungent gas on standing. Such release is incomplete since nuclei remained yellow coloured, even after prolonged evacuation and only became white on heating to about 500 K. In differential scanning calorimetric measurements

on reacted crystals, the only response detected was a single broad endotherm that was sometimes observed at about 370 K. This has been attributed (Galwey & Pöppl 1981) to the volatilization of liquid bromine, if present. No other response peak was found between 310 and 600 K, thus there was no evidence of the decomposition of any intermediate such as a polyhalide. The reason for the persistent yellow coloration of nuclei, even after evacuation, has not been established but is probably because of the retention of liquid bromine trapped as inclusions within product KCl assemblages during growth. This is released only on heating. We also note that after evaporation of liquid bromine from a KBr surface, local spots of brown colour remain, similarly attributable to Br_2 retention as inclusions beneath the retextured crystal surface.

Texture and reactivity of freshly cleaved (100) *faces of reactant* KBr *crystals*

The observations of the texture of reactant surfaces and of the retexturing that occurs on exposure to either halogen or water vapour or both are important in the consideration of reaction mechanisms and are also required for the interpretation of textural features revealed during electron microscopic examinations. In particular, it was necessary to be able to recognize and to distinguish between modifications promoted by water vapour and features characteristic of the reaction of interest.

The pristine reactant surface. S.e.m. examinations, at magnifications up to $\times 20000$, of pristine, freshly cleaved (100) KBr faces showed these to be featureless and planar, except for linear and often aligned step edges (features also seen on cleaved alum crystals (Galwey *et al.* 1981)).

Exposure of reactant (100) KBr *faces to bromine.* (i) *Bromine gas.* Freshly cleaved KBr (100) surfaces underwent modification on exposure to bromine vapour, 0.8 Ps (where Ps is saturated vapour pressure) at 288 K. After short, 2–10 min, exposure the greater proportion of the surface was unchanged, but there was rounding of step edges, and pit (around 0.1–0.2 μm^3) development. Characteristic surface textures are illustrated in figure 1, plate 1. After long exposure to Br_2 vapour (over 30 min in Ps $\approx$ 0.8) textural changes had extended across the complete surfaces and occasional blister-like protuberances had been developed.

(ii) *Bromine liquid.* Liquid bromine invariably caused more profound and extensive textural modification than that resulting from exposure to the vapour. Typical surface roughening is illustrated by figure 2, plate 1. Occasional small red-brown stains in the solid could be observed by transmission microscopy after liquid Br_2 volatilization. These were presumably caused by the retention of included liquid Br_2 droplets, though the quantity of free halogen retained was too small to be detected by titration.

Discussion. Although it has been stated (Trotman-Dickenson 1973*a*) that the alkali halides are, in general, sparingly soluble in liquid Cl_2 or Br_2, the present observations demonstrated that bromine promoted significant textural reorganization of KBr (100) surfaces. Since these effects were detectable even when vapour only (Br_2, Ps $\approx$ 0.8) was admitted, it must be concluded that a strong interaction exists between KBr and Br_2, presumably involving surface condensation or intermediate compound formation. The total quantities of material relocated, were, however, small since the effects could be observed in detail only by using the s.e.m. and were usually at or below the limits of detection of the optical microscope.

Exposure of reactant KBr (100) *faces to water vapour.* KBr surfaces, exposed to water vapour (120 min at 288 K in 0.7 Ps) underwent retexturing, including the rounding of step and other sharp edges and the relaxation of zones of strain. This characteristic retexturing could be

observed and recognized in the s.e.m. but the changes were often below the limits of detection by optical microscopy. Water promoted appreciable surface mobility of lattice components: Walter (1971) has shown that KBr adsorbs about two monolayers thickness of water vapour at 0.45 Ps between 293 and 298 K.

Exposure of reactant KBr (100) *faces to chlorine.* (i) *Chlorine gas.* During kinetic measurements the chlorine pressure was usually not more than 0.1 Ps and after reactions no textural modifications could be detected on surfaces other than those obviously associated with nuclei (and described in context below). At the lowest temperature studied, 256 K, surface modifications similar to those described for exposure to bromine were sometimes detected. These are attributable to the condensation of product halogen (BrCl or Br_2 or both) since they were found on partly reacted crystals.

(ii) *Chlorine gas followed by water vapour.* Preliminary observations showed that after short exposure to Cl_2, under reaction conditions, unnucleated KBr surfaces were appreciably more susceptible to textural modifications promoted by water vapour, than the pristine reactant. This result is sufficiently important to justify the detailed investigation described below.

In comparative experiments, pairs of reactant crystals, one pristine and the other previously exposed to chlorine gas under reaction conditions, were placed together on the thermostatted stage of the vacuum apparatus. Directed across these crystals was a flow of air that contained a controlled pressure of water vapour, passing symmetrically and concurrently (*not* consecutively) across the parallel crystals. The KBr crystal surfaces underwent progressive textural changes which could be observed in the optical microscope used in the reflection mode. Precise comparative studies, in a series of 20 experiments, identified a sequence of progressive and reproducible variations of surface texture. These show that both crystals in each pair undergo an identical general sequence of surface modifications, but that these *always* occurred appreciably earlier and more extensively in the chlorine pretreated specimen. In a typical experiment, the earliest detectable change on KBr surfaces after previous exposure to chlorine gas was the generation of approximately square and probably aligned features, figure 3*a*, plate 2. In contrast, a pristine surface (not pretreated with Cl_2) but otherwise concurrently and identically exposed to water vapour had only undergone rounding of the step edges, figure 3*b*, plate 2. After a longer period of chlorine pretreatment the retexturing was more pronounced, figure 4, plate 2.

Discussion. These observations demonstrate that exposure to chlorine resulted in a change of reactivity of the *total surface* of the KBr crystal and modification was not specifically associated with sites of potential nucleation. The simplest explanation of this behaviour is that chlorine reacted over all the KBr surfaces but the extent of chemical change was limited and only specialized sites were capable of subsequent generation of growth nuclei. This identification of an initial *overall* surface interaction, on exposure of the solid to reaction conditions, is similar to behaviour observed during the onset of dehydration of alums (Galwey *et al.* 1981). This reaction model is not, however, in accordance with the widely accepted view that nucleation processes obeying the power law (including the present reaction, Morrison & Nakayama 1963) involve a localized sequence of consecutive chemical changes (Brown *et al.* 1980).

A consequence of this sensitivity of surfaces, and, particularly, of reacted surfaces, to water promoted modification is that textural changes may occur between sample preparation and examination. Any specimen showing evidence of deterioration during storage, by the appearance of structures characteristic of water promoted modification, were discarded. With care, reliable surface textures could be obtained for examination.

Microscopic examinations

Throughout the work, emphasis was placed on the value of microscopic observations in elucidating reaction mechanisms and, in all, more than 800 photographs were obtained. The representative examples reproduced here were selected so that each illustrated a significant feature which was identified as being both representative and reproducible. The reaction conditions used for the preparation of each individual sample are specified in the figure legend.

We present first the microscopic observations since a knowledge of the structures of both the nucleus and the interface was a necessary prerequisite for the interpretation of the kinetic data. Kinetic and observational measurements were, however, made concurrently with the same samples.

The $KBr + Cl_2$ *reaction at low temperature, under* 400 K

Chlorine reacted with potassium bromide at rates suitable for kinetic measurements in two distinct temperature ranges, separated by an interval of small or negligible reactivity above about 370 K (Morrison & Nakayama 1963; Ivanov & Schachtschneider 1980). Our main emphasis has been on the *low temperature reaction*, studied below 400 K and results are reported in the present section. We have also made a more limited investigation of the *high temperature reaction*, which occurs above 500 K; these results are presented in the next section. We believe that the two rate processes proceed by quite different reaction mechanisms.

Microscopy

Nucleus structures were first characterized by microscopic examinations of product assemblages developed under conditions corresponding to median reactivity, in particular for reactions between 273 and 293 K in 25 kPa Cl_2. Subsequently the effects of variations in chlorine pressure (from 12 to 50 kPa), temperature (from 256 to 325 K) and certain catalysts were determined.

Cleaved nuclei. Rapid cleavage of freshly developed nuclei (for examination of internal structures) often revealed local textural roughening of exposed KBr (100) surfaces that immediately adjoined the interface. In contrast, surfaces more remote from the reaction zones on the same crystals were smooth. When reacted material had been evacuated before exposure, the KBr (100) cleaved surfaces adjoining the reaction zone were usually smooth and always less textured than samples cleaved without prior removal of the volatile product. Accordingly we conclude that the local roughening of KBr beside a nucleus results from contact with bromine vapour, or perhaps even droplets of liquid, released by fracture of the nucleus containing it. It has been shown that Br_2 actively promotes surface retexturing.

We have been unable to confirm that dislocation proliferation occurs at the reaction interface. Etching experiments revealed the presence of numerous line imperfections at all crystal faces examined but there was no evidence that the density increased in KBr zones adjoining the product nuclei. Moreover, the propagation of cracks (indicative of strain relief) beyond nuclei and extending into unchanged reactant was so rare as to be regarded as exceptional. This behaviour contrasts with the dehydration reactions of alums, where there was obvious crack proliferation at nucleus boundaries (Galwey *et al.* 1981).

We have, therefore, no evidence of reactant cracking, or strain distortion capable of generating structural imperfections in KBr adjoining the reaction interface. Local retexturing of the

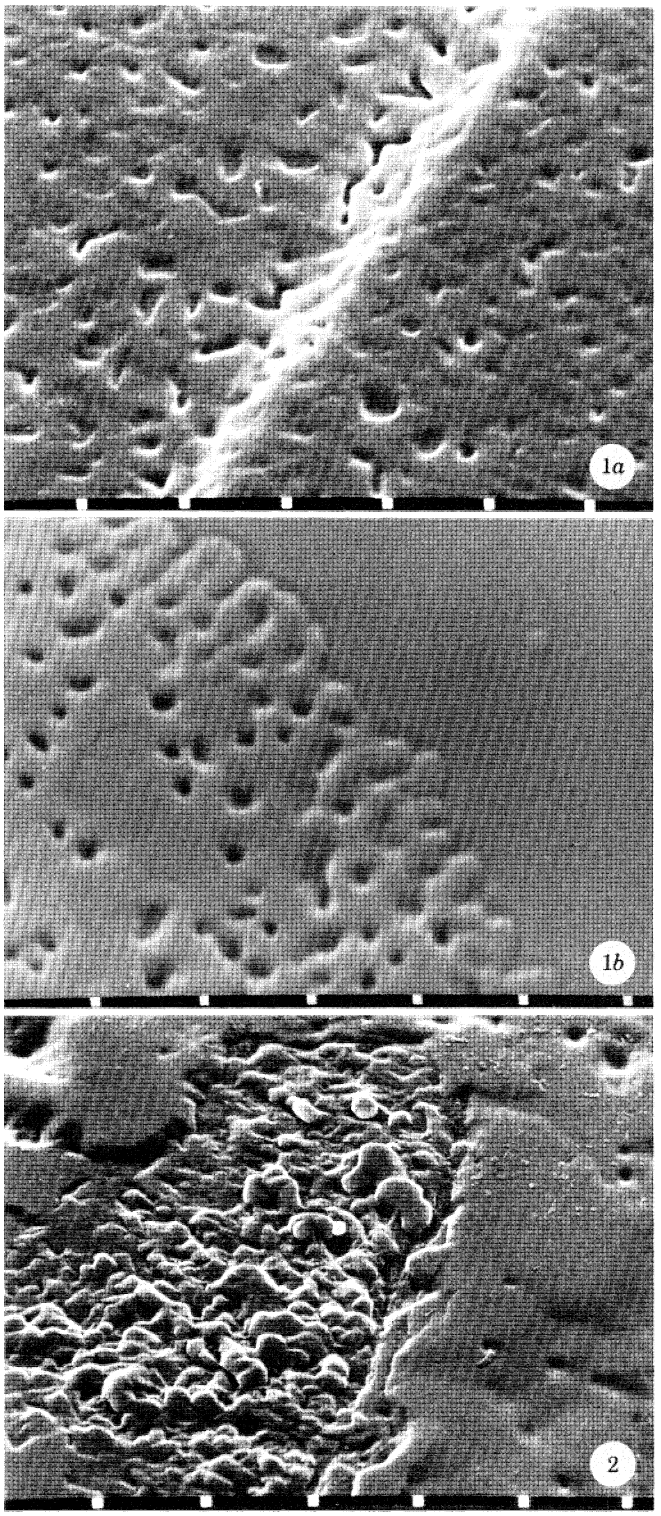

FIGURE 1. KBr surfaces, freshly cleaved and exposed to bromine vapour (0.8 Ps) at 288 K. (*a*) After 7 min exposure to Br_2 the step edges have become rounded, as compared with the pristine faces. Local modification of adjoining surfaces is also evident. (*b*) After 5 min exposure to Br_2, surfaces in the vicinity of step edges had developed rounded features and small pits. Much of the surface between step edges remained unmodified. (On these and other s.e.m. photographs a scale is included at the lower edge: spacings of the scale divisions here are (*a*) 3 μm and (*b*) 1 μm.)

FIGURE 2. S.e.m. photograph of a KBr surface on which a drop of liquid Br_2 had remained for one minute at 288 K before evaporation. The original featureless, flat surface has been extensively modified, though the detailed textures remaining varied somewhat between nominally identical experiments. S.e.m.: spacing of scale divisions is 10 μm.

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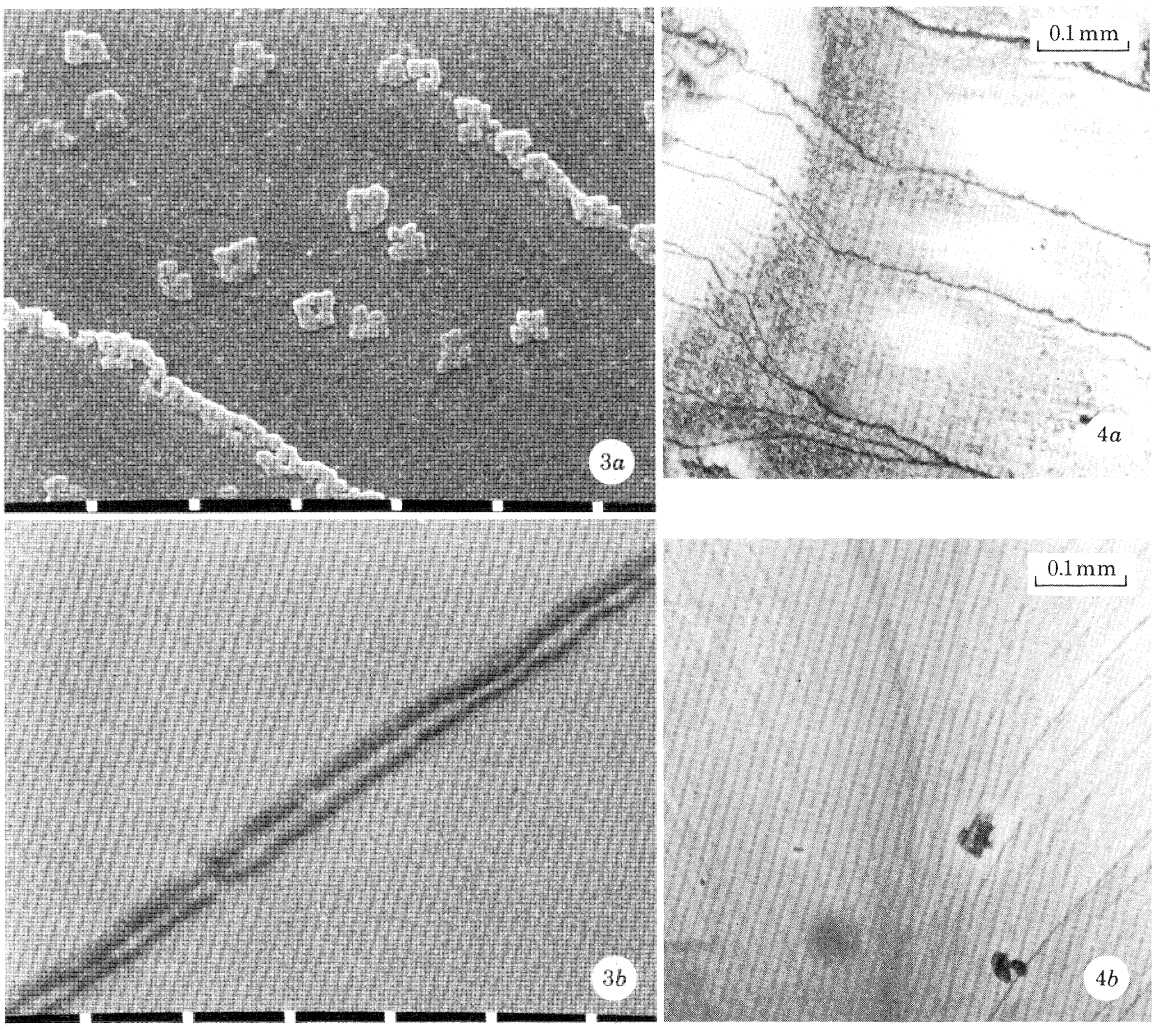


FIGURE 3. Comparative s.e.m. photographs for two differently pretreated KBr surfaces after concurrent exposure to water vapour with a slow increase in pressure from 0.2–0.5 Ps (H_2O) during 60 min. (*a*) This surface, which had previously reacted for 40 min at 290 K in 25 kPa chlorine, underwent a characteristic water vapour promoted textural modification. (*b*) This pristine and unreacted surface was unchanged by its concurrent exposure to the water vapour, except for the rounding of step edges. S.e.m.: spacings of scale divisions are both 3 μm.

FIGURE 4. Comparative optical micrographs also confirmed (see figure 3) that a surface (*a*) previously reacted (160 min at 290 K in 25 kPa chlorine) underwent greater textural modification than a pristine surface (*b*) after both had been identically and concurrently exposed to water vapour (30 min at 288 K in 0.5 Ps (H_2O)).

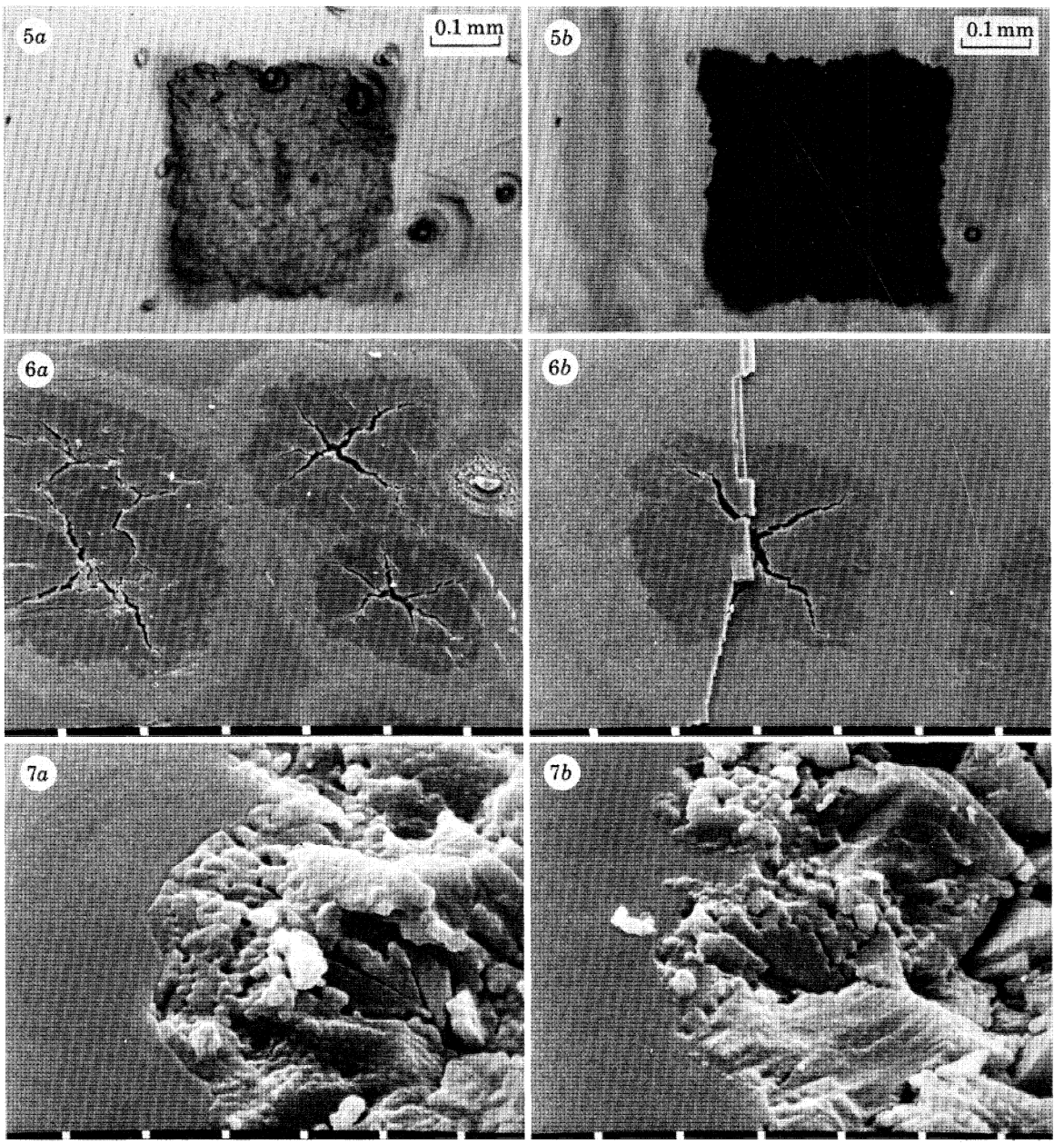


FIGURE 5. Reflection and transmission optical photomicrographs of a small growth nucleus in a partly reacted KBr crystal (1440 min at 273 K in 25 kPa chlorine). The region of surface deformation is slightly smaller than, but corresponds with, the approximately square but irregular outline boundary of the nucleus seen in transmission. Surface cracking had not yet developed.

FIGURE 6. Two areas of a KBr crystal that contains growth nuclei. The surface of each nucleus is distorted and there is approximately diagonal cracking. Around each nucleus there is an aureole of slightly different texture. (240 min tin promoted reaction at *ca.* 290 K in 25 kPa Cl_2.) (*a*) Four nuclei are present with some overlap, a reacted tin residue can be seen near the centre of the right hand side. (*b*) This single nucleus was initiated at a surface step edge and probably within a crack at this discontinuity. S.e.m.: spacings of scale divisions are both 30 μm.

FIGURE 7. The reaction interface at high magnification. To the left are areas of unmodified KBr reactant, exposed by cleavage after nucleus development. These are not penetrated by cracks emanating from nuclei. To the right are product assemblages, KCl crystals often having flat faces and intranuclear pore systems affording pathways for halogen movements. Between these regions is the reaction zone, within which the chemical change occurs and believed to contain liquid during interface advance. Particles here are small, often rounded, presumably participating in dissolution processes, and show some textural resemblances to Br_2 modified KBr (figures 1 and 2). (240 min reaction at 290 K in 25 kPa Cl_2.) Spacings of scale divisions are both 3 μm.

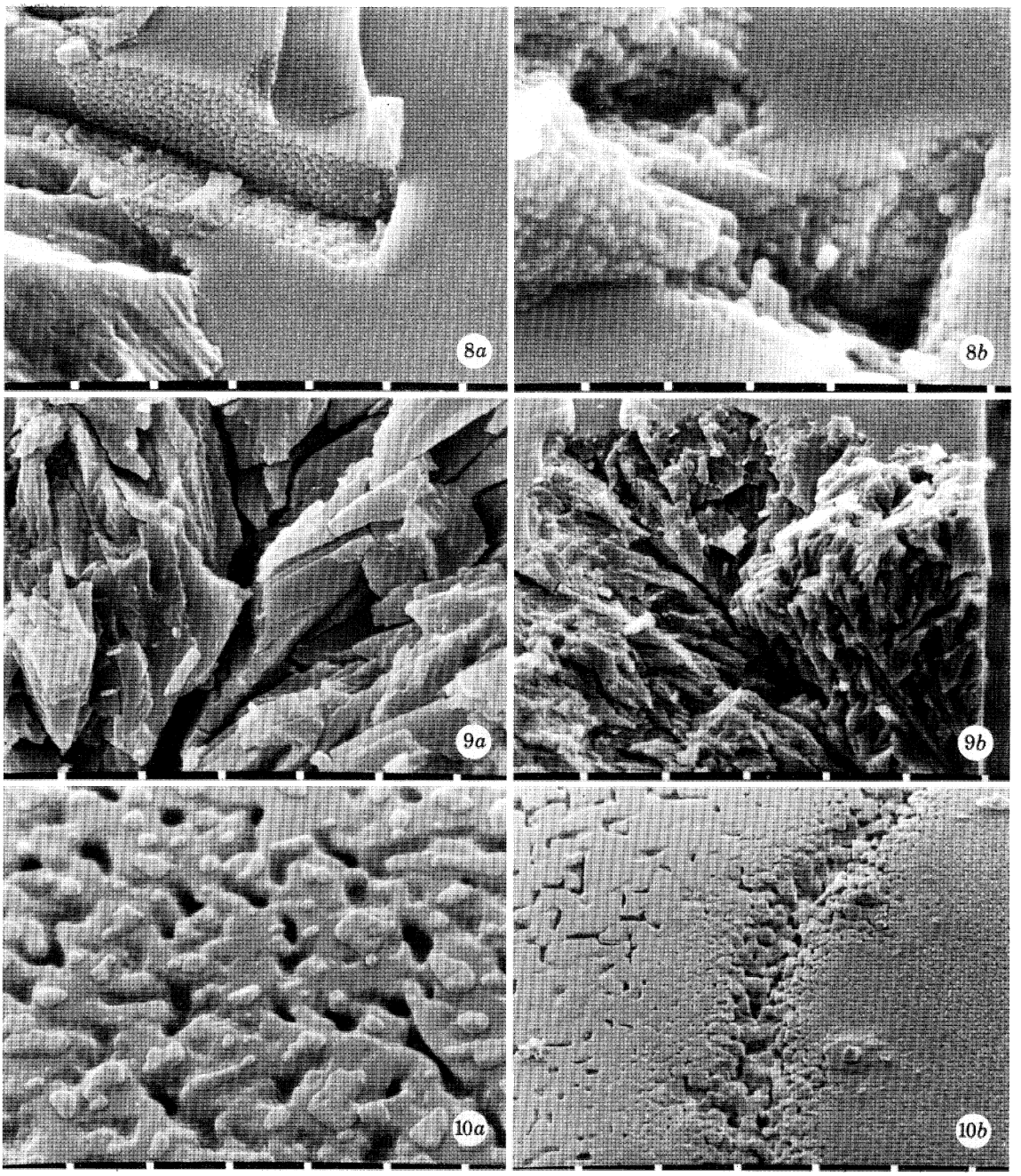


FIGURE 8. Details of interface textures revealed by cleavage of growth nuclei. The appearance, shape and dimensions of the numerous small (*ca.* 0.2 μm) hemispherical protuberances on reactant surfaces are similar, in some respects, to the textures developed by Br_2 modification of KBr surfaces (figure 1, plate 1). The rounded habit of these features is ascribed to participation in dissolution–recrystallization processes involving liquid halogen contained within the intercrystalline channels. This appearance is more readily explained by etching and a dissolution–diffusion mechanism involving a solute than through control by crystallographic forces. The planar areas of active surfaces are not oriented normally to the mean (100) directions of nucleus growth, which is here approximately from left to right. No textural modifications are evident in the crystal face beyond the interface, exposed by cleavage after reaction. (1680 min reaction at 273 K in 25 kPa Cl_2.) S.e.m.: spacings of scale divisions are (*a*) 3 μm and (*b*) 1 μm.

