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STRUCTURE AND FUNCTION OF THE NUCLEI DEVELOPED DURING DEHYDRATION OF THE ALUMS $KAl(SO_4)_2 \cdot 12H_2O$ AND $KCr(SO_4)_2 \cdot 12H_2O$ *

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ABSTRACT

Nuclei developed during the dehydration of the alums $KAl(SO_4)_2 \cdot 12H_2O$ and $KCr(SO_4)_2 \cdot 12H_2O$ have been examined microscopically in detail, to extend a previous kinetic and mechanistic study of this nucleation and growth reaction (A.K. Galwey, R. Spinicci and G.G.T. Guarini, Proc. R. Soc. London, Ser. A, 378 (1981) 477). In the present work it has been observed that the contact interface between reactants and products is coherent and is characterized by no discernible associated crack or pore structure. Reactants and products adhered strongly across this zone of chemical change. The textures observed are described and are entirely consistent with the reaction mechanism proposed previously. In this the rate-controlling process is identified as residual solid product retexturing, promoted by product water temporarily retained within the nucleus, an appropriately structured product assemblage. This conclusion is also consistent with results of a study of an alternative dehydration reaction in which alum crystals were immersed in concentrated sulphuric acid. This reaction was not a nucleation and growth process. Reaction proceeded within an adherent product layer that was initially rapidly established across the entire surface and thereafter advanced inwards at a rapidly diminishing rate.

INTRODUCTION

The most significant mechanistic conclusion that was reached during a recent study [1] of the dehydration of alums ($KAl(SO_4)_2 \cdot 12H_2O$ and $KCr(SO_4)_2 \cdot 12H_2O$) was that the occurrence of reaction preferentially at the reactant–product interface arises as a consequence of the promotion of solid product recrystallization by water temporarily retained within intranuclear channels. This reaction model identifies the nucleus as a structure specifically developed to impede the removal of the volatile product, thereby retaining a sufficient concentration of available water in the vicinity of the reaction zone to enable the product phase to reorganize. This reaction mechanism [1] contrasts with previously accepted views [2,3] that regard the

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* Dedicated to Professor W.W. Wendlandt on the occasion of his 60th birthday.

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solid products, which constitute the nucleus, as offering no impedance to volatile product escape. This conclusion was based on the observation that interface advance proceeds at a constant rate and does not diminish with effective increase in product layer thickness. These differences can be reconciled, however, if it is accepted that intranuclear water vapour escape channels *beyond* the immediate reaction zone are large and offer little impedance to product movement. This new interpretation [1] of behaviour explains these nucleation and growth processes as reactions in which water loss is an autocatalytic process occurring within specifically developed subsurface structures. We also note that this proposed participation by fluids is consistent with parallel behaviour described for the mechanisms of two other nucleation and growth reactions involving solid reactants: the decomposition of ammonium perchlorate [4] and the reaction between potassium bromide and chlorine gas [5].

During the previous study [1] it was observed, through microscopic examinations, that the outer faces of reactant crystals were not detectably changed by exposure to vacuum dehydration conditions. However, on subsequent admission of water vapour, at less than saturation pressure, such crystal faces underwent superficial retexturing. This is positive evidence that the volatile product promotes superficial structural reorganization following alum crystal evacuation. Similar recrystallization may be expected to occur in the presence of water at the active reactant–product contact zone. This water is retained because the rate of diffusive escape is restricted within the narrow channels characteristic of the region of chemical change at each nucleus boundary. The controlling factor in sustaining dehydration at the peripheries of all growth nuclei is identified, therefore, as the restructuring of the solid products. The active interface texture is not readily established on relatively perfect external crystal faces, from which the irreversible loss of water is rapid. In consequence the nucleation step is difficult and only occurs at a limited number of suitable, highly specialized surface sites.

The present communication reports two extensions of the previous kinetic and mechanistic study of alum dehydrations [1]. Firstly, we report a novel microscopic examination of the detailed structure of the reaction interface. From these observations we demonstrate that the residual products retain coherent contact with the reactant across the zone of chemical change and that no crack structure could be identified within or in advance of the interface. Secondly, a study has been made of an alternative dehydration reaction, in which the alum surface was reacted directly with concentrated (and alum-presaturated) sulphuric acid. The chemical changes occurring during this solid–liquid interaction proceed at an interface through a rate process that does not involve the generation of separate and discrete nuclei. We conclude that the present observations generally support the mechanism proposed previously [1], though with some modifications that are discussed below.