FIGURE 9. Habits of crystals towards the centres of nuclei tended to be less regular than those adjoining reaction zones. Intercrystalline pore systems permit gas transport to and from the reaction zone by large channels connected with the fine tributary systems. Immediately behind the active reaction zone KCl crystals are often slab-like, oriented in (111) directions with respect to the reactant KBr. (240 min reaction at 290 K in 25 kPa Cl_2.) S.e.m.: spacings of scale divisions are (*a*) 3 μm and (*b*) 10 μm.

FIGURE 10. (*a*) The outer crystal surface of a nucleus that had been exposed to water vapour after reaction. (*b*) Along the surface boundary of the nucleus a depression developed, attributable to the enhanced solubility of the finely divided product first formed and possibly also the presence of free halogen: here the right hand side is the nucleus surface. (Before exposure to water vapour the crystal had reacted 200 min at 291 K in 25 kPa Cl_2.) S.e.m.: spacings of scale divisions are (*a*) 3 μm and (*b*) 30 μm.

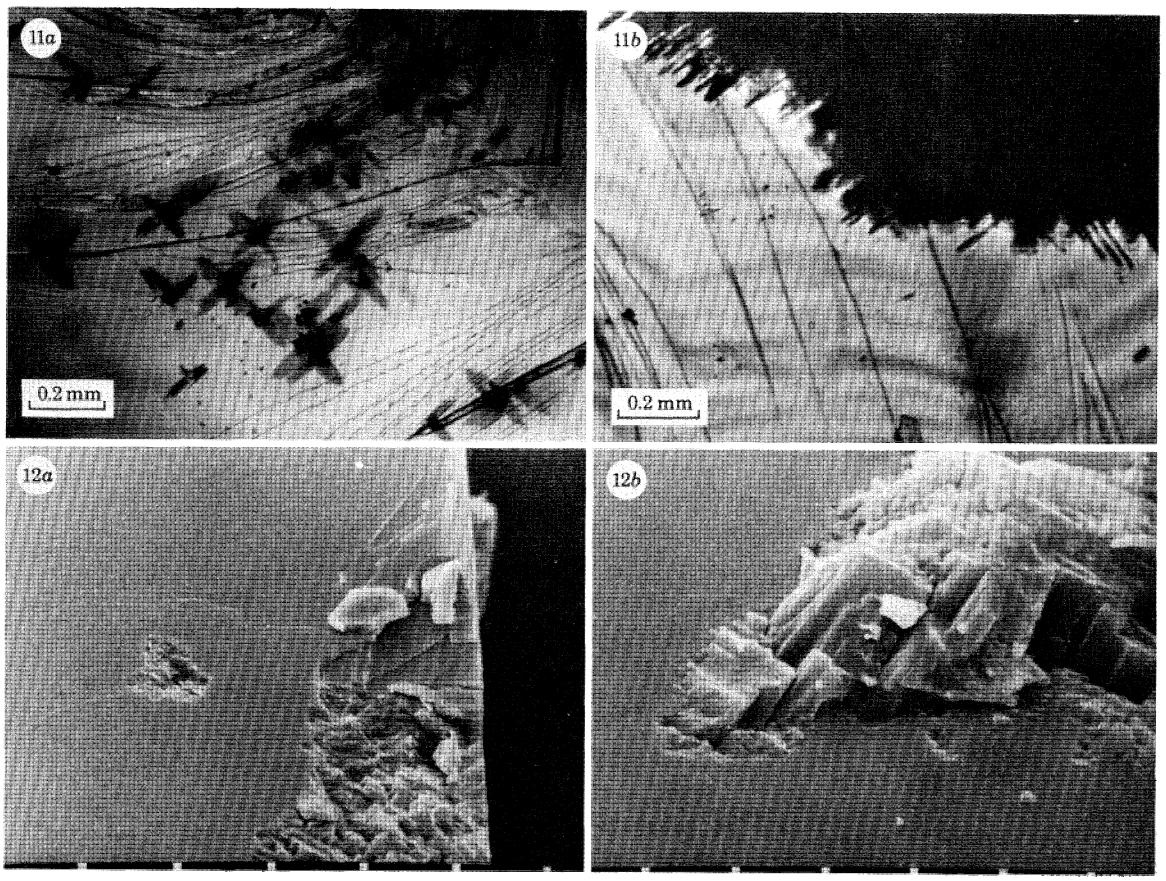


FIGURE 11. Optical micrographs of the fibre-like structures oriented in (111) directions, developed during the latter stages of tube reactions. (*a*) Small square-outline nuclei extended into the crystal ((111) directions) to form X-shaped structures. (1440 min reaction at 273 K in 25 kPa Cl_2.) (*b*) Shows the fibre-like development of product in the later stages of growth of large nuclei. (4320 min reaction at 293 K in 25 kPa Cl_2.)

FIGURE 12. Textures of X-shaped nuclei revealed by (100) cleavage of reacted KBr. (*a*) The zone of (111) development is well separated from the section of a surface nucleus. The texture of the top of this advancing zone included rounded features resembling those found at advancing interfaces (figure 8, plate 4). (*b*) The (111) orientation of product KCl crystals and the associated pore structures of the fibre-like prolongations are shown. (These crystals were tube reactions for 1320 min at 273 K in 25 kPa Cl_2.) S.e.m.: spacings of scale divisions are (*a*) 10 μm and (*b*) 3 μm.

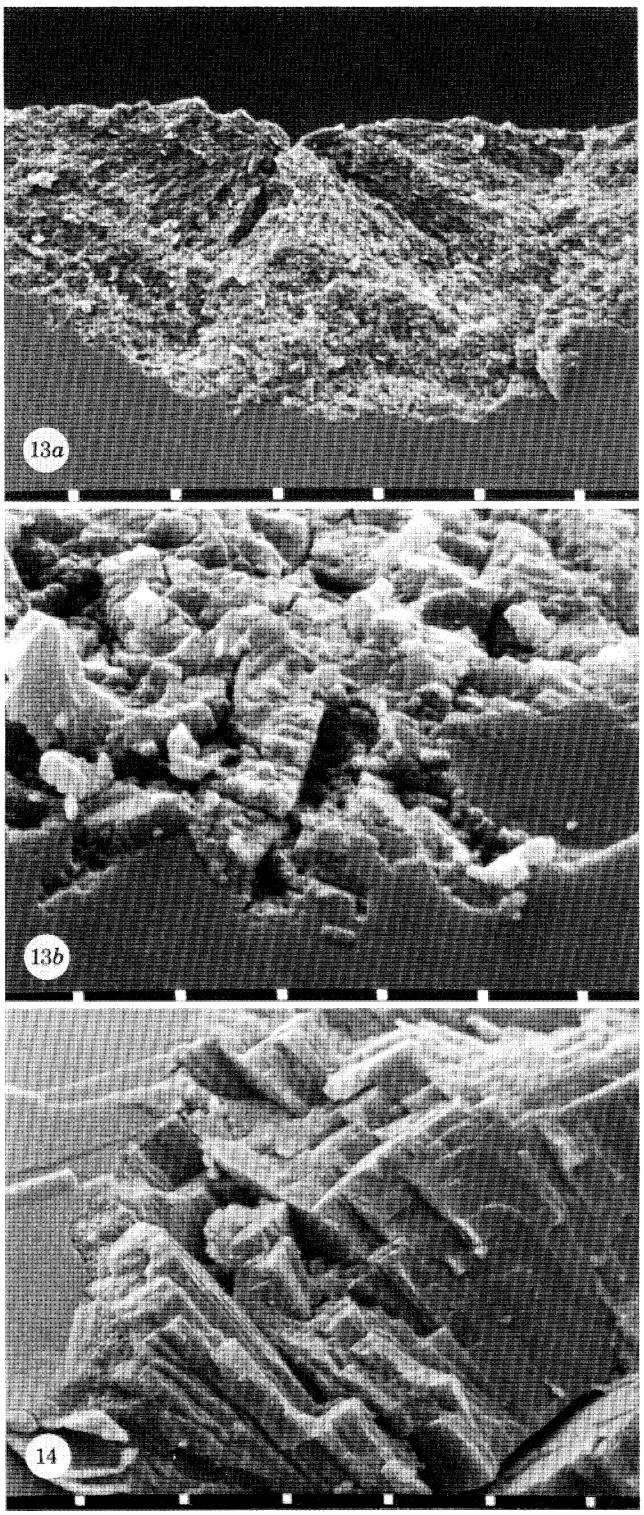


FIGURE 13. (*a*) Section of an approximately hemispherical nucleus developed during reaction in a relatively low chlorine pressure (12 kPa Cl_2). (*b*) At higher magnifications it is seen that the KBr–KCl interface is most irregular, crystallites are small (3–5 μm) and product crystal alignments in the (111) directions are less obvious (1360 min reaction at 291 K in 12 kPa Cl_2). S.e.m.: spacings of scale divisions are (*a*) 30 μm and (*b*) 3 μm.

FIGURE 14. Section of nucleus developed by reaction in 50 kPa Cl_2 showing the large (*ca.* 10 μm), slab-like, (111) oriented KCl crystals in the vicinity of the reaction interface (1360 min reaction at 291 K in 50 kPa Cl_2). S.e.m.: spacings of scale divisions are 10 μm.

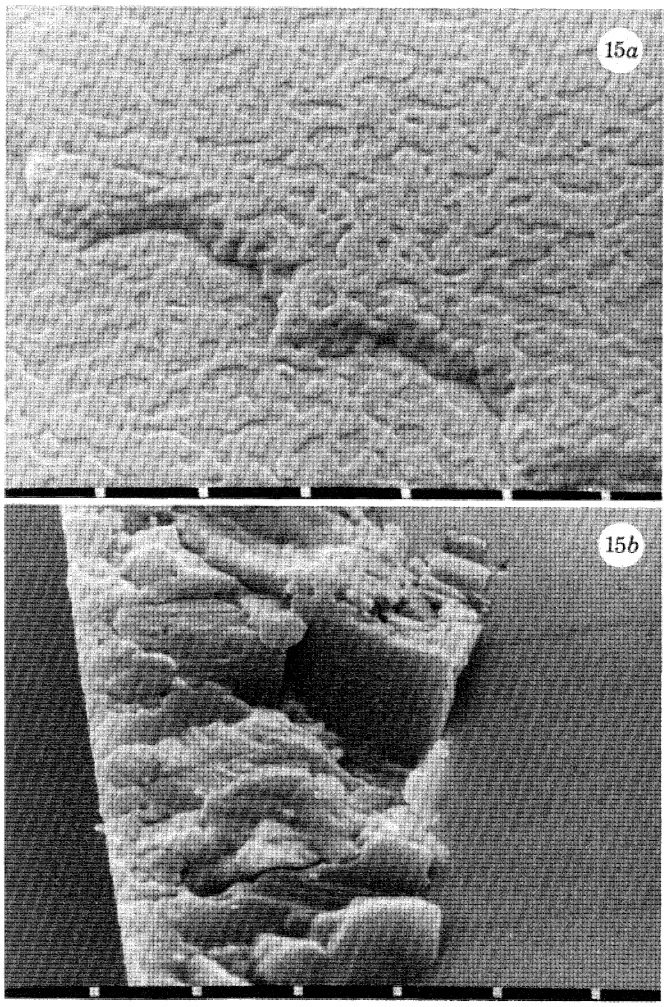


FIGURE 15. Textures developed during reactions at low temperature (256 K). (*a*) Textural modification of the reactant surface here is ascribed to halogen condensation. (*b*) This cleaved section of a nucleus reveals the pitted surface of large KCl product crystals, oriented in (111) direction. (1260 min reaction at 256 K in 25 kPa Cl_2.) S.e.m.: spacings of scale divisions are both 3 μm.

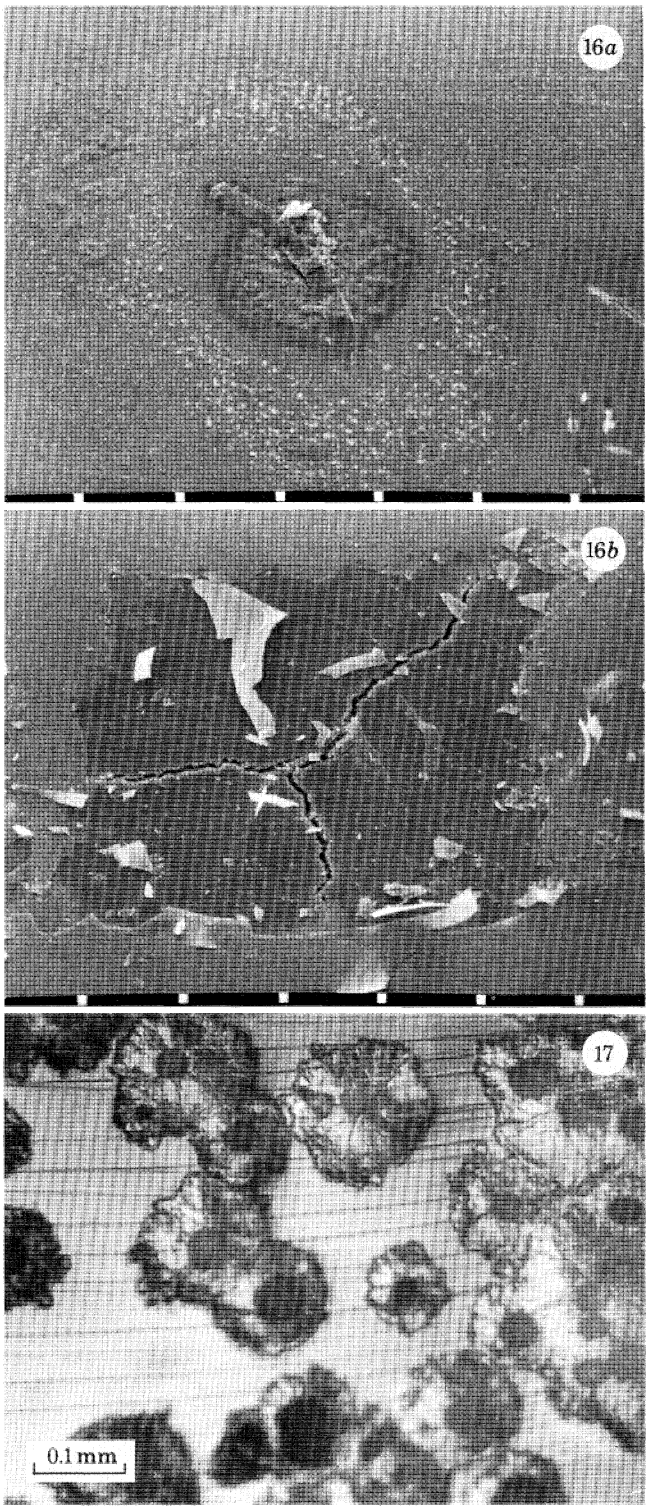


FIGURE 16. Surface textural changes due to excess tin on reactant surfaces. (*a*) A residue from a reacted tin particle (oxide?) is surrounded by a region of textural modification. (*b*) Elsewhere on the same surface, a surface layer, of presumably modified structure, has become detached over an area that coincides with a growth nucleus. Neither texture was ever observed during unpromoted reactions. (Two reaction intervals: 115 min at 283 K continued with 85 min at 325 K, both in 25 kPa Cl_2.) S.e.m.: spacings of scale divisions are both 30 μm.

FIGURE 17. Optical reflection micrograph for a lead promoted reaction: the nuclei are unusual in having circular outlines. No reaction was apparent after 18700 min at 380 K in 25 kPa Cl_2, tube reaction, but, after cooling the reaction shown occurred during 180 min at 273 K.

cleaved face near the reaction zone after fracture of a halogen-containing nucleus is, however, satisfactorily explained by interaction with the halogen released.

Reactions at 273–293 K *in* 25 kPa Cl_2. Product nuclei were usually approximately square with irregular boundaries, typical reflection and transmission optical photomicrographs are shown in figure 5, plate 3. Surface cracking was not yet evident on this example but the diagonal disposition of cracks, characteristic of nucleus surfaces, is shown in figure 6, plate 3. (Surface cracks on nuclear material appear only after appreciable growth.) The nucleus in figure 6*b*, plate 3, was apparently generated at a step edge, possibly within a cleft at this surface discontinuity. Cleavage sections of nuclei were approximately rectangular in outline.

The KBr–KCl contact was usually irregular, typical textures are shown in figure 7, plate 3. Although the mean directions of interface advance correspond with principal crystal axes, the KBr–KCl interface was not composed of planar (100) (etc.) surfaces. The uneven growth of product crystals oriented in the (111) direction resulted in the development of imperfect, serrated nucleus boundaries. Three zones of different textures across the reaction interface can be distinguished from the photomicrographs (figure 7, plate 3). To the left of these illustrations there is an unmodified cleaved KBr (100) surface. To the right the polycrystalline zones were identified as nuclei and shown by electron dispersive analysis to be composed of KCl, and contain no appreciable quantity of KBr. Such intranuclear assemblages were penetrated by crack systems permitting reactant (Cl_2) access and product (BrCl) escape. The active reaction interfacial zone between these is composed of small irregular crystals with rounded surface textures and this is identified as the region of the liquid halogen promoted chemical change.

Further characteristics of nucleus and interface textures are illustrated in figures 8 and 9, plate 4. Discussions of the features observed and treatments of the reactant specimens photographed are recorded in the figure legends. In the immediate post-reaction zone, crystals of KCl product were often in the form of slabs oriented (111) with respect to the KBr reactant. Toward the centre of each nucleus crystal habits were much less regular and the assemblages were penetrated by an interconnected system of channels of various sizes (figure 9).

Exposure of partly reacted crystals to water vapour modified the surface textures of nuclei (figure 10, plate 4).

In tube reactions the quantity of chlorine available was insufficient to effect complete reaction of the KBr crystals used. Under these conditions, during the final stages of growth, the existing nuclei developed what appeared, in the optical microscope, to be bundles of fibres oriented in the (111) direction with respect to the KBr host crystal. The downward penetration of these made it difficult to obtain satisfactory optical photomicrographs, but some characteristic features are shown in figure 11*a*, plate 5. Similar development of fibre-like processes was also observed during the final stages of growth of large nuclei (figure 11*b*, plate 5). In the s.e.m. these fibre-like growths could be examined only in section, revealed by (100) cleavage: representative photomicrographs are shown in figures 12*a* and *b*, plate 5. In figure 12*a* the tip of a (111) fibre-like growth is well separated from the compact nucleus. Parallel, (111) oriented KCl crystals, within a fibre development, penetrated by channels, are shown (in section) in figure 12*b*.

Variation of chlorine pressure (12–50 kPa). In 12 kPa Cl_2, nuclei were approximately hemispherical. In transmission, outlines were often almost circular and typical sections are shown in figure 13, plate 6. The irregular and prolific but random direction of advance of product from

the interface accounts for the equal rate of growth of nuclei in all directions, and results in the observed hemispherical development.

At higher pressures of reactant, 50 kPa Cl_2, nuclei were approximately rectangular in outline, but distorted by some preferred growth in the (111) directions. Boundary edges were, therefore, slightly concave and the relatively large (often over 10 μm) slab-like product KCl crystals (figure 14, plate 6), were oriented in the (111) directions.

Variations of reaction temperature (256–325 K). Low temperature reactions (256 K) were often accompanied by surface textural modification (figure 15*a*, plate 7), attributable to halogen condensation or reaction in a superficial liquid film. Sections of nuclei developed under these conditions were composed of large, aligned (111) KCl crystals, the surfaces of which were often pitted (figure 15*b*, plate 7).

No parameter could be identified that would provide a quantitative size measurement for the often irregular assemblages of product crystallites. The qualitative evidence was that, in 25 kPa Cl_2, KCl crystals formed in low temperature reactions (273 K) were larger (around 3 μm section edge by more than 20 μm length) than those formed at higher temperatures (up to 325 K), for which crystallite dimensions did not usually exceed 5 μm.

Textural changes for reactions with catalysts. Excess *tin* (as $SnCl_4$) catalyst (see later) resulted in the extensive surface textural modifications illustrated in figure 16*a*, plate 8; such changes were not apparent when smaller quantities of tin were present. After reaction the residue from a tin particle (originally identified by optical microscopy) adhered to the crystal face (figure 16*a*). This is surrounded by a circular zone of local surface distortion. Elsewhere on the same crystal the surface layer of a nucleus has become detached and fragmented (figure 16*b*, plate 8).

Lead did not interact with chlorine at ambient temperature but reaction was initiated by heating (see below). The nuclei that subsequently developed were circular in outline and included a rounded central zone within which nucleation had occurred (figure 17, plate 8).

Reaction kinetics

Induction periods. Induction periods, t_i, were measured by extrapolation of the linear rates of growth of the first formed nuclei to the time of zero diameter. These values of t_i showed considerable irreproducibility, with variations up to $\pm 50\,\%$ between nominally identical experiments (see also Morrison & Nakayama 1963). Results reported below were obtained from 120 experiments, in 25 kPa Cl_2, many of which were performed in duplicate.

Reactions without additives. Mean measured induction periods are summarized in table 1. The time required to initiate the low temperature reaction increased with temperature and no nuclei were developed in many tube reactions held at 373–380 K for over 10000 min. Indeed, in the two samples held at this temperature for the longest time, approximately 27000 min (19 d), there was no evidence of reaction but, after cooling to 273 K, nuclei appeared rapidly (under 60 min).

Values of t_i for reactions of pellets (crushed and compressed KBr) in the vacuum apparatus were relatively very short: the mean t_i was 25 min, from measured values between 0 and 55 min.

Bromine. Surfaces pretreated by being covered with liquid Br_2, subsequently removed by evacuation, nucleated more rapidly than pristine surfaces. At 298 K, t_i values were 120–1000 min and over 3000 min respectively.

Iodine. Small crystals of KI, deposited on a reactant KBr crystal by evaporation from dilute

solution in ethanol, rapidly reacted on admission of chlorine to release I_2. The induction period to the KBr reaction thereafter was reduced to between 60 and 360 min at 293 K.

Tin(IV) chloride. $SnCl_4$ was found to be a most effective nucleation promotor, always reducing the induction period and it was used for this purpose throughout our kinetic measurements. Reasons for selecting this compound for study are discussed below. $SnCl_4$ was usually formed *in situ* on the cleaved KBr surface by reaction of a *small* amount (perhaps 2 ng) of metallic tin with the chlorine admitted.

TABLE 1. INDUCTION PERIODS (t_i) TO ONSET OF REACTION IN 25 kPa Cl_2 AND IN THE ABSENCE OF ANY ADDITIVE

apparatus*	temperature/K	average† induction period t_i/min
t	256	1200
t	273	1200
v	283	1200
v	293	4300
v	313	8600
t	383	> 27000
t	493‡	30
t	620‡	< 10

* *v*: vacuum apparatus; *t*: tube reaction.

† *Average* values of induction periods are listed; there were significant variations between successive measurements.

‡ High temperature reactions: see later in text.

Values of t_i for $SnCl_4$ promoted reactions in the vacuum apparatus were between 50 and 250 min, increasing somewhat with temperature across the interval studied, 283–317 K. The average t_i for $SnCl_4$ promoted tube reactions at 273 K was 50 min. (Compare with data in table 1.)

Microscopic studies of these $SnCl_4$-promoted reactions showed that nucleation occurred preferentially at sites of surface damage, such as intentionally introduced scratches, texturally reorganized regions remaining after evaporation of a placed $SnCl_4$ droplet, or where an Sn particle had reacted with Cl_2. Experiments were also made in which the metallic tin was placed on the apparatus wall, rather than the KBr crystal as more usually adopted. The short induction periods in these experiments were similar to those characteristic of the usual $SnCl_4$ promoted reaction, though larger numbers of nuclei were formed. This demonstrates the mobility of the active promotor (b.p. of $SnCl_4$ is 387 K).

Tin was effective as a nucleation promotor only when very small quantities were available. When excess Sn was present the KBr surface underwent complete retexturing but no recognizable nuclei were formed in periods of up to 1000 min at 293 K.

Other catalysts. Induction periods were also reduced following the addition of small amounts of Ge or Pb, but initial heating was also required, presumably to effect chlorination of the metal to $GeCl_4$ or $PbCl_4$. These promotors are, however, less active than $SnCl_4$. Arsenic, in contrast, poisoned the reaction, presumably through stable surface compound formation with KBr, an influence that continued into subsequent experiments, perhaps by retention of $AsCl_3$ on the reaction vessel walls.

Discussion. The evidence that intranuclear liquid halogen provides the solvent within which the chemical change occurs provides the starting point for mechanistic consideration of the

above observations. We identify an essential step in nucleation as the generation of a suitable liquid medium within a crack that penetrates the reactant crystal. During subsequent growth of nuclei this liquid becomes a mixture of halogens (Cl_2, BrCl and Br_2) retained within fine intercrystalline pores.

In the absence of a promotor, the long induction periods to reaction are explained as follows. Halogen product (Br_2 or BrCl or both) is slowly released by reaction of Cl_2 with all KBr surfaces until sufficient is present to result in condensation in a suitable crystal crack. This droplet of liquid constitutes the germ nucleus from which a growth nucleus is subsequently developed. The observed increase in t_i with reaction temperature (table 1) is necessary, therefore, because the vapour pressure required for condensation must similarly rise. The rapid initiation (60 min) of reaction at 273 K, on cooling after long periods without nucleation at 373 K, is accounted for by condensation of the relatively large amount of halogen that had been released under the more severe reaction conditions. There were some indications that tube reactions nucleated more rapidly than reactions in the vacuum apparatus; this is attributable to retention of the product bromine within a smaller reaction volume.

A study of the *surface* reaction $KBr + Cl_2$ (hitherto unsuspected) has not been attempted. This rate process must, however, be slow and restricted in extent compared with the nucleation and growth process, at least in this temperature range. Moreover, it was accompanied by no detectable surface retexturing, though there remains the possibility that such chemical changes may contribute to micro-crack development within which the liquid condensation leading to nucleation can occur. The observation that water vapour promoted retexturing of chlorine pretreated and pristine KBr surfaces are different (figures 3 and 4) provides our principal evidence that Cl_2 has interacted chemically with the total surface area of the KBr crystal. Presumably the superficial KCl (or solid halide mixture) produced provides an effective barrier that inhibits continued product layer growth.

This model is also consistent with the observed considerable irreproducibility of t_i values. Initial bromine release is expected to be sensitive to the total reactant surface area, damaged and imperfect regions contributing disproportionately. Moreover, the disposition and dimensions of those superficial cracks within which condensation can occur may vary from one specimen to another. These parameters cannot be effectively controlled or defined and, therefore, behaviour varies between apparently identical specimens of reactant. Reactions of pellets were initiated rapidly. This is consistent with the large areas and often damaged surfaces of the imperfect reactant crystals together with the diversity of sizes of channels, cracks and pores that exist within the compressed particle assemblages.

An additive promoting nucleation would, from the above arguments, be required either to provide a suitable liquid medium or to induce surface cracking or both. Liquid bromine, showing some promotional properties, is known to retexture KBr surfaces and may be adsorbed on the reactant. Similarly KI reacts with Cl_2 to yield ICl (a less volatile liquid than Br_2) which can similarly provide a liquid reaction medium and promote nucleation.

We predicted from these considerations that a nucleation promotor would be a liquid capable of dissolving halogens and perhaps capable of compound formation with KCl. This prediction was fulfilled by the activity exhibited by $SnCl_4$ (m.p. 240 K, b.p. 387 K, known to form complex halides) which was a most effective initiator of reaction. Values of t_i were markedly reduced whether the $SnCl_4$ was prepared on the reactant surface or on the apparatus walls, demonstrating the mobility of the participating species. Reaction may be initiated within

existing cracks but the liquid is also capable of promoting textural modification of the surface. A similar condensation mechanism of reaction initiation, by production of an active liquid medium, is observed with $GeCl_4$ and $PbCl_4$ which are chemically similar compounds.

We conclude, therefore, that nucleation proceeds through the generation of a drop of suitable liquid within a surface crack. The reaction medium may be either the condensed bromine product, released during the initial surface reaction, or an additive that is capable of dissolving both halogen and halide reactants.

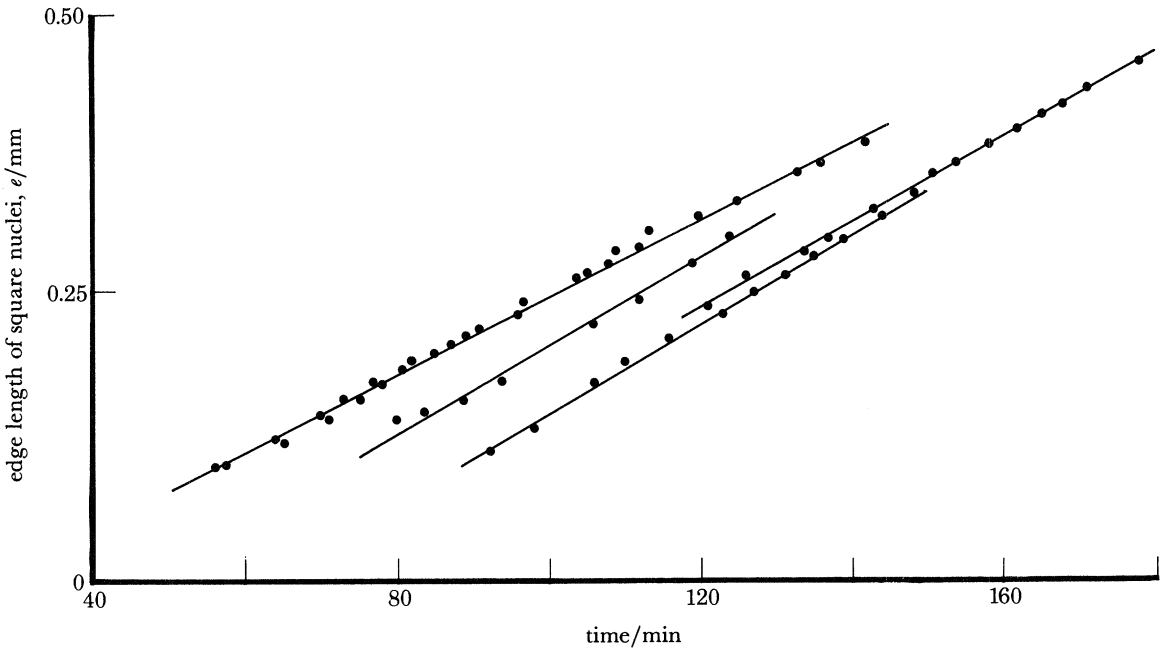


FIGURE 18. Plots of edge lengths e of the approximately square nuclei against time from measurements by optical microscopy. The rate of interface advance is constant and the rates of concurrent growth of the five nuclei are equal (the uppermost line here includes data for two nuclei). These rates were independent of nucleus size: k_g values for large nuclei (even when $e > 1$ mm) were equal to those for the concurrent growth of later-formed, smaller nuclei ($e < 0.2$ mm). The size range during which measurements could be satisfactorily continued for a selected nucleus was always unpredictable since the boundaries of first-formed nuclei usually used for kinetic measurements were often obscured through overlap with later-formed neighbours. (Reaction in the vacuum apparatus at 309.7 K in 25 kPa Cl_2, tin promoted.)

Growth rates of nuclei

Reactions between 273 *and* 320 K *in* 25 kPa *chlorine.* Throughout the kinetic studies, the edge length e of the approximately square nuclei is the most convenient parameter for growth rate measurements with the optical microscope. Rates of interface advance were constant and rate coefficients for growth, k_g, reported here refer to advance of the KBr–KCl contact ($k_g = \frac{1}{2}(de/dt)$). Figure 18 shows typical linear plots of e against time for the constant rate of growth of five nuclei on a (100) KBr cleavage face. Growth rates (k_g values) for nuclei that develop on the same reactant face, or for the concurrent reaction of different crystals in the same environment, were closely similar. This very satisfactory reproducibility is seen in figure 18, where all five k_g values were 0.030 ± 0.002 μm s^{-1}, the variation was small (± 7 %). There were, however, much greater variations (*ca.* ± 30 %) between different experiments, even when fragments of the same KBr crystals were reacted under nominally identical conditions. Accordingly, reliable

k_g values, and their limits of variation, were obtained from measurements for a large number of nuclei involving several experiments. Our observations are summarized in table 2.

No detectable influence of nucleation promotors could be found in comparative measurements of k_g for reactions in the absence of additives and with *small* amounts of $SnCl_4$ or Br_2. All k_g values were within similar ranges for both vacuum apparatus and tube reactions (table 2).

TABLE 2. RATES OF INTERFACE (KBr–KCl) ADVANCE DURING GROWTH OF NUCLEI IN THE LOW TEMPERATURE REACTION (273–318 K)

(All reactions in 25 kPa Cl_2, Sn promoted.)

apparatus*	temperature/K (± 0.5 K)	mean k_g†/(μm s^{-1})	average variation of k_g†/(μm s^{-1})	number of nuclei measured	number of separate experiments involved
v	283	0.021	0.007	104	24
v	293	0.038	0.009	51	10
v	318	0.036	0.011	67	12
t	273	0.022	0.010	25	6
t	283	0.023	0.002	6	2
t‡	293	0.042	0.004	6	2
t§	373	< 0.0001	—	18	6

* *v*: vacuum apparatus, *t*: tube reaction.
† Rate of interface (KBr–KCl) advance.
‡ Promoted by I_2, not $SnCl_4$.
§ Growth of nuclei previously developed at 273 K.

Kinetic studies for reactions in pellets were less straightforward. Ill-defined nuclei were formed in linear arrays at sub-surface channels within which product condensation was possible. The mean k_g value (for 29 nuclei measured in 9 experiments) was 0.032 ± 0.010 μm s^{-1} (at 293 K in 25 kPa Cl_2) which is somewhat less than the reaction under these conditions in a crystal (table 2).

Variation of reaction rate with temperature. From the data in table 2 it is concluded that the temperature coefficient of k_g between 273 and 318 K is small, corresponding to an apparent activation energy E value of less than 50 kJ mol^{-1}.

Since k_g values were not reliably reproducible between successive experiments, the effects of temperature on reaction rate were measured within individual reactions. To achieve this, the water supply to the thermostatted stage, supporting the reactant crystal, was exchanged between two constant temperature baths maintained (± 0.2 K) at 283 and at 325 K. Kinetic plots of e against time were linear, except for small changes in slope at the temperature discontinuity. Typical observations for the growth of two nuclei, at 325 K and at 283 K, are shown in figure 19; here the apparent value of E is negative. In nine separate experiments a total of 14 measurements were obtained for the rate changes which resulted from the 42 K temperature variation. (In each experiment 2–5 nuclei were measured during reaction in 25 kPa Cl_2, tin initiated.) The mean apparent activation energy calculated from these k_g values was 10 kJ mol^{-1}: there was significant scatter of measurements but all values were less than 25 kJ mol^{-1} and some were slightly negative (see, for example, figure 19). Therefore, the temperature coefficient of this reaction is small, corresponding to $E \approx$ 20–40 kJ mol^{-1}.

Discontinuous variations in temperature during reaction resulted in the appearance of a textural change within each nucleus, which persisted during further growth.

Rates of nucleation and of growth diminished to very small, effectively zero, values at 373 K (Ivanov & Schachtschneider 1980). Nuclei, established during 80 min reaction at 273 K in 25 kPa Cl_2, underwent no perceptible growth in 1500 min further heating at 373 K (these are the tube reactions referred to in the last row of table 2).

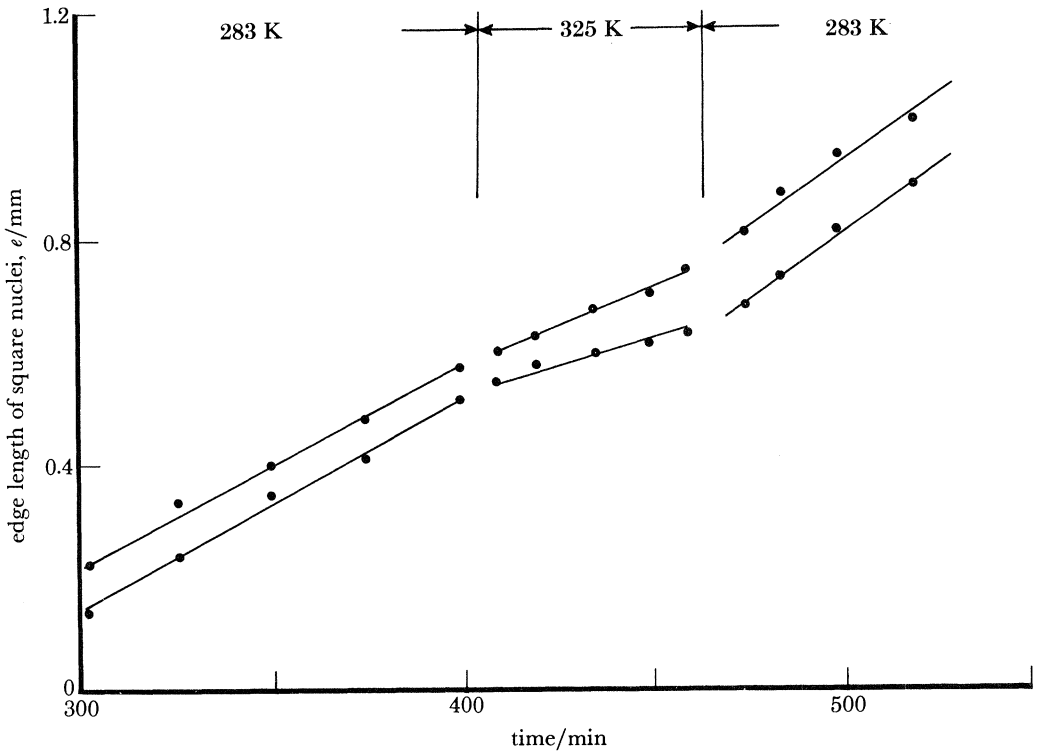


FIGURE 19. Effect of temperature variation on rate of an individual reaction; e is plotted against time for the concurrent growth of two nuclei during a continued reaction at 283, at 325 and again at 283 K. k_g values (unusually) diminished slightly after the discontinuous temperature increase and returned again to the original value on restoring the earlier reaction conditions. (Vacuum apparatus reaction in 25 kPa Cl_2, tin promoted.)

Variation of reaction rate with chlorine pressure. Reaction rates increased with the pressure of reactant chlorine, expressed generally by

$$k_g = k'(P_{Cl_2})^{0.8}.$$

Limits of variation of the exponent were 0.7–1.0. Typical plots of e against time for reaction at 283 K in 12, 25 and 50 kPa Cl_2 are shown in figure 20. Rate changes occurred within a few minutes of each pressure adjustment, showing that interface equilibration was relatively rapid.

Nucleus shape varied with reactant Cl_2 pressure. Under our preferred reaction conditions, 25 kPa Cl_2, product assemblage outlines were approximately square, though corners were rounded and edges were irregularly serrated. In 12 kPa Cl_2 the rounding of corners had increased with the production of almost circular nuclei and these edges were relatively smooth. At higher reactant Cl_2 pressures, 50 kPa Cl_2, nuclei showed preferred development in the (111) directions so that mid-edges were slightly concave and the outline edges were noticeably more irregular.

Influence of interruption of reaction with evacuation. During the Cl_2 pressure dependency experiments nucleus growth continued after pressure reduction only if the gaseous reactant was

withdrawn slowly. If chlorine removal was abrupt, or the sample was evacuated, there followed a period of quiescence, sometimes extending to a second induction period, before resumption of the growth of established nuclei.

When the original conditions of reaction were restored soon (in under 5 min) after Cl_2 removal, the earlier rate of interface advance was rapidly resumed. After longer periods of evacuation (over 60 min), however, induction periods to continued nucleus development were

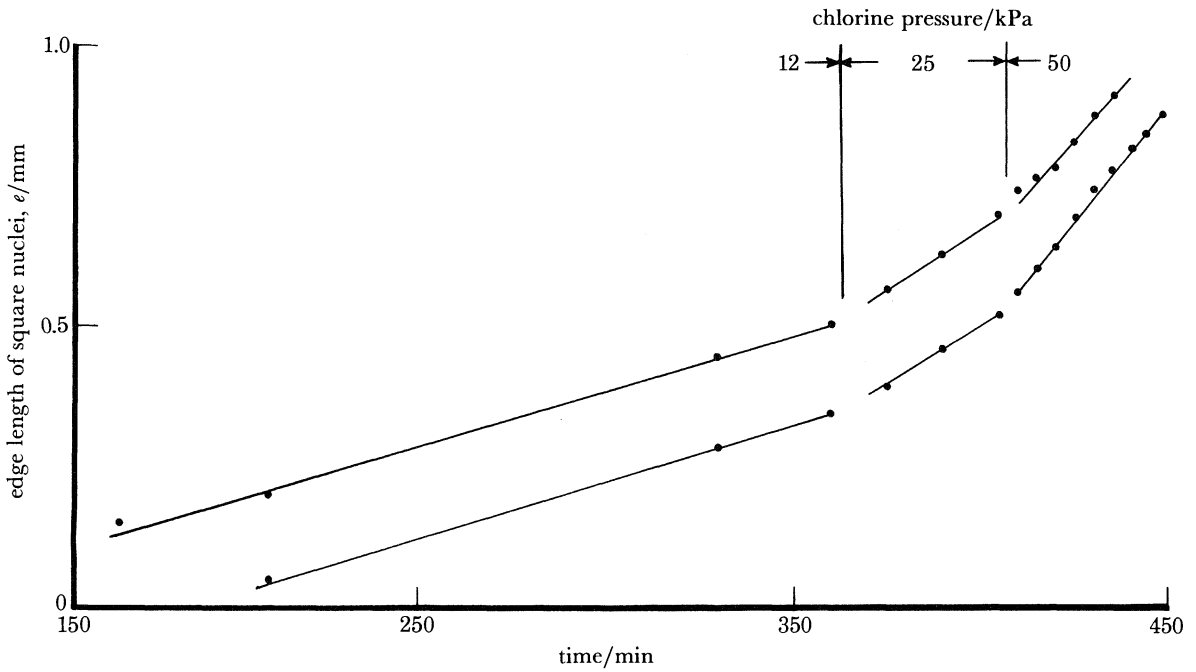


FIGURE 20. Influence of variation of chlorine pressure on reaction rate. Plots of e against time for concurrent growth of two nuclei in 12, 25 and 50 kPa Cl_2. (Vacuum apparatus reaction at 283 K, tin promoted.)

sometimes greater than those originally found (figure 21). This can be attributed to $SnCl_4$ removal and a reduced rate of Br_2 release from reactions on the outer KBr surfaces which had been covered by KCl formed during the first reaction period. Furthermore, as shown in figure 21, k_g values during the resumed reactions were appreciably less ($\times$ 0.3–0.5) than those before interruption. Growth rates of nuclei formed only during a resumed reaction were the same as those of the continued development of older nuclei (i.e. were relatively slow). It is significant that growth rates of all nuclei act in concert: the later generated nuclei exhibit behaviour comparable with the properties modified by evacuation of those formed earlier.

The observed effects of evacuation are readily explained by the slow removal during pumping of the active liquid participant at the interface. The pore structure of nuclei must thereby be modified by solute deposition and the rate of continued growth is changed, following, of course, the period required for accumulation of the liquid needed to promote resumed interface advance. Nuclei in evacuated samples remained yellow, attributable to halogen retention as inclusions within the product assemblage.

Discussion. The essential feature of the mechanism we propose for this reaction is that liquid halogen is condensed within the intercrystalline channels of the nucleus at the KBr–KCl

interface. Product halogen ($BrCl \rightleftharpoons \frac{1}{2}Br_2 + \frac{1}{2}Cl_2$) and dissolved reactant (Cl_2) move in opposite directions along the channels of what we have described as a *fluid-flux* nucleus (Galwey 1982). Evidence that liquid halogen is present in nuclei has been discussed earlier (orange coloration, halogen content, interface structure, liquid catalyst ($SnCl_4$) and effect of evacuation).

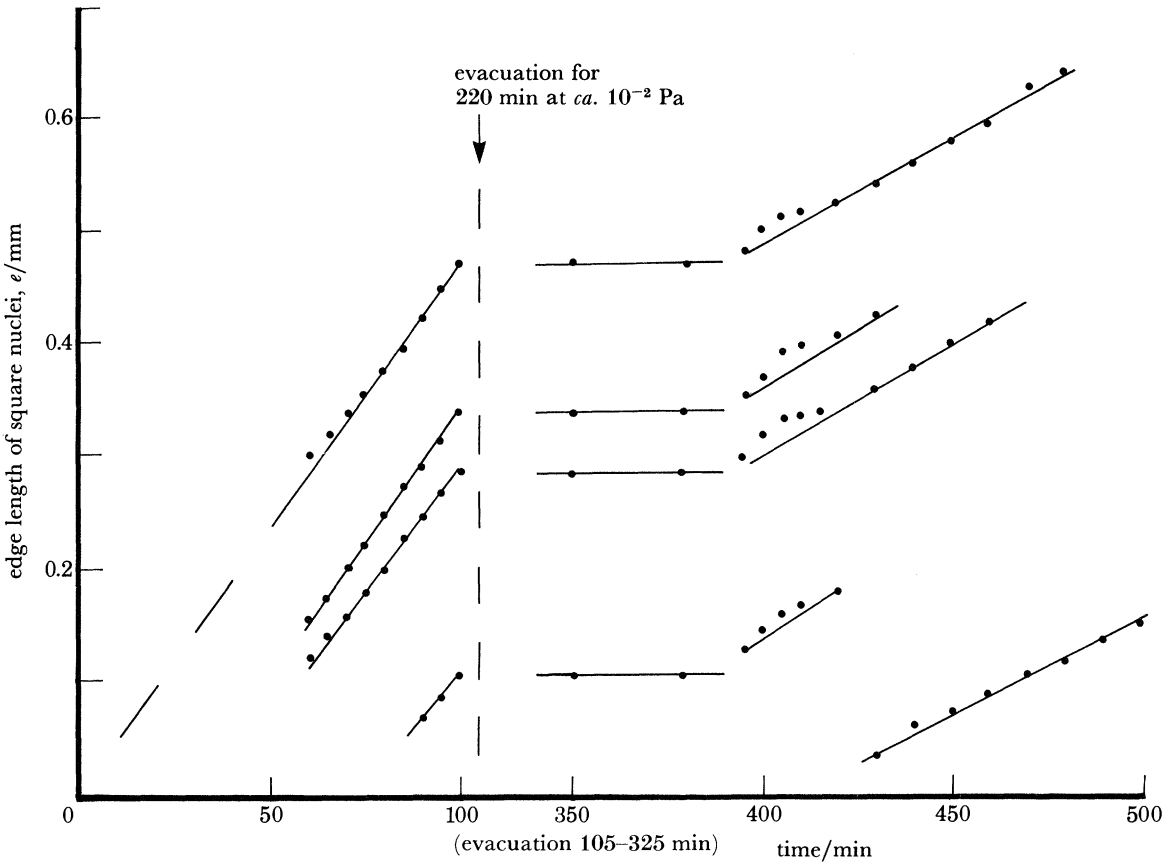


FIGURE 21. Effect of interruption by evacuation on reaction rate. Plots of e against time for a reaction with a period of pumping (under 10^{-2} Pa between 100 and 320 min). Growth of nuclei continues only after a further induction period, from 320 to 390 min, and proceeds at a slower rate. A nucleus formed during the second period of reaction grows at the slower rate, characteristic of the resumed reaction. (Vacuum apparatus reaction at 293 K in 25 kPa Cl_2, tin promoted.)

We identify the liquid halogen as the medium within which this relatively low temperature chemical change (reaction (1)) can occur without the necessity for generating high energy intermediates, such as chlorine atoms. The sequence of chemical steps is that reactant dissolution is followed by solution equilibria involving the polyhalide anion, $[BrCl_2]^-$, and product deposition. Salts that contain the $[BrCl_2]^-$ ion have been referred to by Trotman-Dickenson (1973*b*).

$$KBr(s) \rightleftharpoons K^+ + Br^- \text{ (reactant dissolution)},$$
$$Br^- + Cl_2 \rightleftharpoons [BrCl_2]^- \rightleftharpoons Cl^- + BrCl,$$
$$K^+ + Cl^- \rightleftharpoons KCl \text{ (product deposition)}.$$

Interface advance. The constant rate of nucleus growth (figure 18) implies that reaction occurs at an interface wherein conditions do not systematically change during its movement. This is

consistent with the microscopic observations. The chemical changes occur in the liquid occupying the fine pore structure adjoining the KBr–KCl contact. Thereafter, diffusive transport within the relatively larger intercrystalline pores within the nucleus centre is much more rapid. Thus product accumulation does not offer progressively increasing impedance to the countercurrent transport processes that participate.

k_g values were closely similar for nuclei that grow concurrently, even on separate crystals. This reproducibility (figure 18) is in contrast with the much larger variations found for interface advance rates in successive, though nominally identical, experiments (table 2). This pattern of behaviour requires the involvement of a mobile participant, controlling the interaction between separated nuclei. The most obvious parameter capable of such control is the effective prevailing pressure of product (BrCl or Br_2 or both), probably determined by the average crack dimensions within all coexisting active interface domains. Once this controlling pressure has been established during the sensitive nucleation stage, condensation will occur thereafter in pores of similar dimensions. This initiates conditions for similar growth rate and ensures comparable behaviour during concurrent development of nuclei in the same environment. In successive experiments, however, there may be differences in the sizes of cracks within which nucleation is initiated and this results in some variation of k_g values between these different experiments. This is also consistent with our observations that interruption of reaction by evacuation resulted in a change in rate of the resumed rate process and that later evolved nuclei conformed to the prevailing (i.e. modified) growth kinetics.

Temperature. The unusually small temperature coefficient of reaction rate is explained by control through either a diffusion process within the intercrystalline fluid channels or temperature dependent displacements of the equilibria specified above. We cannot determine the relative importance of these effects from the evidence available. It is possible, however, to exclude from consideration all mechanisms that involve control by a single step of large activation energy. The marked reduction in rate of this low temperature reaction on heating to *ca.* 370 K is easily explained by volatilization of the reactant fluid medium from the interface.

Cl_2 *pressure.* The observed rise in reaction rate with increase in pressure of Cl_2 reactant is in accordance with expectation. The liquid reaction products provide an almost ideal solvent for Cl_2 and increased concentrations of this reactant will displace equilibria, enhance reaction rates and thus result in the more rapid growth of nuclei.

Since BrCl is unstable at reaction temperatures (Surles & Popov 1969), we conclude that Br_2 is the predominant product. Its vapour pressure at 293 K is *ca.* 16 kPa and calculations suggest that this may be reduced further, by perhaps 2 kPa, on condensation in the narrow channels within the reaction zone. The temporary retention of liquid under reaction conditions is, therefore, reasonable, since evaporation is opposed by the (usually) larger pressure of chlorine prevailing during kinetic studies.

Product orientation. A general observation from the microscopic examinations of nucleus structures was that the slab-like crystals of product KCl were preferentially oriented in the (111) directions with respect to the reactant KBr (see figures 11, 12, 14 and 15). There were also indications that (111) KBr surfaces were developed during reactant erosion at the active interface. Wyckoff (1963) lists the unit cell edges of KBr and KCl as 0.6600 and 0.6293 nm respectively. Scale drawings were used to compare quantitatively cation distributions at KBr (111) and KCl (100) faces, but no marked coincidences were apparent, capable of explaining this topotactic relation between reactant and product. It was noted, however, that $2\times$ (the

(111) K^+–K^+ spacing in KBr) (1.866 nm) is close to 3 × (the unit cell edge in KCl) (1.888 nm), though we are not convinced that this can be accepted as a satisfactory explanation for the observed topotactic relation.

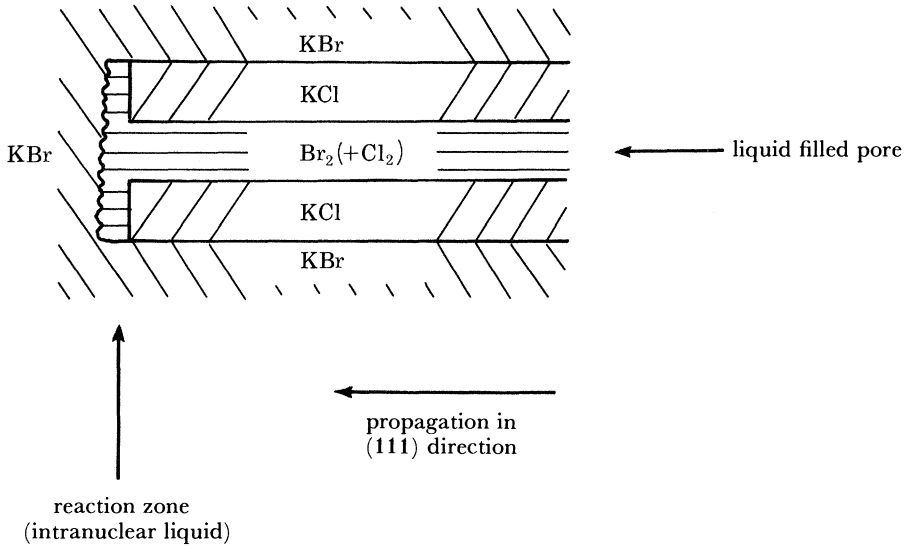


FIGURE 22. Diagrammatic representation of a longitudinal section of a single (111) oriented channel of an X-nucleus.

X-*shaped nuclei.* We regard X-shaped nuclei (figure 11) as the most pronounced manifestation of the preferred (111) orientation of product KCl crystals. One-dimensional nucleus development was apparent principally during the final stages of tube reactions, when the quantity of bromine released was large, sufficient to occupy the greater portion of the intercrystalline channels with liquid. This solvent is regarded as promoting growth in the (111) direction of individual KCl crystals, and inhibiting the crack development that results in branching leading to nuclei of square outline. The structure of one such channel is shown diagrammatically in figure 22: typical X-nucleus development usually involved groups of (111) oriented parallel KCl crystals and channels.

Nucleus shapes. Under the conditions used for kinetic measurements, the pressure of Cl_2 was greater and the availability of Br_2 was less than as described for the X-nuclei above. We suggest that in 25 kPa Cl_2 there was the possibility of *divergent* or branching growth of channels at the interface. Thus a pore of the type represented in figure 22 could bifurcate at the tip with an angle of divergence of 70.5° to yield two daughter structures both oriented in (111) directions. Random and frequent division of this type will then yield the serrated edge rectangular outline nuclei observed. The approximately planar boundary surfaces are oriented parallel to the principal axes of the host KBr but are composed of KCl crystals oriented in the (111) directions. Therefore, the rate of crystal development in the product structure is $\sqrt{3}e$. (The values in table 2 refer to growth in (100) etc. directions.)

During reactions in the higher pressures of chlorine (50 kPa) a slight increase in the retention of halogen within nuclei results in some reduction in ease of channel branching discerned as an apparent enhancement of growth in (111) directions. This may result from the influence of retained solvent, though less significant here than in the X-nuclei. At lower reactant pressures,

12 kPa Cl_2, halogen retention is less, KCl product crystals are smaller and less aligned, so that product formation proceeds outwards at equal rates in all directions to yield the less serrated, hemispherical nuclei.

Thus control of nucleus development, through the amount of liquid retained in the pores, explains the unusual dependence of nucleus shape (hemisphere, half-cube or X-shape) on reaction conditions obtaining.

Kinetics of nucleation

Since two previous studies of nucleation kinetics have been reported, we have made no further quantitative measurements. Morrison & Nakayama (1963) showed that on an untreated surface nucleation obeyed the power law, $N = (kt)^n$, with wide variations in n (often $n > 6$). In the presence of an uncharacterized promotor, Morrison & Tuzi (1966) fitted their results to the empirical relation, $N = At^3[1 - \exp(-Ct)]$. This corresponds to an initial obedience to the power law with $n = 4$, later reducing to $n = 3$. Qualitatively we confirm that nucleation is a strongly acceleratory process and that reactivity varies appreciably between nominally identical experiments.

These observations are consistent with our proposed mechanism if the nucleation rate is controlled by the prevailing pressure or the availability of Br_2 product. The initial induction period occurs during the slow general surface reaction yielding bromine, which must accumulate in sufficient quantity to condense in suitable pores, before there is recrystallization and subsequent generation of growth nuclei. The bromine released from the development of each compact nuclei varies with the third power of time. If this is the dominant factor, the power law obedience of nucleation rate with $n > 3$ is explained if nucleus production continues. The observed acceleratory rate of nucleation is entirely consistent with our proposed reaction model: nucleation follows product halogen condensation in a suitable surface crack.

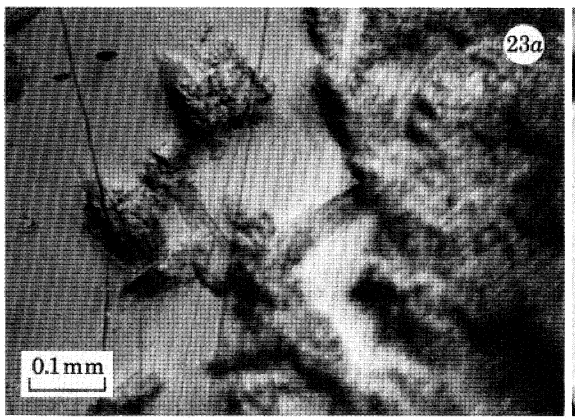
The high temperature $KBr + Cl_2$ *reaction, over* 450 K

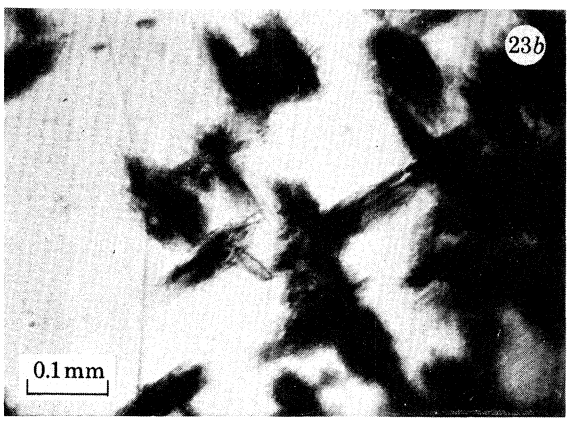
We confirm the observations by Morrison & Nakayama (1963), that a nucleation and growth reaction occurred above *ca.* 450 K to yield irregularly shaped product assemblages having some preferred (111) orientation. Typical structures are shown in figure 23, plate 9.

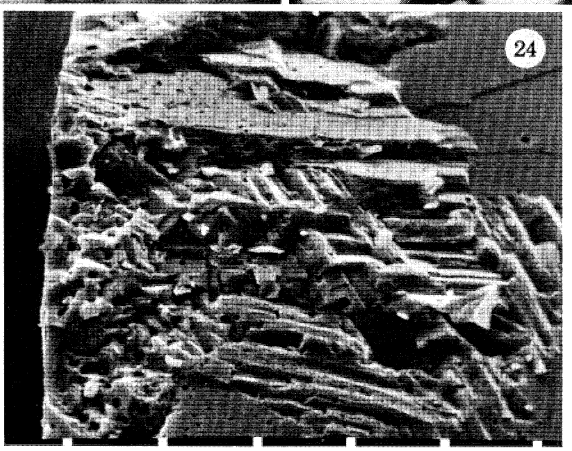
Reaction kinetics

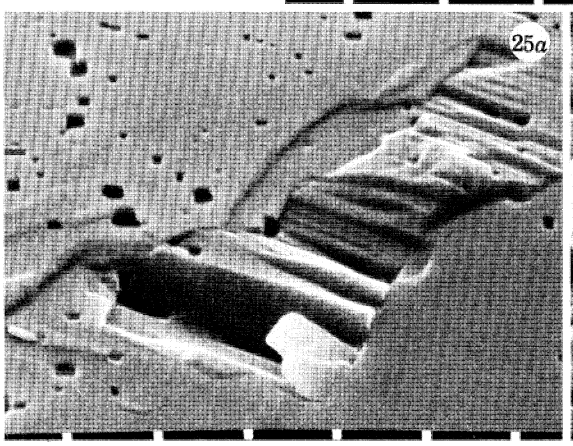
No parameter capable of quantitatively measuring the size of each irregular nucleus-type structure (figure 23), developed during the high temperature reaction, could be recognized. Consequently, no measurements of nucleus growth rates could be undertaken. It was clear, however, that the numbers of such nuclei present increased with time, approximately obeying the linear law, though irreproducibility of data made precise characterization difficult. Mean initial rates of nucleation in 25 kPa Cl_2 were 0.01 ± 0.01 and 0.1 ± 0.1 nuclei mm^{-2} min^{-1} at 493 and 620 K respectively. There was no induction period to reaction (table 1).

In their gravimetric measurements of the overall rate of reaction, Morrison & Nakayama (1963) report that at 773 K reaction initially proceeds at a constant rate and subsequently ($\alpha > 0.1$) becomes deceleratory. It is not easy to reconcile this kinetic behaviour with the observed three-dimensional growth of ill-defined product assemblages.









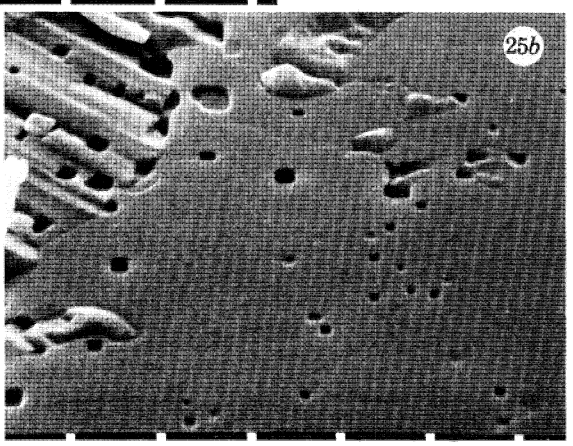


FIGURE 23*a*, *b*. Reflection and transmission optical micrographs of the nuclei developed during the high temperature reaction. Shapes of nuclei were variable and outlines highly irregular, with some preferred development in the (111) directions. (95 min reaction at 611 K in 25 kPa Cl_2.)

FIGURE 24. Cleavage section of crystal after high temperature reaction. The interior is penetrated by an extensive pore system in which three textural zones can be distinguished. Immediately below the surface little order can be recognized in the KCl product crystallite assemblage. The inner region of the retextured material shows preferred (111) orientation of the product crystals; two interpenetrant systems can be seen. Beyond this zone of obvious recrystallization, the reactant is penetrated by continuation of the system of pores, channels and holes. (120 min reaction at 620 K in 25 kPa Cl_2.) S.e.m.: spacings of scale divisions are 10 μm.

FIGURE 25. Cleavage section at inner limit of superficial retextured zones produced during the high temperature reaction. The (100) surface exposed on fracture is penetrated by numerous holes, never observed during many examinations of cleavage faces of unreacted KBr. The boundaries of the recrystallized zones are irregular and no reaction interface could be identified. (Crystal reacted under same conditions as for figure 24.) S.e.m.: spacings of scale divisions are both 3 μm.

(*Facing p.* 178)

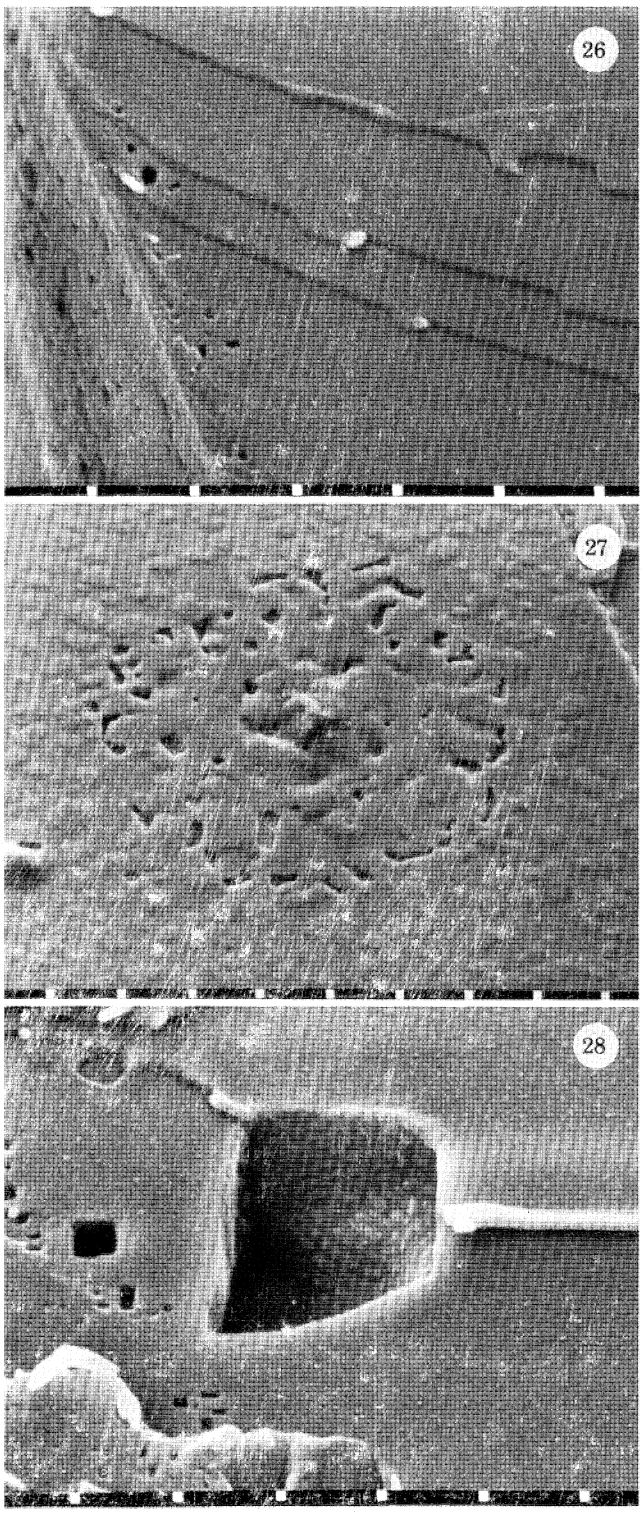


FIGURE 26. Subsurface holes developed during the high temperature reaction in a zone remote from any recrystallization nucleus. (Same crystal as in figure 24.) S.e.m.: spacings of scale divisions are 3 μm.

FIGURE 27. Surface texture modification during the high temperature reaction. The nucleus periphery is characterized by the pattern of holes which provide routes for reactant access and product escape. (40 min reaction at 610 K in 25 kPa Cl_2.) S.e.m.: spacings of scale divisions are 10 μm.

FIGURE 28. An unusually large hole, revealed on cleavage, in unrecrystallized reactant near a high temperature nucleus. The rounded features on internal surfaces are reminiscent of interface textures in low temperature reactions. (90 min reaction at 610 K in 25 kPa Cl_2.) S.e.m.: spacings of scale divisions are 3 μm.

Microscopic observations

The novel textural feature revealed by s.e.m. examinations was the extensive subsurface system of channels that apparently indiscriminately permeated regions of recrystallized product and unrecrystallized solid alike. From systematic observations of cleavage sections traversing established nuclei, we distinguished the three textural zones illustrated in figure 24, plate 9. The outer portion of the nucleus is composed of an irregular coherent assemblage of small KCl crystallites, penetrated by an extensive system of holes of square cross section. The inner portion of this recrystallized region, comprised of slab-like crystallites, shows alignment in (111) directions: two interpenetrant alignments are apparent in figure 24, plate 9. This preferred orientation again parallels the product disposition characteristic of the low-temperature reaction. An important difference, however, was the absence of intranuclear channel development (figure 9) during the high temperature reaction. Within the third zone, behind the irregular periphery of the retextured zones, the unchanged (100) faces characteristic of the reactant KBr were penetrated by numerous holes, 0.2–10 μm in diameter. These were square in cross section, their sides being aligned with the principal KBr crystal axes. No coherent reaction interface could be recognized: typical contacts between recrystallized and planar cleavage faces are illustrated in figure 25, plate 9.

Intracrystalline hole development was also observed in surface regions that did not immediately adjoin established nuclei (figure 26, plate 10). Unlike the low temperature reaction, nucleus surfaces did not crack (see figure 6), but outlines were indicated by a pattern of holes affording channels for the movement of volatile reactant to and product escape from the reaction zone (figure 27, plate 10). It is also seen from figures 26 and 27 that the high temperature reaction is accompanied by surface roughening.

The unusually large channel shown in figure 28 occurred in an unrecrystallized zone in close proximity with a nucleus. Wall textures are very similar to those developed at interfaces during low temperature reactions (see figure 8). In another crystal there was evidence of a particularly long channel, detected intermittently across a cleavage surface for a distance of 0.25 mm beyond a nucleus, though the constant cross section was only *ca.* 1 μm. This pore is assumed continuous, though tortuous, since it was associated with a linear step edge of the fracture face and no other holes were observed in the surrounding areas.

Electron dispersive analysis of recrystallized zones confirmed that these were composed of KCl product. The unretextured but pore penetrated faces exposed on cleavage were shown to contain chloride. This confirms that subsurface reaction occurs *before* onset of the structural reorganization identified as nucleus development (figure 23).

Discussion

To reconcile the kinetic evidence that reaction is initially zero order (or slightly acceleratory) (Morrison & Nakayama 1963) with the observations indicating a nucleation and growth process (figure 23), we propose the following reaction mechanism, which also takes cognizance of the textural structures found in figures 23–28. The central feature of our model is that the development of each channel is accompanied by the production of a surrounding zone of chloride (product KCl). This is positively supported by the analytical data. Pores are initiated at surfaces and progress inwards, and it is only after a sufficient local concentration of chloride has been generated that reorganization occurs forming the slab-like, (111) oriented, crystals of KCl

product. Subsequent development (growth) of such nuclei is irregular but subject to control by crystallographic factors (figure 24) and by local fluctuations in extent of reaction arising from the vagaries of channel distribution. Thus the aggregate dimensions of microscopically detectable product assemblages (nuclei) does not provide a measure of the total quantity of chloride formed. The paradox in the first sentence above is resolved because gravimetry and microscopy are measuring different parameters, total extent of reaction (1) and quantity of KCl product that has recrystallized respectively.

Pore development is identified as an indispensible component of the reaction mechanism since these are definitely absent from the reactant but advance inwards and proliferate during the high temperature rate process. While the s.e.m. micrographs reveal holes in cleaved crystal faces only, we identify these as sections of a system of interconnecting tortuous channels, penetrating and permeating the reaction zone, thus providing the connection between unchanged KBr and the gaseous reactant outside the crystal. We accept the view of Boldyrev & Ivanov (1976) that dislocations represent sites of enhanced reactivity and suggest that channels develop along line imperfections. The present chemical change, unlike many tarnishing reactions, yields a volume of product that is *less* than the volume of reactant from which it was derived. Accordingly, reactions at the wall of each channel must result in an increase in pore diameter and there is evidence that such surfaces are retextured (figure 28), as, indeed, are the external crystal faces. The stresses associated with reaction are, however, insufficient to cause obvious cracking of either reactant or product. Reaction associated with subsurface pore development is familiar from studies of ammonium perchlorate decomposition (Herley *et al.* 1970), though the only probable similarity with the present reaction is that chemical change propagates preferentially along line imperfections.

The above evidence demonstrates that KBr is pseudomorphically replaced by KCl without the participation of stress induced cracking within the crystal. Crystalline KCl product is precipitated and such aggregates grow through the acquisition of chloride. This model assumes that there is considerable mobility of the *anions* within the crystal structure, an unexpected feature since both participating negative ions are larger than the cation (ionic radii are K^+: 0.131; Br^-: 0.196; Cl^-: 0.181 nm). Moreover, pore development must arise through shrinkage of the surrounding lattice and we estimate that the replacement (KCl in place of KBr) required for their development corresponds to reaction thicknesses extending to over one thousand lattice units. However, both KBr and KCl contain Schottky defects, that permit some anionic mobility, and this may be further enhanced by the formation of K(Br, Cl) solid solution by reaction in regions adjoining pores that contain the reactant Cl_2. The chloride component of this solid solution is continually precipitated by the development of topotactically oriented KCl crystals, the microscopically observed nuclei (figure 23).

The initial approximately zero order rate process, followed by later deceleration (Morrison & Nakayama 1963), is explained by this mechanism of pore development accompanied by local solid formation if diffusion control of gas within the pores operates only during the later stages. While this model explains the overall pattern behaviour satisfactorily, properties of the solid solutions and the migrating entities within them have not been fully characterized here.

Conclusions

The feature of this reaction that first attracted our interest was that the low temperature gas + solid interaction proceeded by a nucleation and growth mechanism, rather than by the development of a product barrier layer, observed in many tarnishing reactions (Brown *et al.* 1980). Mechanistic details of this reaction have been discussed above; here we comment on these conclusions in the context of currently accepted theory.

An important result reported here is that reaction is initiated over *all* reactant surfaces and the *onset* of chemical change is not restricted to specific sites of surface imperfection. It follows, therefore, that nucleation (again, Galwey *et al.* 1981) occurs only after much more extensive superficial change than the completion of a small number of localized individual bond redistribution steps, as has often been assumed in theoretical explanations of nucleation kinetics (Brown *et al.* 1980).

The participation of intranuclear liquid, located within interparticulate channels of the product assemblage, is a reaction model that has not found favour in recent fundamental mechanistic discussions of reactions of solids. The participation of dissolution–precipitation phenomena, together with associated homogeneous reactions, proposed here, contrasts with the rather rigid solid structures envisaged in the Polanyi–Wigner theory (Brown *et al.* 1980). The retention of liquid at the reaction zone (Galwey 1982) offers an attractive explanation of nucleation and growth phenomena, so that the nucleus is identified as a specialized structure developed *to retain* the solvent necessary to promote the chemical change. Alternative reaction pathways become available that involve dissolved (here ionic) intermediates; reactivity in the liquid phase is often enhanced (Bawn 1955; Galwey & Hood 1982) since the stabilizing influence of crystal structure forces are relaxed and reactants have greater freedom to adopt the reaction configuration, etc. For the present reaction, the availability of a suitable solvent for the reactants has been demonstrated.

Previous reservations that concerned the value of mechanisms involving intranuclear product retention have been based on an expectation of increasing impedence with growth (Garner 1955). However, here we attribute the constant rate of interface advance, figure 18, to the maintenance of constant conditions within a thin reaction zone, thickness perhaps 10 μm, figure 7. The diffusion of gases through the wider channels of the nucleus centre (figure 9) to the edge of this active region is relatively rapid and not rate controlling. Variations in reaction conditions are expected to influence the volume of participating liquid and were shown to generate an unexpected diversity of nucleus shapes (hemispherical, half-cube and X-shaped). These resulted from reactant pressure-dependent changes in the tendency towards alignment of product KCl crystals in (111) directions with respect to the KBr host lattice.

The influence of temperature on reaction rate was complicated: rate processes were identified in two separate temperature intervals and these proceeded by different reaction mechanisms. The value of the activation energy for the low temperature reaction could not be satisfactorily measured, though all values of E determined were small, under 50 kJ mol^{-1}. Since the temperature coefficient of reaction rate here is expected to be a complex parameter, including contributions from several factors, the magnitude of E cannot be used as evidence for identifying a specific rate controlling step. Such contributory factors include some or all of the following: rates of KBr dissolution and KCl deposition; solubilities of intermediates and perhaps their diffusion mobilities; the rates of homogeneous reactions. The investigation of the high

temperature reaction was less comprehensive but it was demonstrated that behaviour was quite different from that characteristic of the low temperature reaction.

The study emphasizes the importance of using microscopic observations to complement kinetic measurements and interpretations. The complexity of interfacial chemistry in reactions of solids is again demonstrated.

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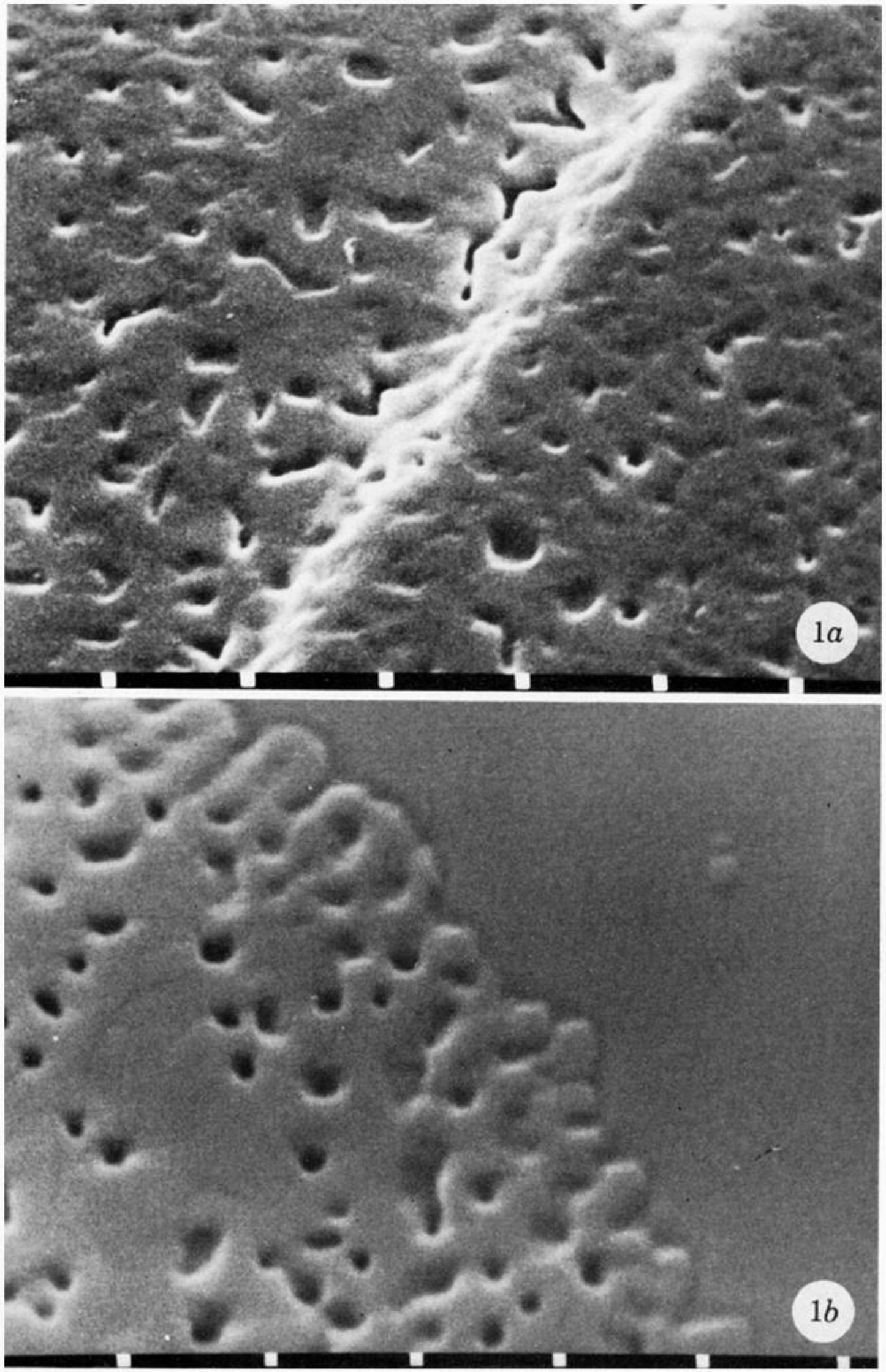


FIGURE 1. KBr surfaces, freshly cleaved and exposed to bromine vapour (0.8 Ps) at 288 K. (*a*) After 7 min exposure to Br_2 the step edges have become rounded, as compared with the pristine faces. Local modification of adjoining surfaces is also evident. (*b*) After 5 min exposure to Br_2, surfaces in the vicinity of step edges had developed rounded features and small pits. Much of the surface between step edges remained unmodified. (On these and other s.e.m. photographs a scale is included at the lower edge: spacings of the scale divisions here are (*a*) 3 μm and (*b*) 1 μm.)

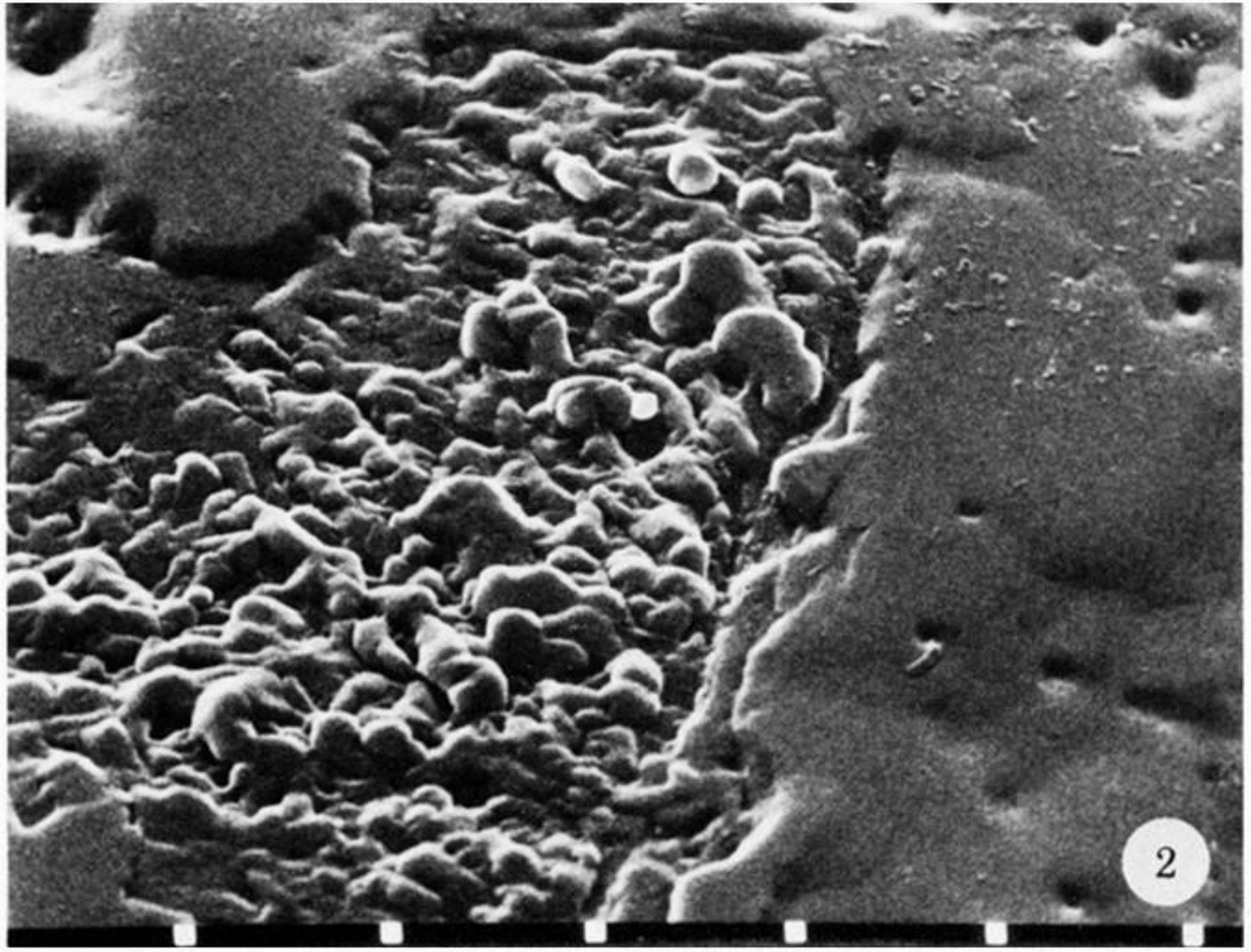


FIGURE 2. S.e.m. photograph of a KBr surface on which a drop of liquid Br_2 had remained for one minute at 288 K before evaporation. The original featureless, flat surface has been extensively modified, though the detailed textures remaining varied somewhat between nominally identical experiments. S.e.m.: spacing of scale divisions is 10 μm.

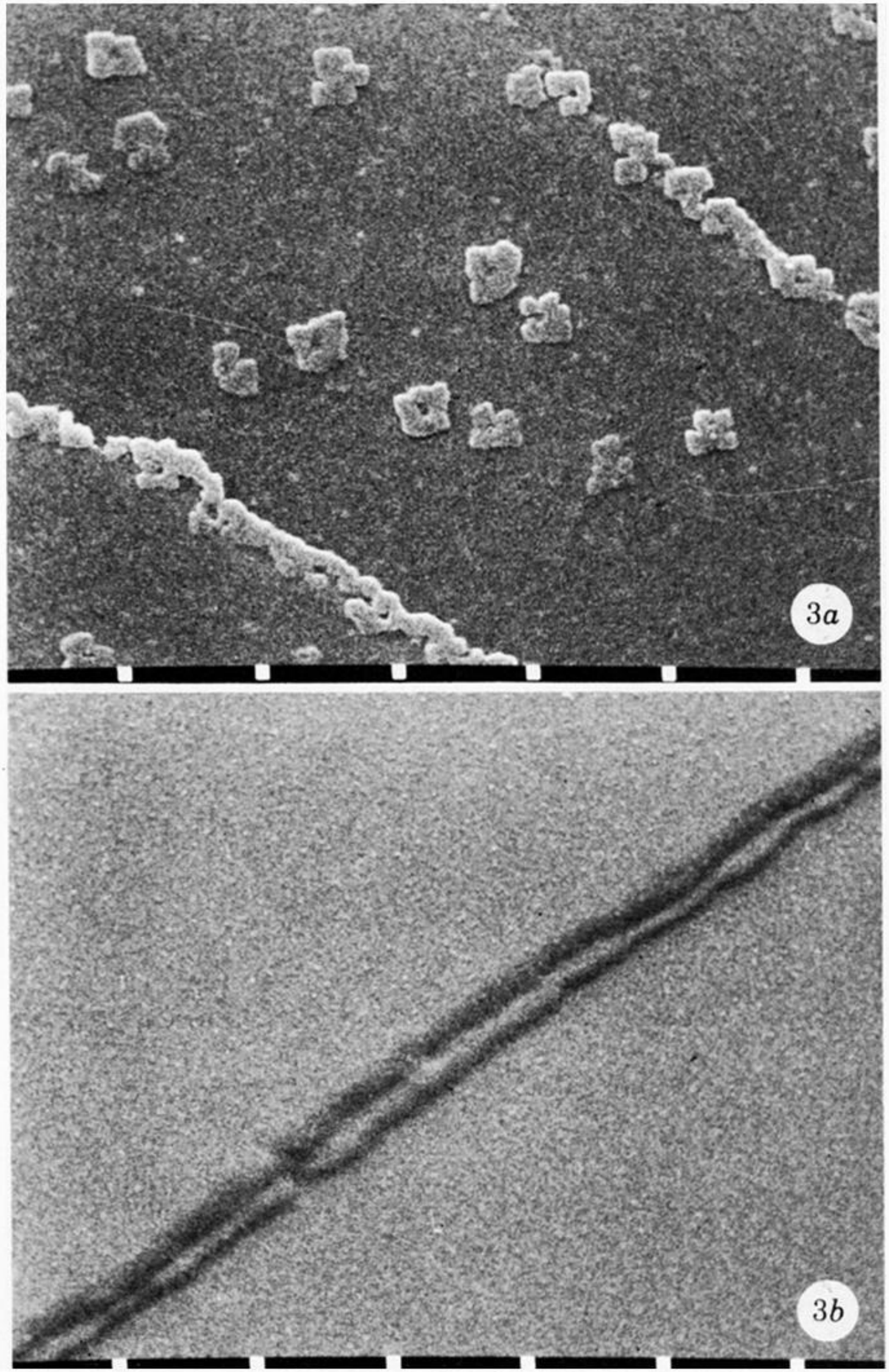
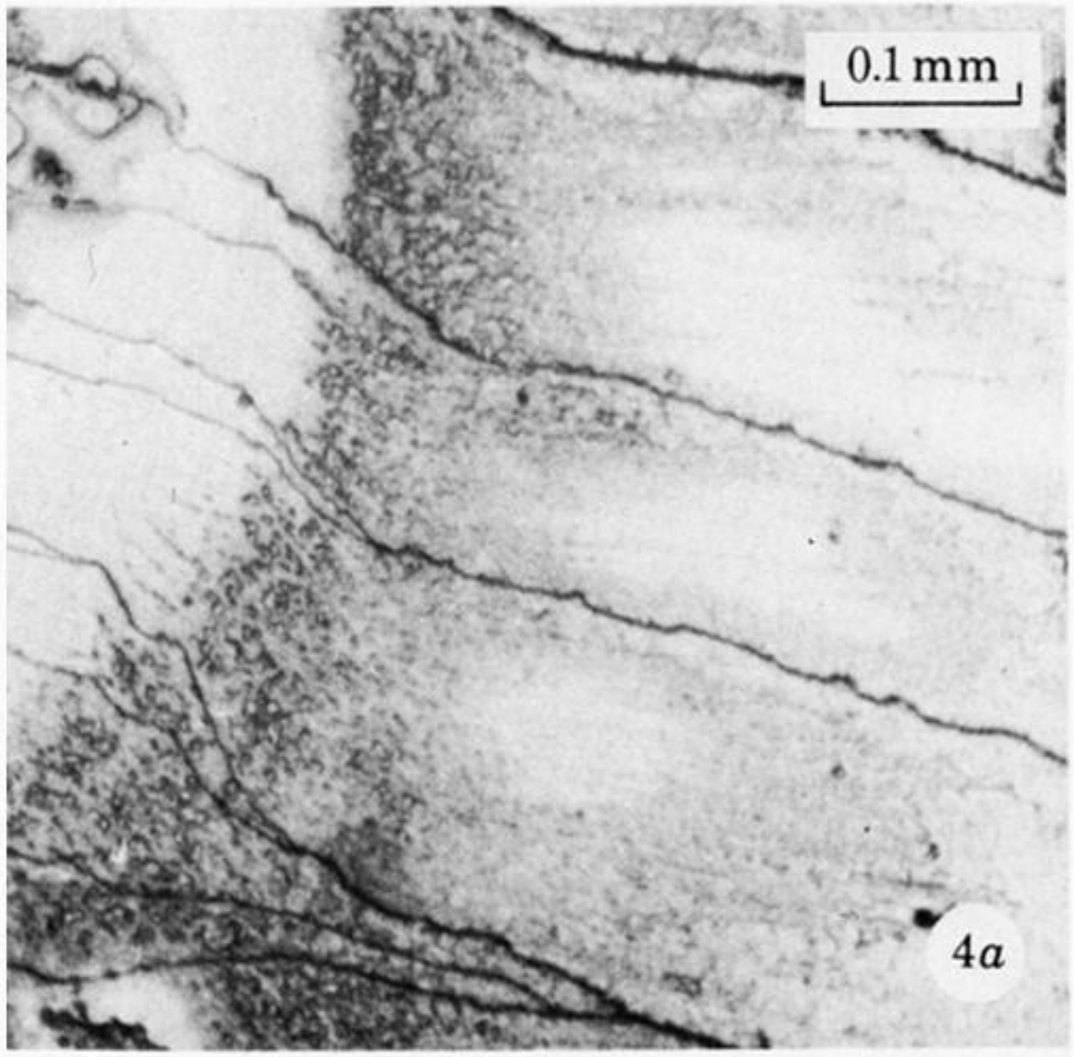


FIGURE 3. Comparative s.e.m. photographs for two differently pretreated KBr surfaces after concurrent exposure to water vapour with a slow increase in pressure from 0.2–0.5 Ps (H_2O) during 60 min. (*a*) This surface, which had previously reacted for 40 min at 290 K in 25 kPa chlorine, underwent a characteristic water vapour promoted textural modification. (*b*) This pristine and unreacted surface was unchanged by its concurrent exposure to the water vapour, except for the rounding of step edges. S.e.m.: spacings of scale divisions are both 3 μm.



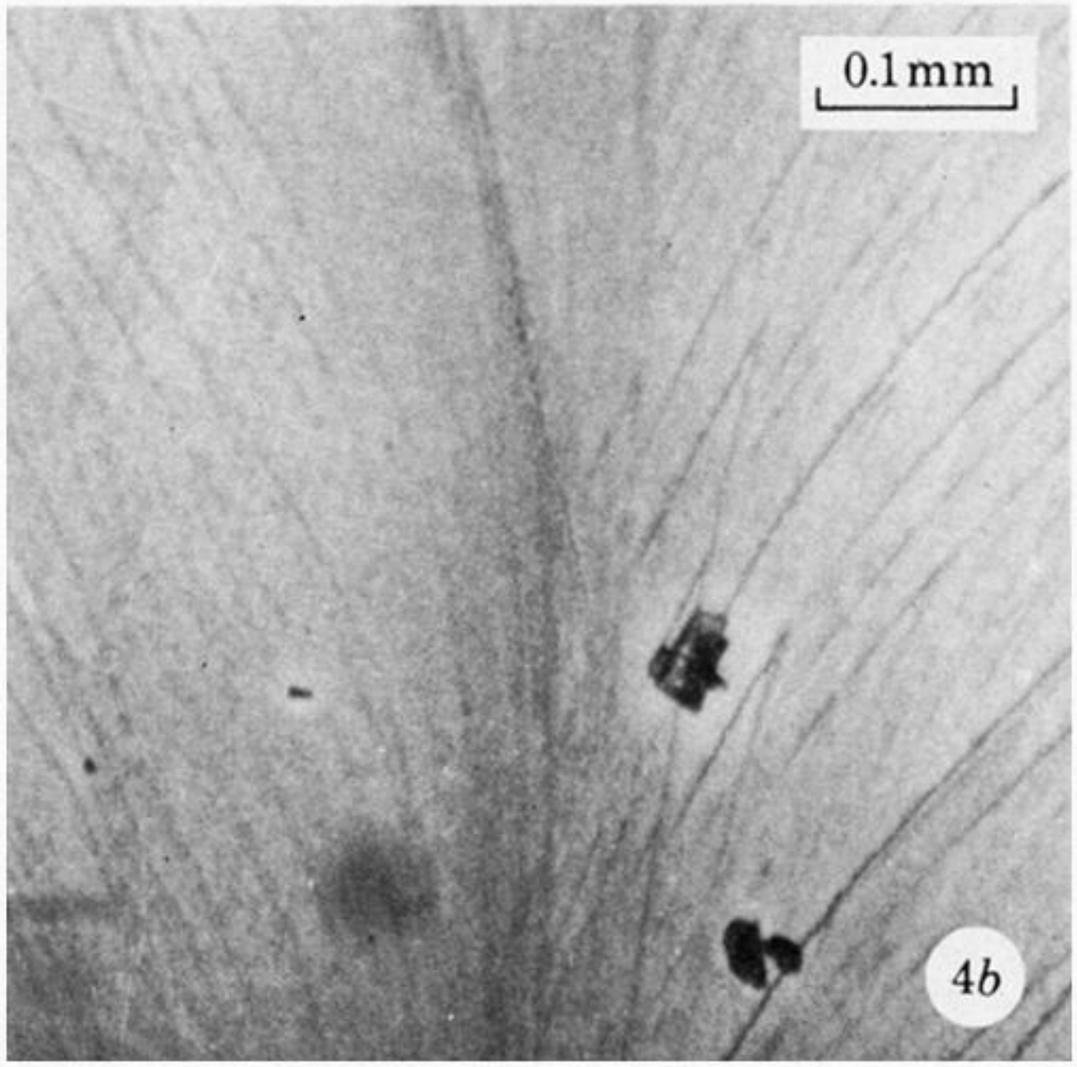


FIGURE 4. Comparative optical micrographs also confirmed (see figure 3) that a surface (*a*) previously reacted (160 min at 290 K in 25 kPa chlorine) underwent greater textural modification than a pristine surface (*b*) after both had been identically and concurrently exposed to water vapour (30 min at 288 K in 0.5 Ps (H_2O)).

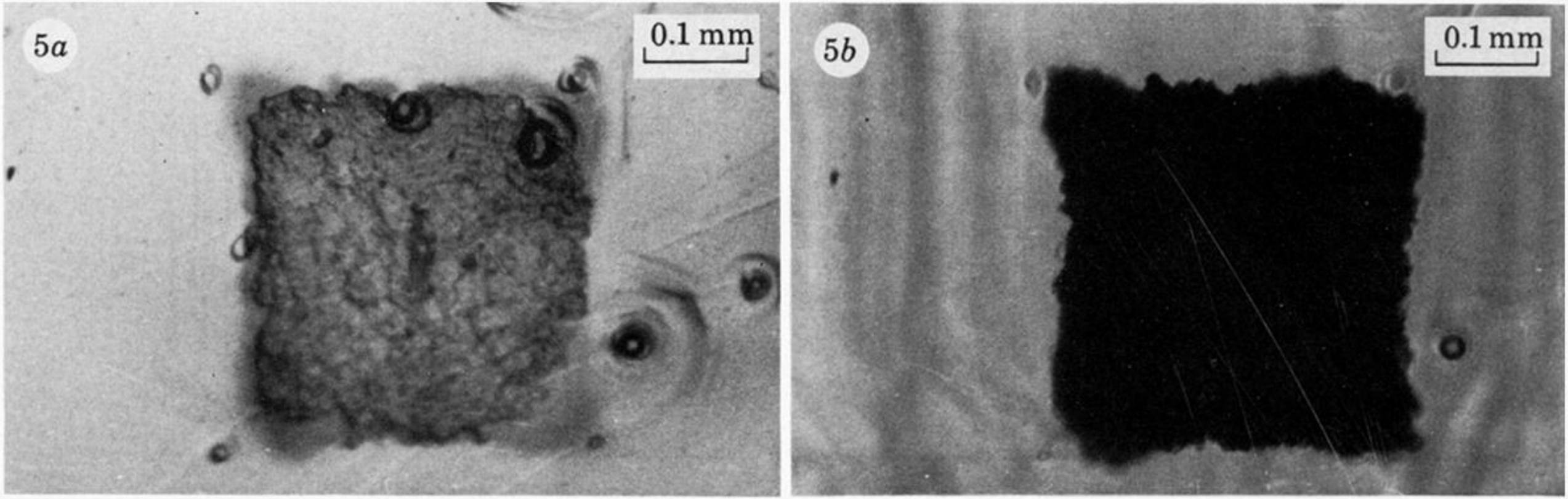


FIGURE 5. Reflection and transmission optical photomicrographs of a small growth nucleus in a partly reacted KBr crystal (1440 min at 273 K in 25 kPa chlorine). The region of surface deformation is slightly smaller than, but corresponds with, the approximately square but irregular outline boundary of the nucleus seen in transmission. Surface cracking had not yet developed.

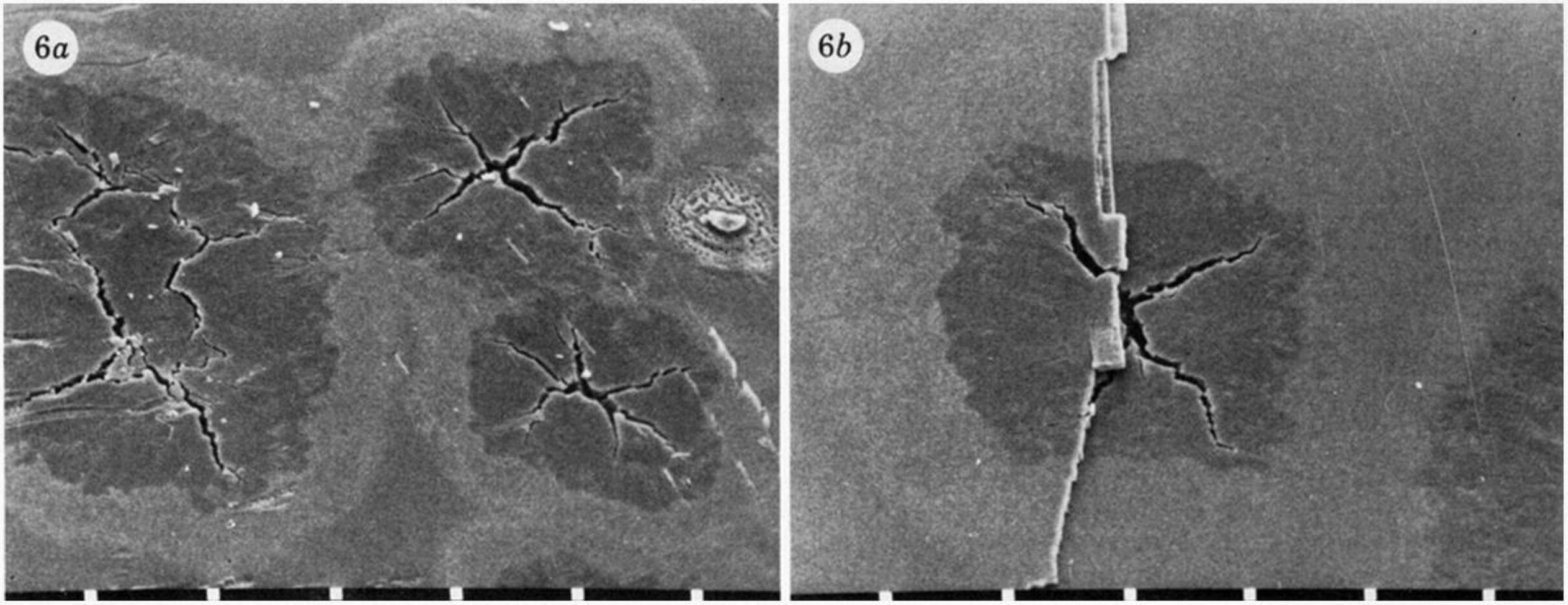


FIGURE 6. Two areas of a KBr crystal that contains growth nuclei. The surface of each nucleus is distorted and there is approximately diagonal cracking. Around each nucleus there is an aureole of slightly different texture. (240 min tin promoted reaction at *ca.* 290 K in 25 kPa Cl_2.) (*a*) Four nuclei are present with some overlap, a reacted tin residue can be seen near the centre of the right hand side. (*b*) This single nucleus was initiated at a surface step edge and probably within a crack at this discontinuity. S.e.m.: spacings of scale divisions are both 30 μm.

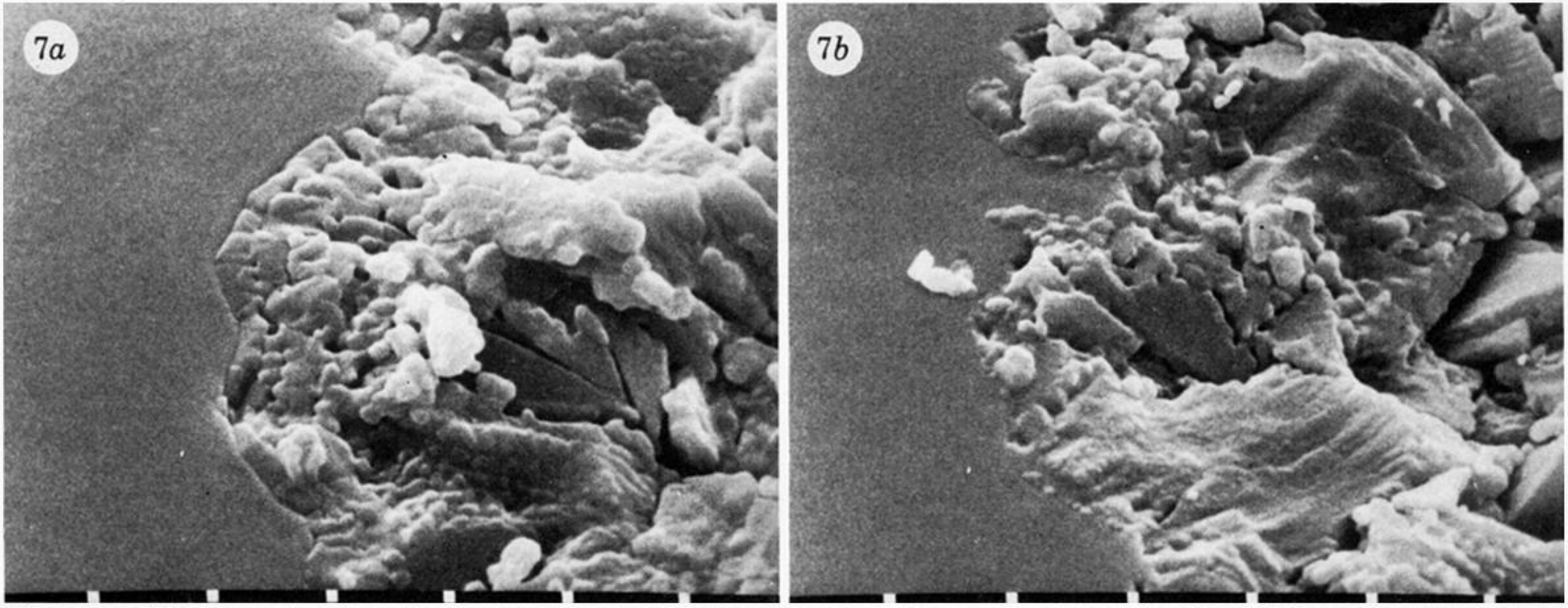
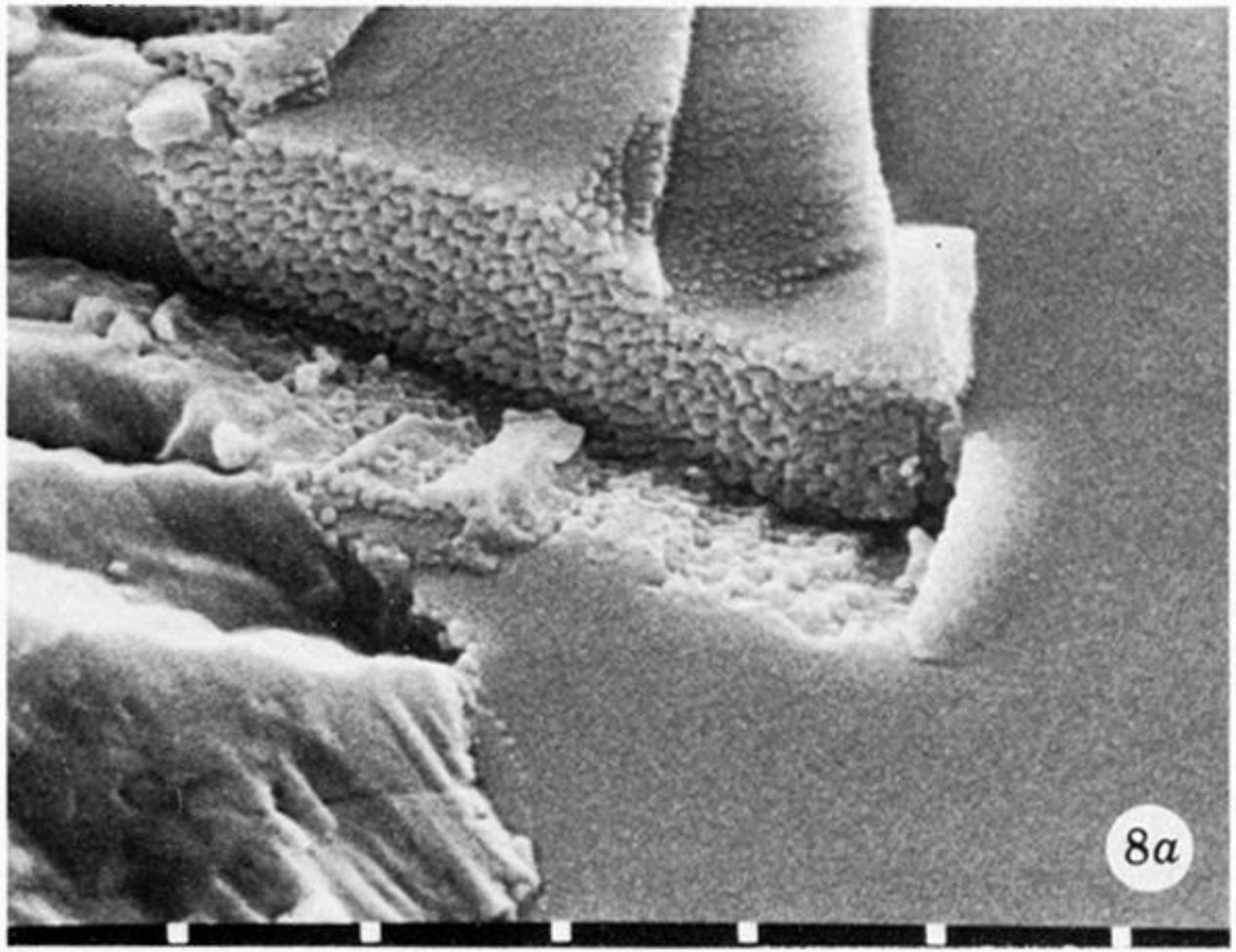


FIGURE 7. The reaction interface at high magnification. To the left are areas of unmodified KBr reactant, exposed by cleavage after nucleus development. These are not penetrated by cracks emanating from nuclei. To the right are product assemblages, KCl crystals often having flat faces and intranuclear pore systems affording pathways for halogen movements. Between these regions is the reaction zone, within which the chemical change occurs and believed to contain liquid during interface advance. Particles here are small, often rounded, presumably participating in dissolution processes, and show some textural resemblances to Br_2 modified KBr (figures 1 and 2). (240 min reaction at 290 K in 25 kPa Cl_2.) Spacings of scale divisions are both 3 μm.



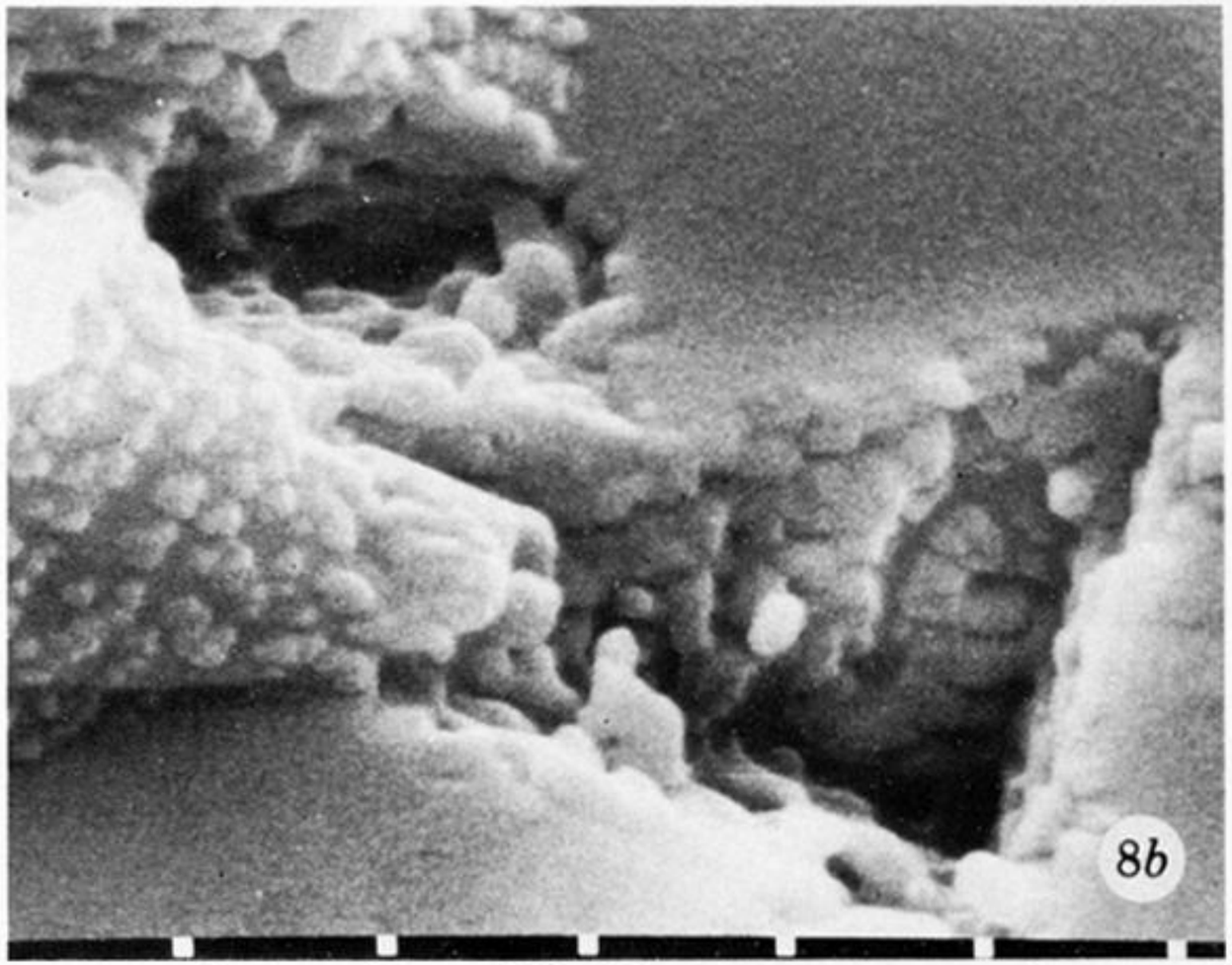


FIGURE 8. Details of interface textures revealed by cleavage of growth nuclei. The appearance, shape and dimensions of the numerous small (*ca.* 0.2 μm) hemispherical protuberances on reactant surfaces are similar, in some respects, to the textures developed by Br_2 modification of KBr surfaces (figure 1, plate 1). The rounded habit of these features is ascribed to participation in dissolution–recrystallization processes involving liquid halogen contained within the intercrystalline channels. This appearance is more readily explained by etching and a dissolution–diffusion mechanism involving a solute than through control by crystallographic forces. The planar areas of active surfaces are not oriented normally to the mean (100) directions of nucleus growth, which is here approximately from left to right. No textural modifications are evident in the crystal face beyond the interface, exposed by cleavage after reaction. (1680 min reaction at 273 K in 25 kPa Cl_2.) S.e.m.: spacings of scale divisions are (*a*) 3 μm and (*b*) 1 μm.

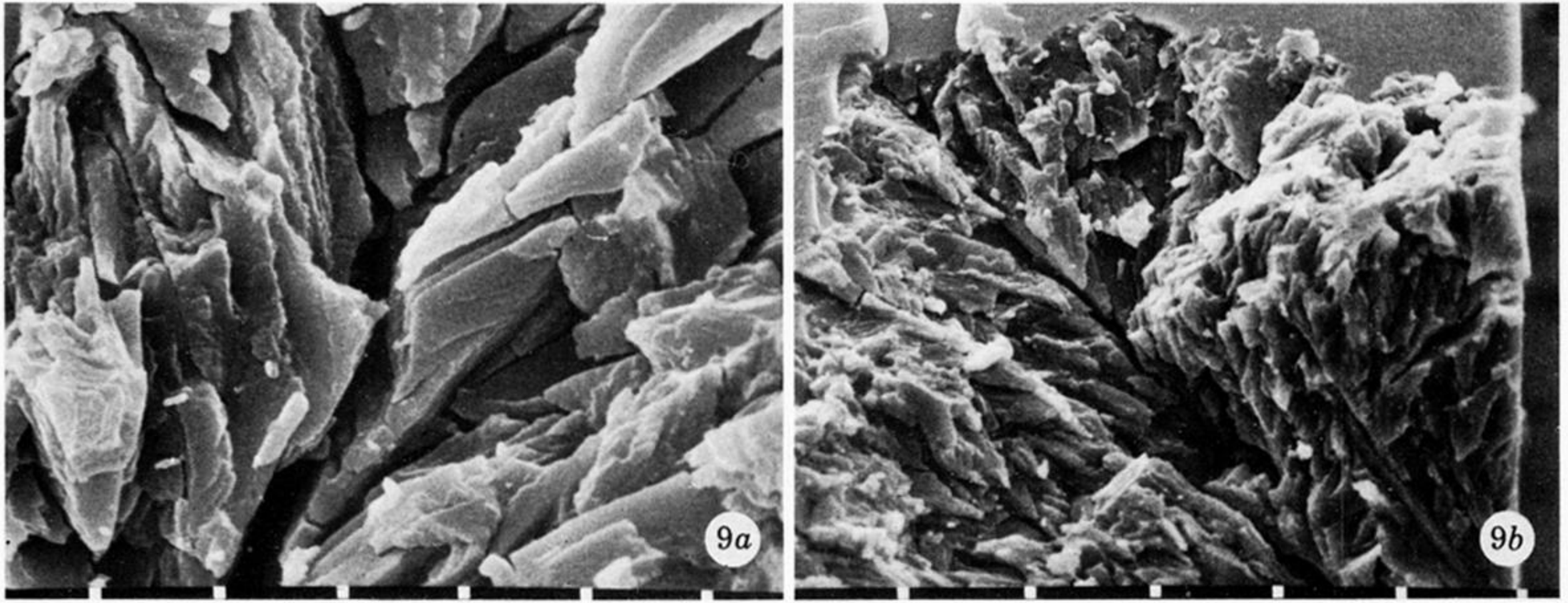


FIGURE 9. Habits of crystals towards the centres of nuclei tended to be less regular than those adjoining reaction zones. Intercrystalline pore systems permit gas transport to and from the reaction zone by large channels connected with the fine tributary systems. Immediately behind the active reaction zone KCl crystals are often slab-like, oriented in (111) directions with respect to the reactant KBr. (240 min reaction at 290 K in 25 kPa Cl_2.) S.e.m.: spacings of scale divisions are (*a*) 3 μm and (*b*) 10 μm.

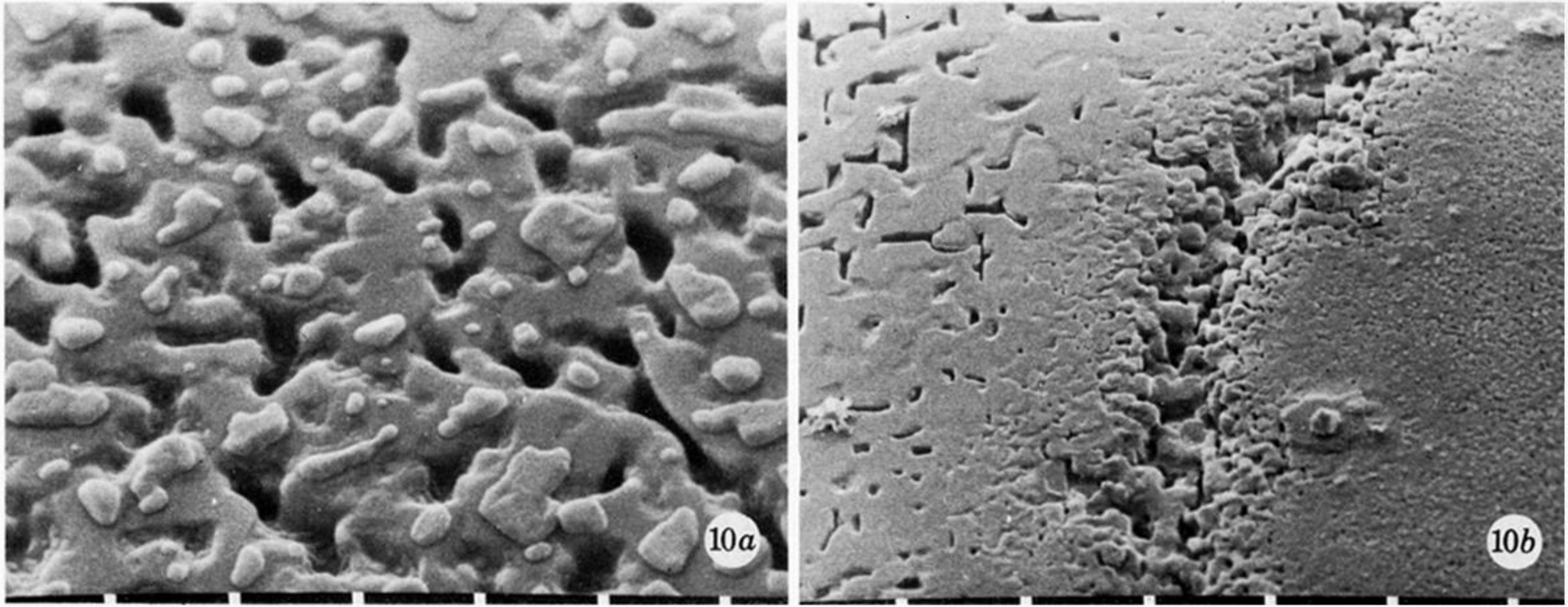


FIGURE 10. (*a*) The outer crystal surface of a nucleus that had been exposed to water vapour after reaction. (*b*) Along the surface boundary of the nucleus a depression developed, attributable to the enhanced solubility of the finely divided product first formed and possibly also the presence of free halogen: here the right hand side is the nucleus surface. (Before exposure to water vapour the crystal had reacted 200 min at 291 K in 25 kPa Cl_2.) S.e.m.: spacings of scale divisions are (*a*) 3 μm and (*b*) 30 μm.

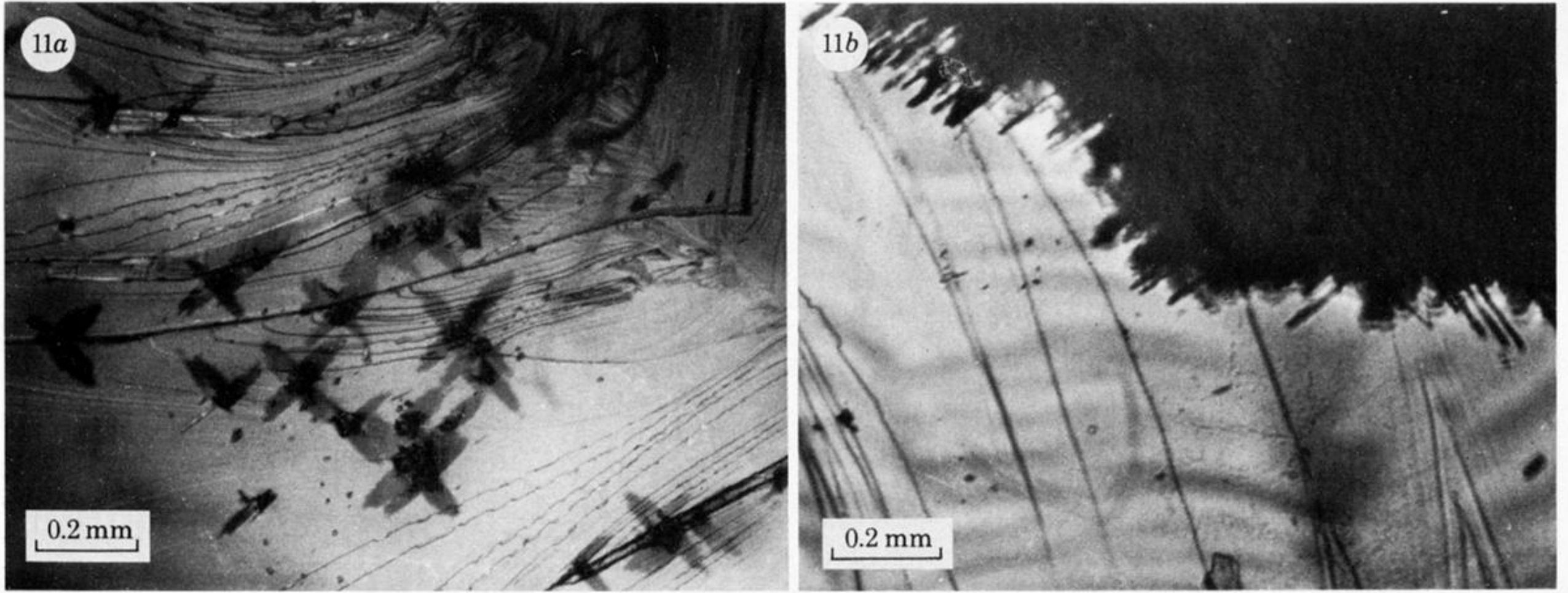


FIGURE 11. Optical micrographs of the fibre-like structures oriented in (111) directions, developed during the latter stages of tube reactions. (*a*) Small square-outline nuclei extended into the crystal ((111) directions) to form X-shaped structures. (1440 min reaction at 273 K in 25 kPa Cl_2.) (*b*) Shows the fibre-like development of product in the later stages of growth of large nuclei. (4320 min reaction at 293 K in 25 kPa Cl_2.)

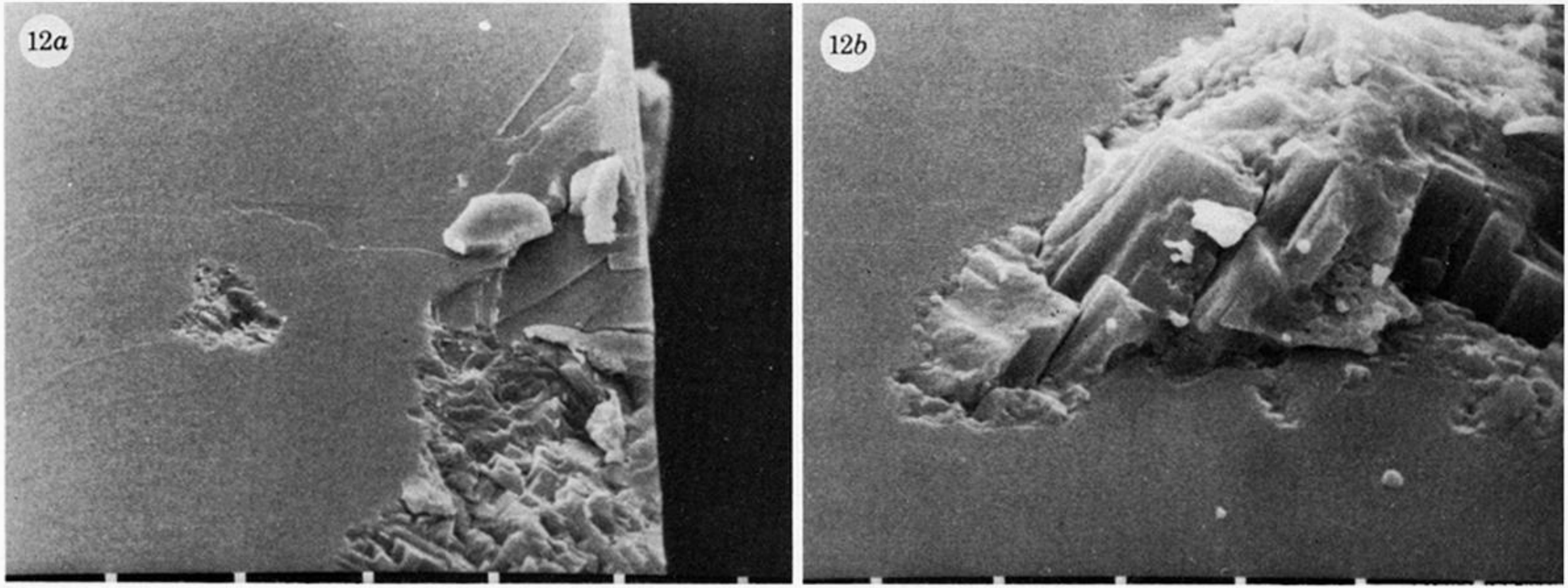


FIGURE 12. Textures of X-shaped nuclei revealed by (100) cleavage of reacted KBr. (*a*) The zone of (111) development is well separated from the section of a surface nucleus. The texture of the top of this advancing zone included rounded features resembling those found at advancing interfaces (figure 8, plate 4). (*b*) The (111) orientation of product KCl crystals and the associated pore structures of the fibre-like prolongations are shown. (These crystals were tube reactions for 1320 min at 273 K in 25 kPa Cl_2.) S.e.m.: spacings of scale divisions are (*a*) 10 μm and (*b*) 3 μm.

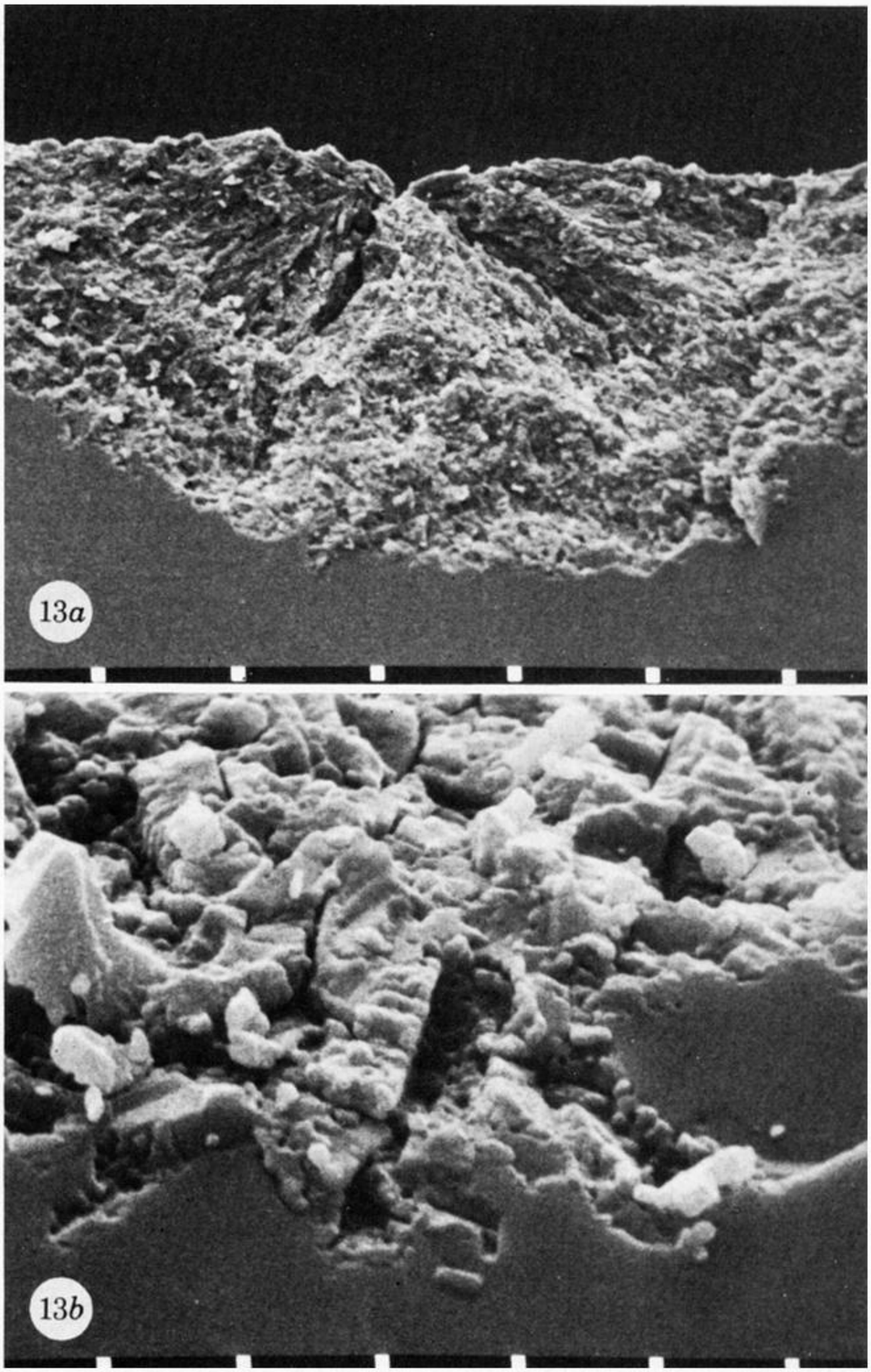


FIGURE 13. (*a*) Section of an approximately hemispherical nucleus developed during reaction in a relatively low chlorine pressure (12 kPa Cl_2). (*b*) At higher magnifications it is seen that the KBr–KCl interface is most irregular, crystallites are small (3–5 μm) and product crystal alignments in the (111) directions are less obvious (1360 min reaction at 291 K in 12 kPa Cl_2). S.e.m.: spacings of scale divisions are (*a*) 30 μm and (*b*) 3 μm.

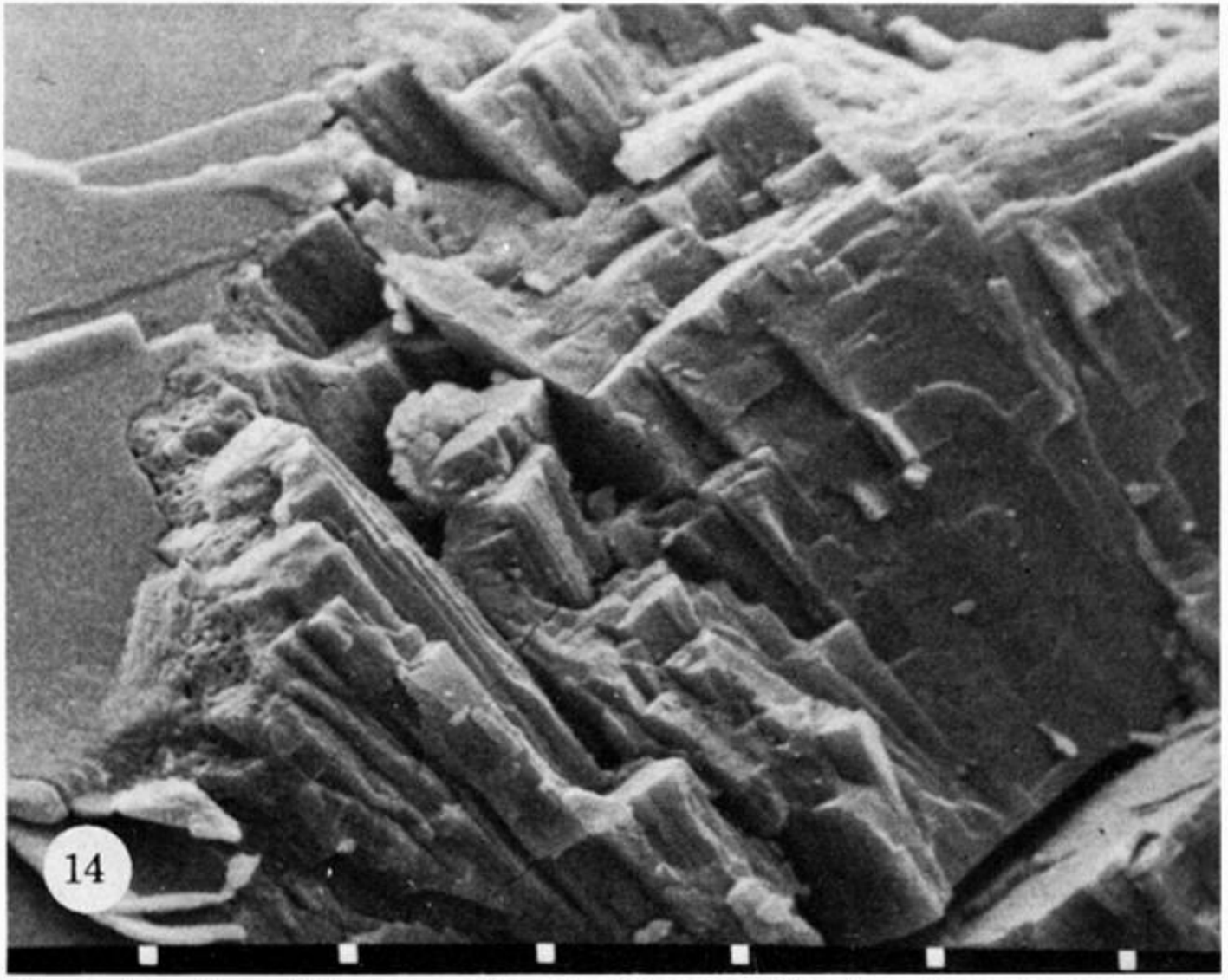
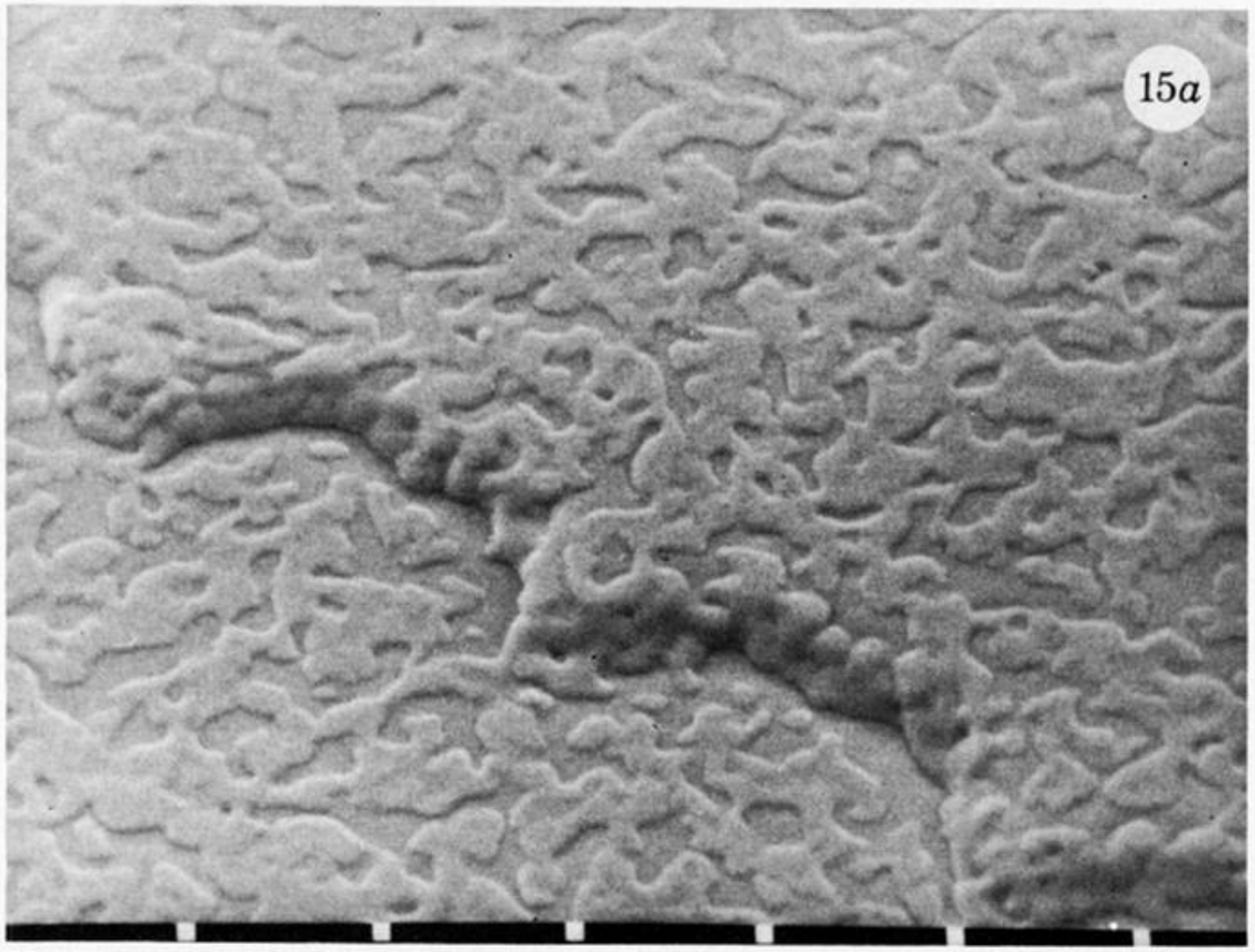


FIGURE 14. Section of nucleus developed by reaction in 50 kPa Cl_2 showing the large (*ca.* 10 μm), slab-like, (111) oriented KCl crystals in the vicinity of the reaction interface (1360 min reaction at 291 K in 50 kPa Cl_2). S.e.m.: spacings of scale divisions are 10 μm.



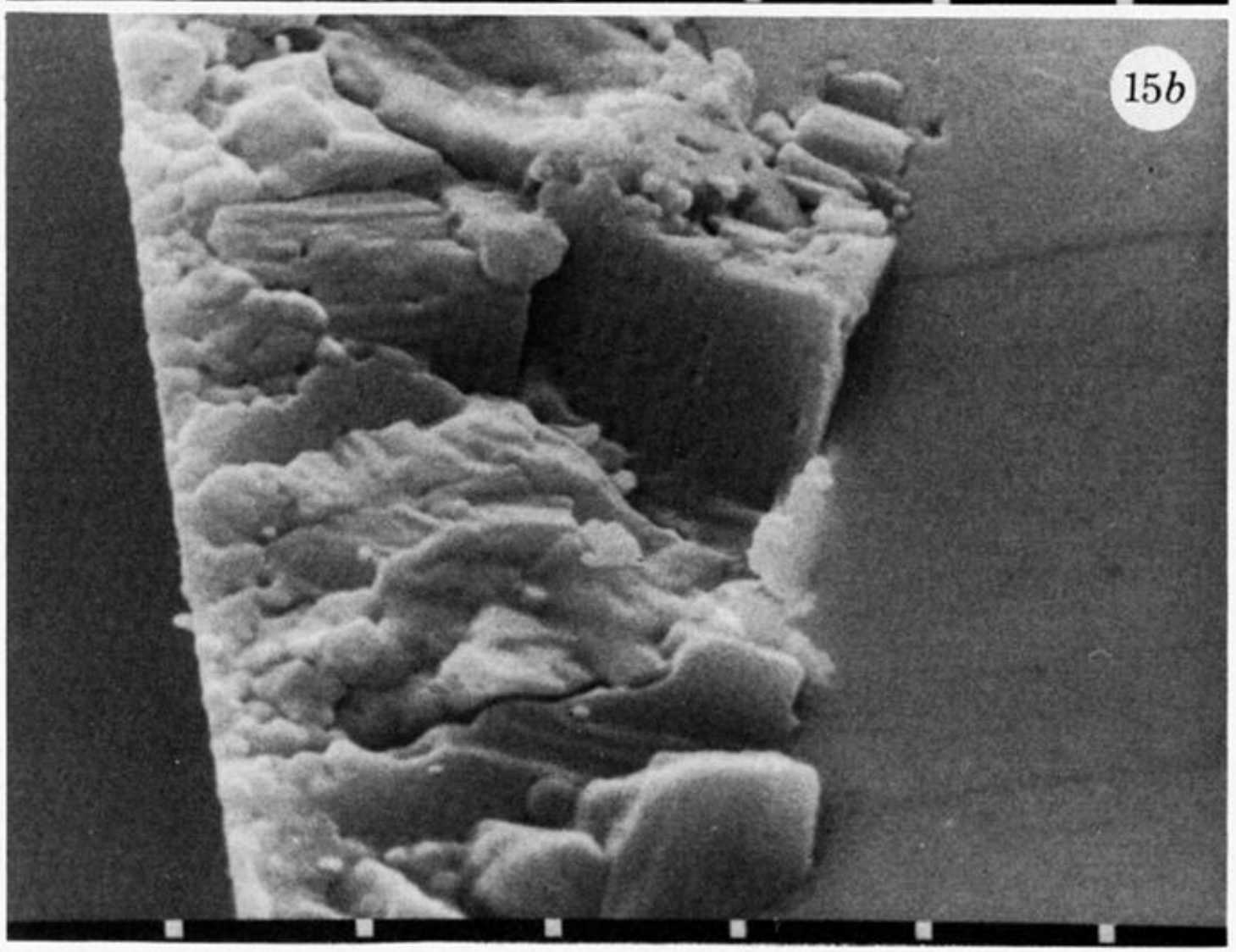


FIGURE 15. Textures developed during reactions at low temperature (256 K). (*a*) Textural modification of the reactant surface here is ascribed to halogen condensation. (*b*) This cleaved section of a nucleus reveals the pitted surface of large KCl product crystals, oriented in (111) direction. (1260 min reaction at 256 K in 25 kPa Cl_2.) S.e.m.: spacings of scale divisions are both 3 μm.

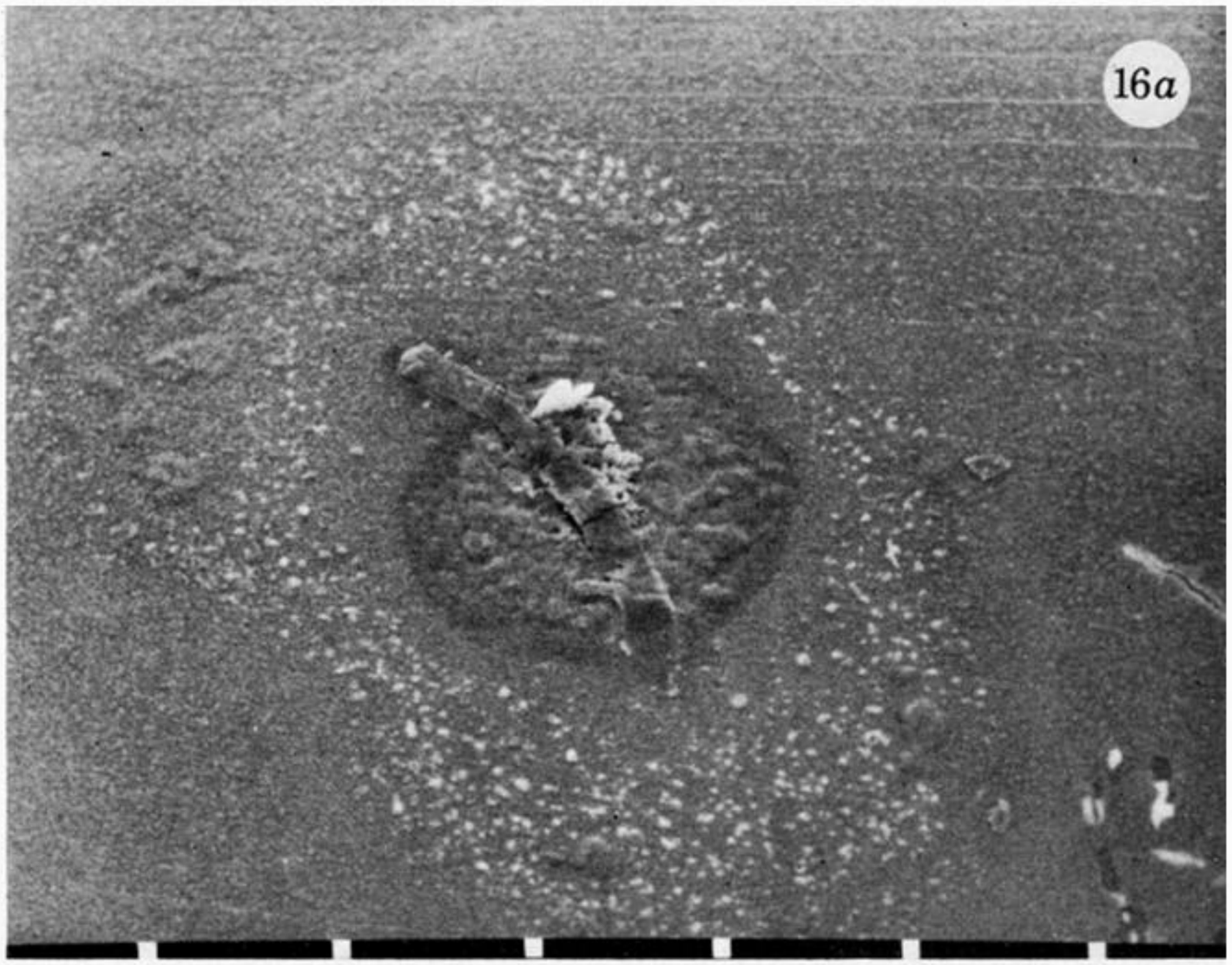


FIGURE 16. Surface textural changes due to excess tin on reactant surfaces. (*a*) A residue from a reacted tin particle (oxide?) is surrounded by a region of textural modification. (*b*) Elsewhere on the same surface, a surface layer, of presumably modified structure, has become detached over an area that coincides with a growth nucleus. Neither texture was ever observed during unpromoted reactions. (Two reaction intervals: 115 min at 283 K continued with 85 min at 325 K, both in 25 kPa Cl_2.) S.e.m.: spacings of scale divisions are both 30 μm.

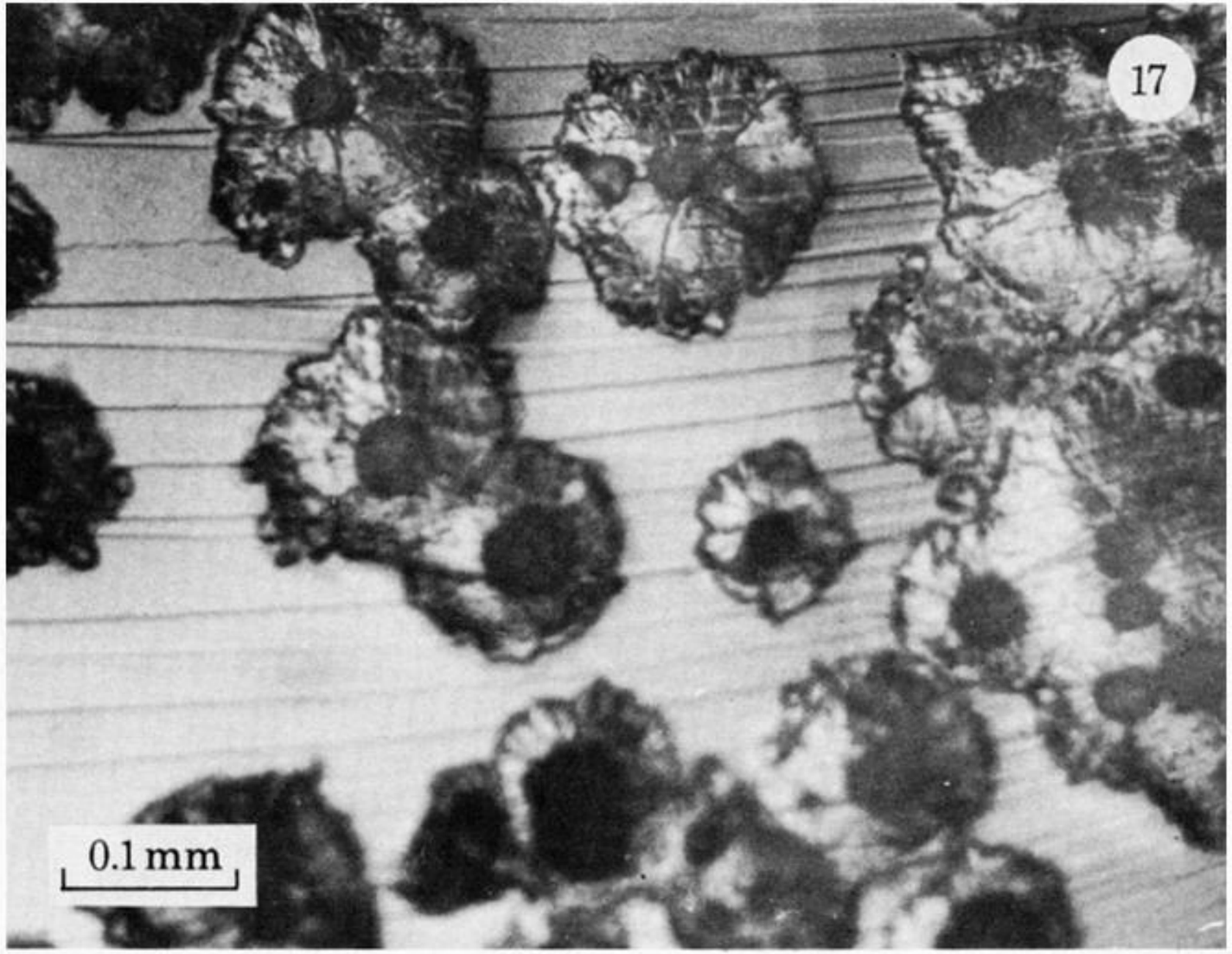


FIGURE 17. Optical reflection micrograph for a lead promoted reaction: the nuclei are unusual in having circular outlines. No reaction was apparent after 18700 min at 380 K in 25 kPa Cl_2, tube reaction, but, after cooling the reaction shown occurred during 180 min at 273 K.

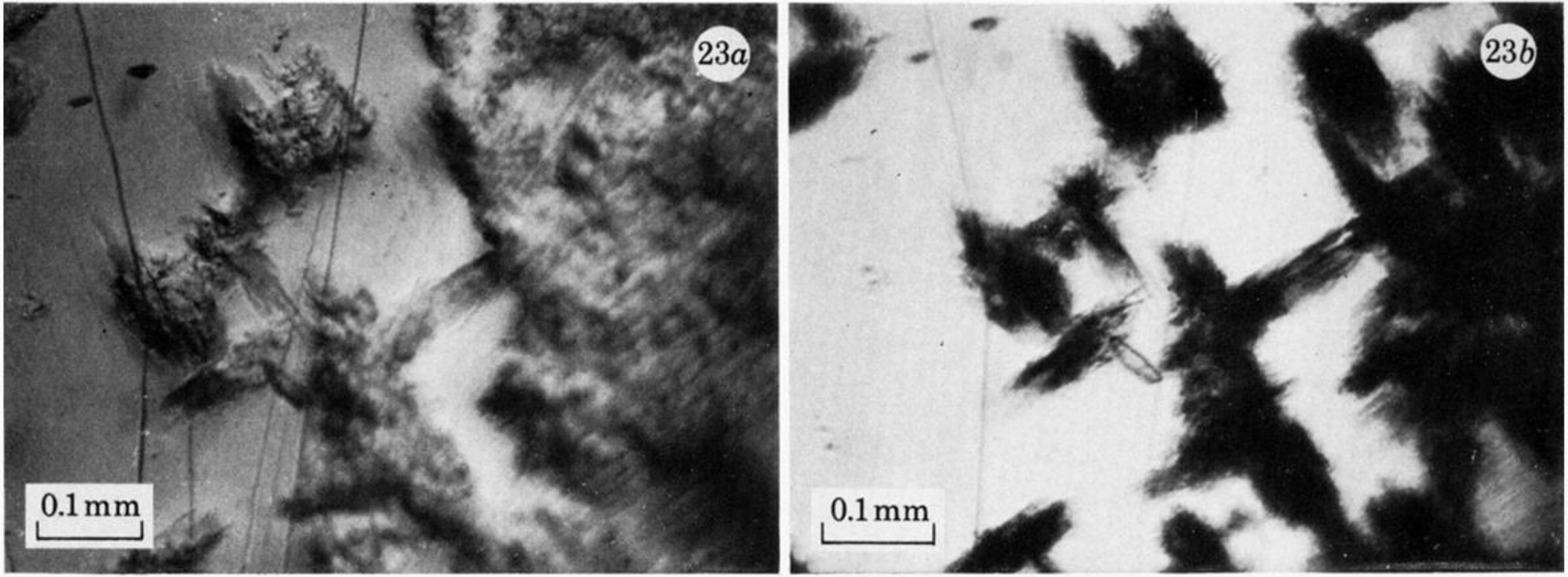


FIGURE 23*a*, *b*. Reflection and transmission optical micrographs of the nuclei developed during the high temperature reaction. Shapes of nuclei were variable and outlines highly irregular, with some preferred development in the (111) directions. (95 min reaction at 611 K in 25 kPa Cl_2.)

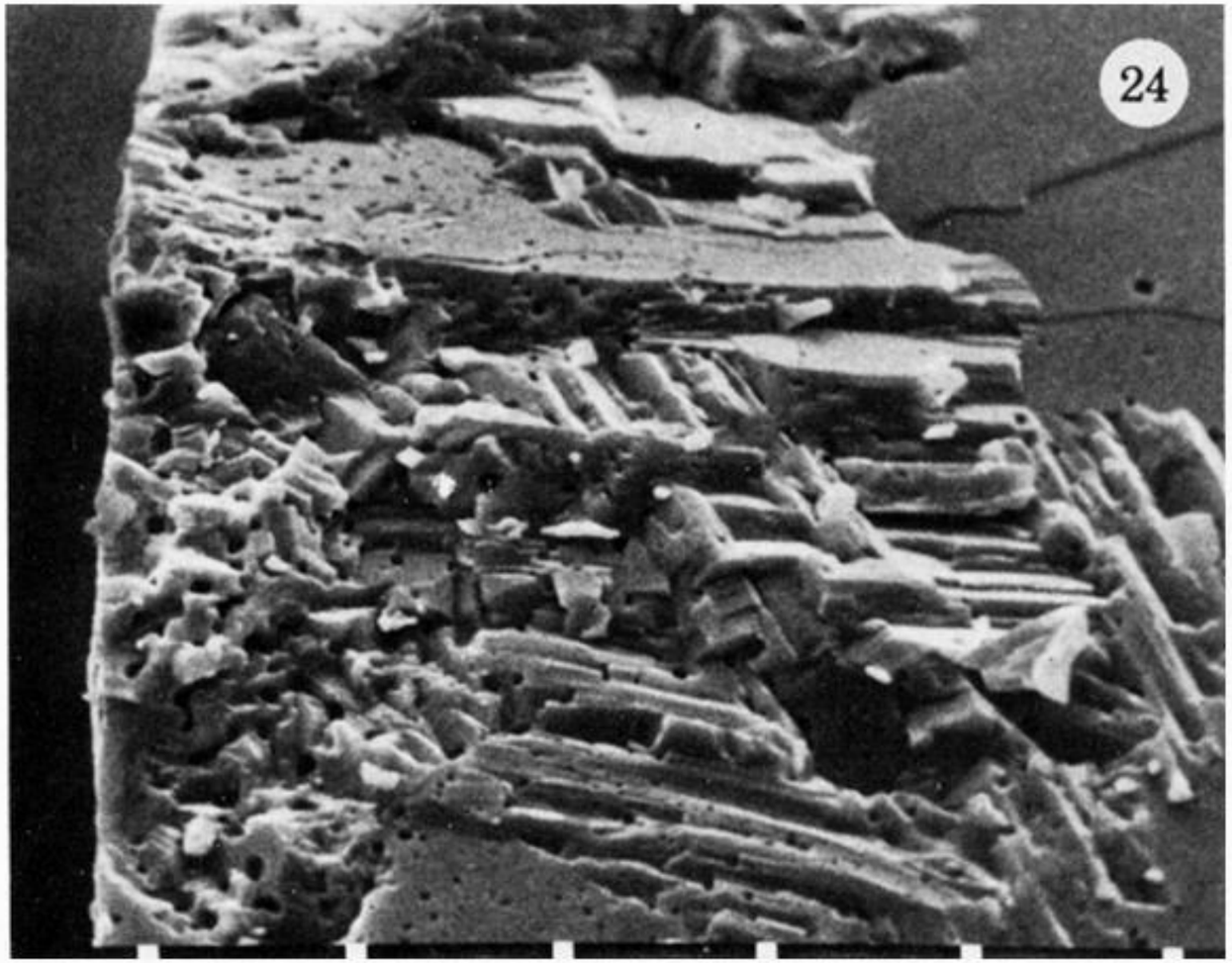
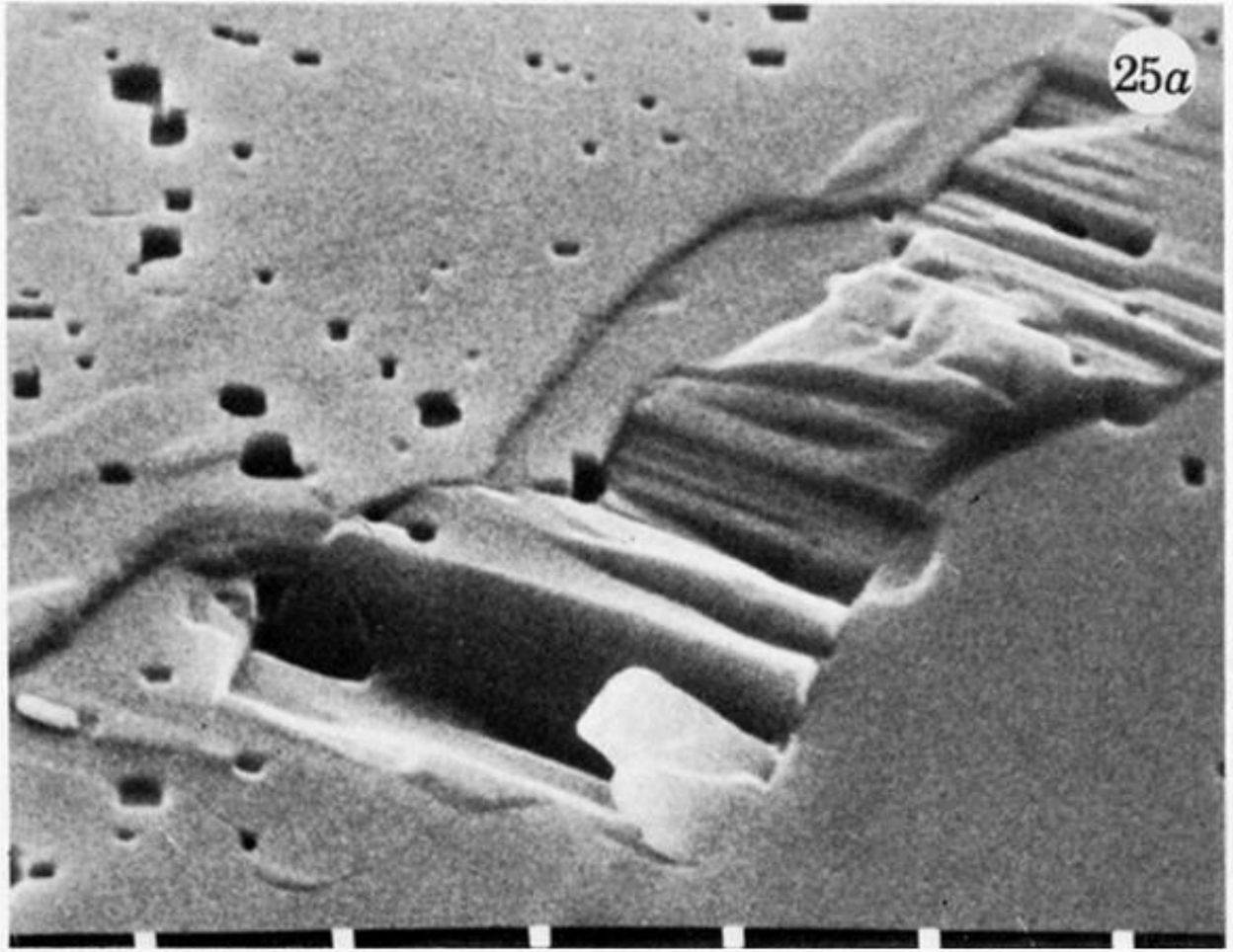


FIGURE 24. Cleavage section of crystal after high temperature reaction. The interior is penetrated by an extensive pore system in which three textural zones can be distinguished. Immediately below the surface little order can be recognized in the KCl product crystallite assemblage. The inner region of the retextured material shows preferred (111) orientation of the product crystals; two interpenetrant systems can be seen. Beyond this zone of obvious recrystallization, the reactant is penetrated by continuation of the system of pores, channels and holes. (120 min reaction at 620 K in 25 kPa Cl_2.) S.e.m.: spacings of scale divisions are 10 μm.



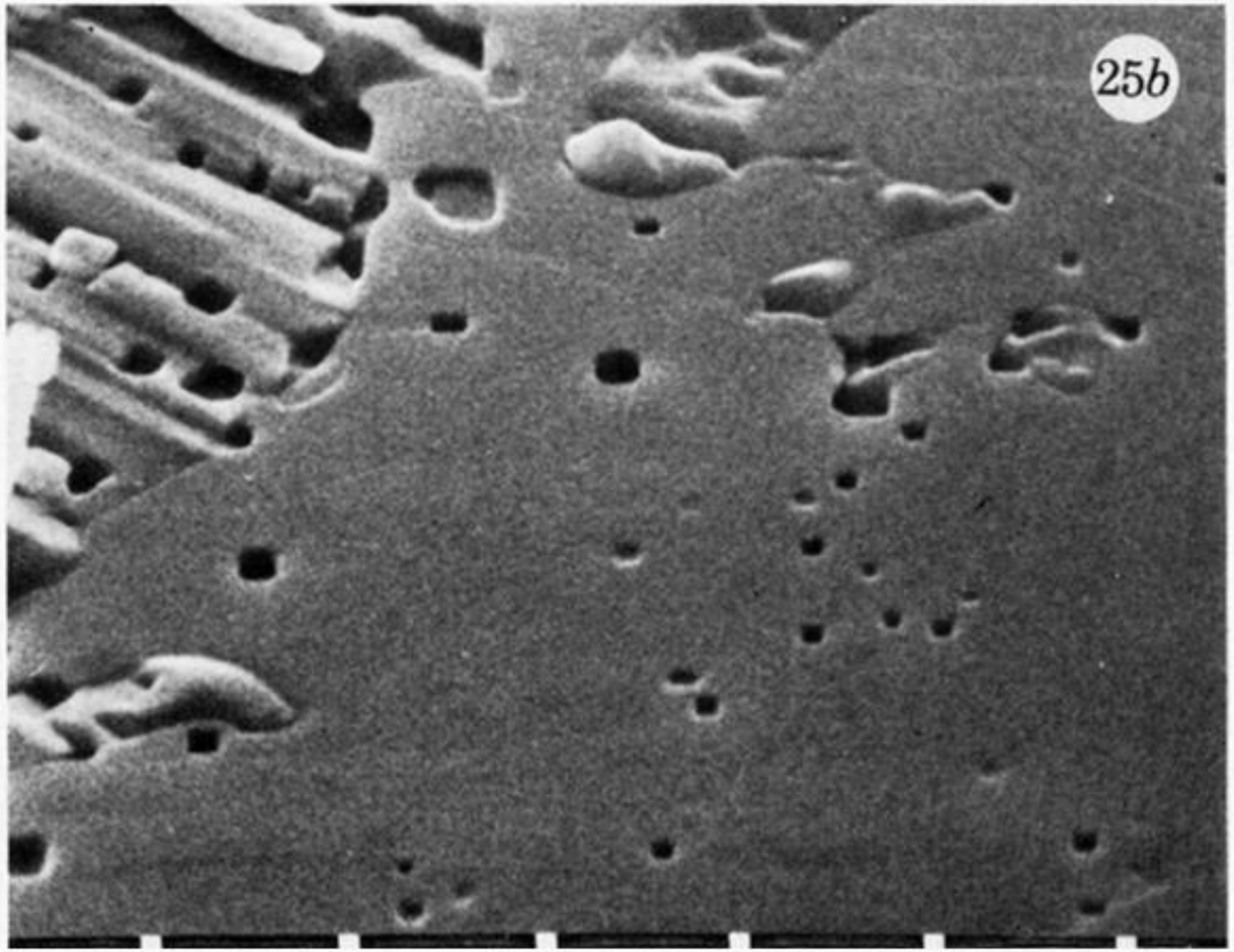


FIGURE 25. Cleavage section at inner limit of superficial retextured zones produced during the high temperature reaction. The (100) surface exposed on fracture is penetrated by numerous holes, never observed during many examinations of cleavage faces of unreacted KBr. The boundaries of the recrystallized zones are irregular and no reaction interface could be identified. (Crystal reacted under same conditions as for figure 24.) S.e.m.: spacings of scale divisions are both 3 μm.

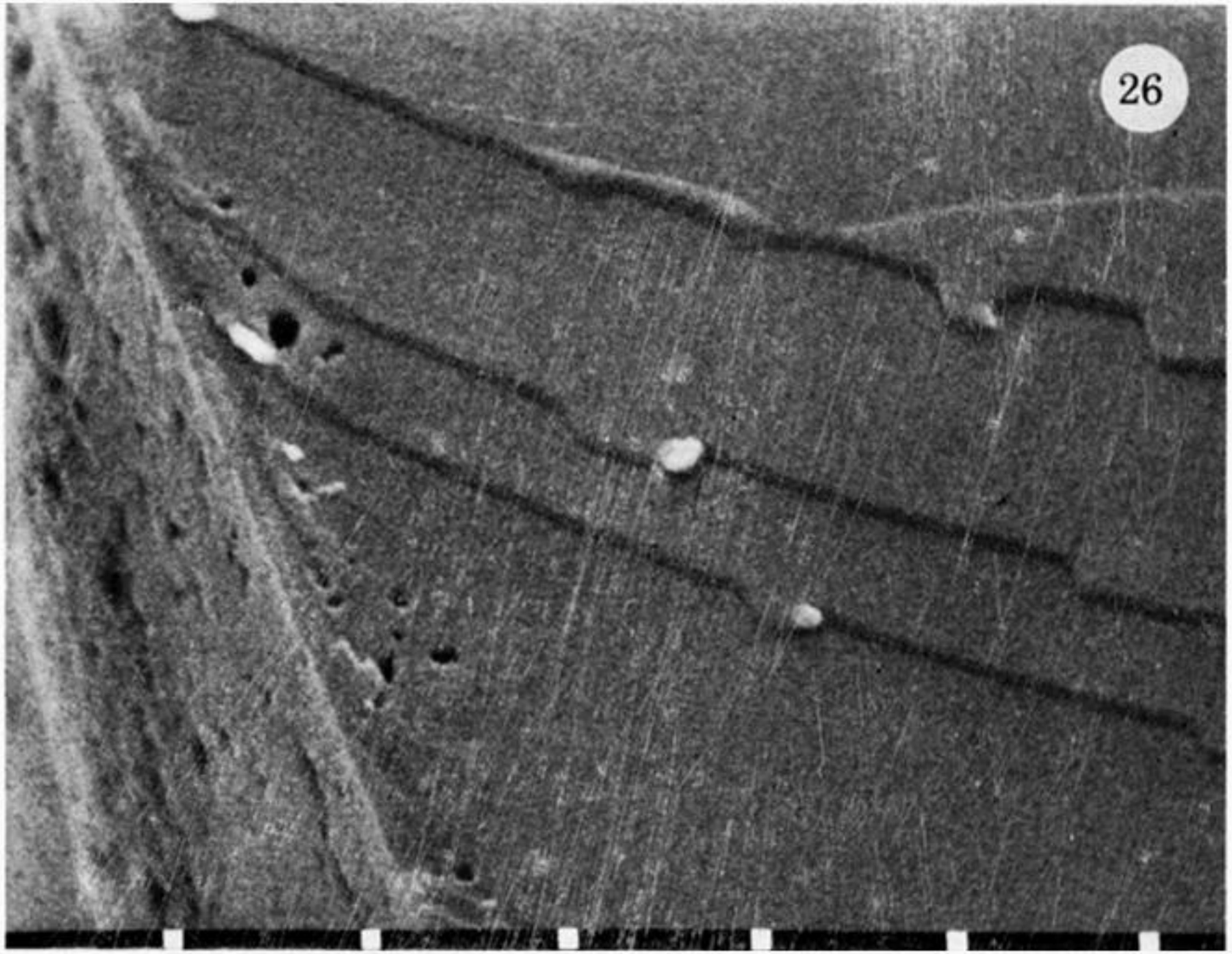


FIGURE 26. Subsurface holes developed during the high temperature reaction in a zone remote from any recrystallization nucleus. (Same crystal as in figure 24.) S.e.m.: spacings of scale divisions are 3 μm.

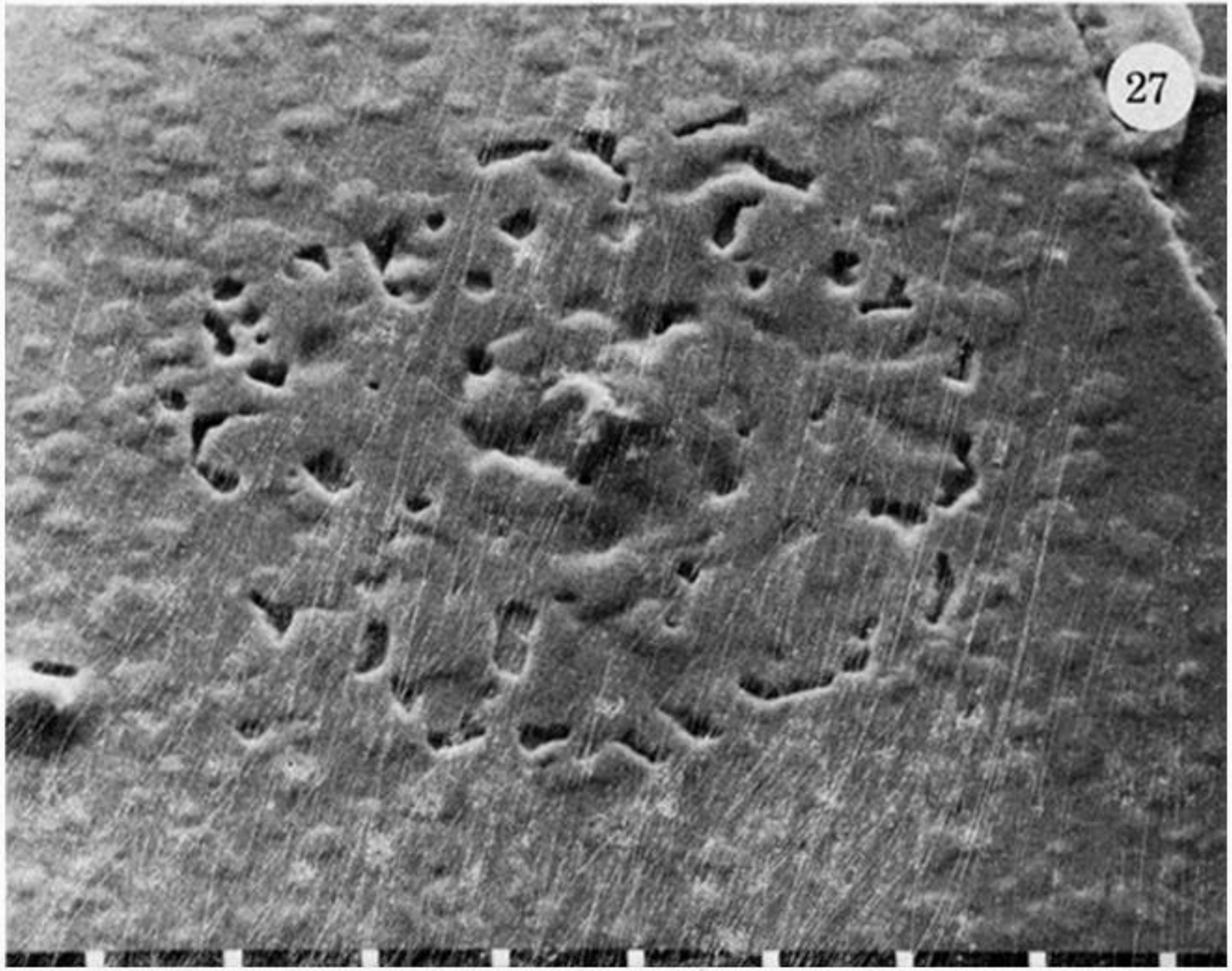


FIGURE 27. Surface texture modification during the high temperature reaction. The nucleus periphery is characterized by the pattern of holes which provide routes for reactant access and product escape. (40 min reaction at 610 K in 25 kPa Cl_2.) S.e.m.: spacings of scale divisions are 10 μm.

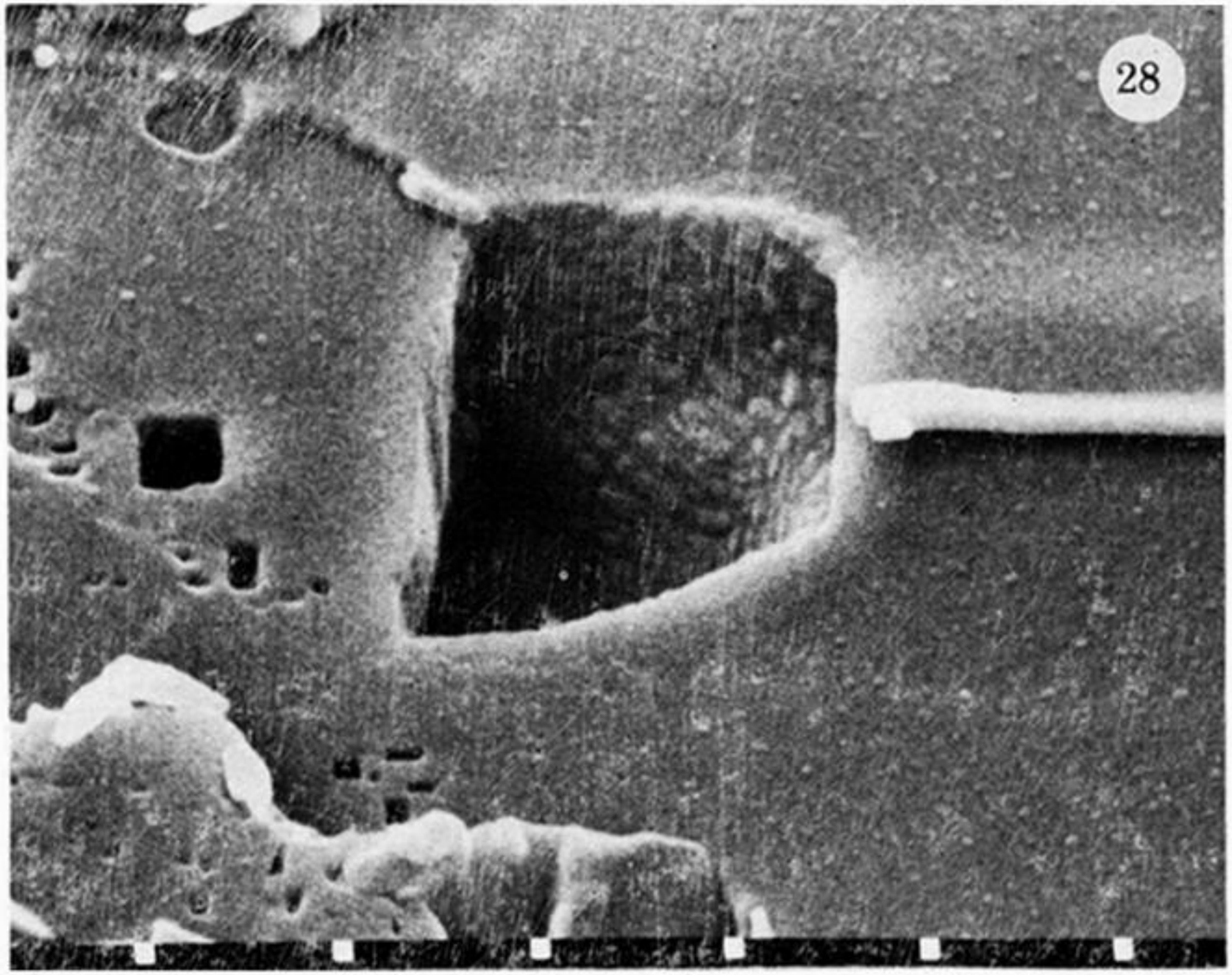


FIGURE 28. An unusually large hole, revealed on cleavage, in unrecrystallized reactant near a high temperature nucleus. The rounded features on internal surfaces are reminiscent of interface textures in low temperature reactions. (90 min reaction at 610 K in 25 kPa Cl_2.) S.e.m.: spacings of scale divisions are 3 μm.