MICROSCOPIC EXAMINATION OF INTERFACE STRUCTURE

Experimental

The previous microscopic studies [1,6,7] included the use of a replication technique [6] to examine intranuclear crack structures developed during alum, particularly $KCr(SO_4)_2 \cdot 12H_2O$, dehydration. Suitable large, single alum crystals were dehydrated sufficiently to develop growth nuclei and the surface of interest was covered with a solution of formvar in chloroform. This liquid spread across the external crystal face and also penetrated the intranuclear crack structure. After the polymeric material had set and hardened, the alum reactant and the residual dehydration products were removed by dissolution in water. The replica of the surfaces of interest was subsequently examined in a scanning electron microscope. Significant features of the nucleus textures observed have already been described and discussed [1].

Using this method, the replicating fluid penetrates the intranuclear crack system from the surface hole of each nucleus. Accordingly, access to the innermost zones of each product assemblage may be restricted. Thus we cannot be certain as to whether this method gives reliable replication of the reactant–product contact; the texture of this zone of chemical change is of greatest importance in the formulation of the reaction mechanism.

The present article describes textures observed from replicas prepared by a method in which the replicating fluid was brought directly into contact with the exposed interface in section, thereby enhancing its accessibility to the features of greatest interest. Here alum crystals, prepared identically to those used in previous work [1], were partially dehydrated with the development of growth nuclei. Such crystals were at once cleaved to reveal sections of dehydration nuclei (within seconds of removal from vacuum apparatus). The replicating fluid was immediately placed on areas of interest, including reactant–product contacts. After drying and hardening, the alum and reaction products were removed by dissolution and the replica examined in a scanning electron microscope. [1,6,7]

Intranuclear structure and texture of reaction interface

The textures of typical sectioned and subsequently replicated nuclei, developed during $KCr(SO_4)_2 \cdot 12H_2O$ dehydration, are shown in Fig. 1. The open structure of thin interconnected sheets represents the replicant-filled intranuclear cracks of the former nucleus. The right-hand side of the photograph is the cleaved crystal face. Of greatest interest in the present context is the zone where the cleaved reactant contacts the intranuclear solid product. Three representative photographs of this zone at higher magnifications are shown with alternative perspectives in Fig. 2. The relatively smooth

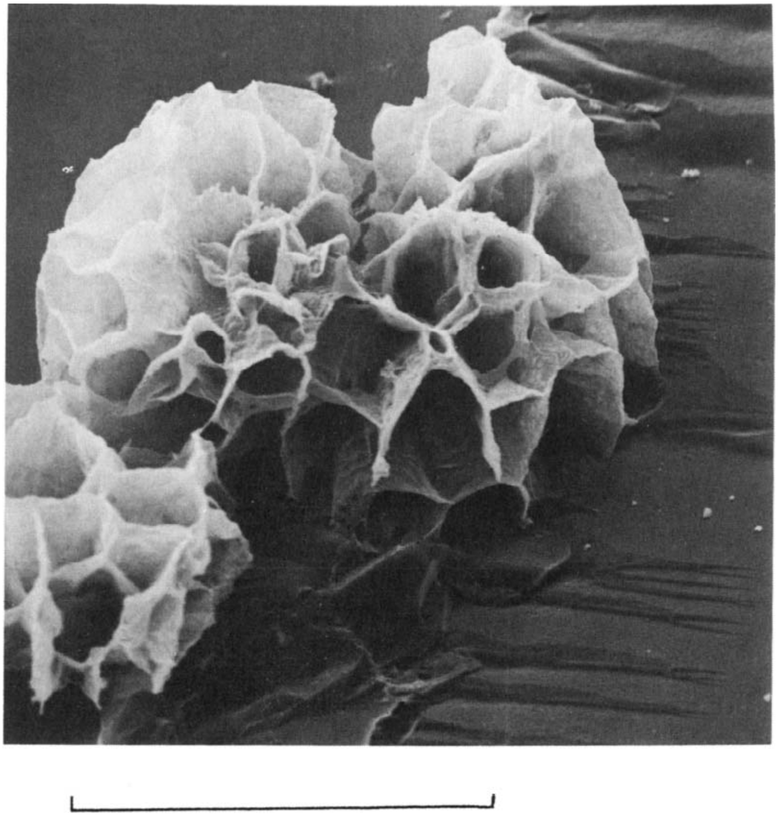

Fig. 1. Scanning electron micrograph of replica of $KCr(SO_4)_2 \cdot 12H_2O$ dehydration nucleus; the crystal was cleaved after reaction but before replication. The intranuclear crack system is evident as the open structure (the gaps between cracks were formerly filled with solid product assemblages). The exposed surface of unchanged reactant is seen on the right-hand side. The cleavage surface propagates across the nucleus. Scale bar, 100 μm.

areas are sections of unchanged reactant; the former intranuclear cracks appear on the replica as laminar features. Two bifurcations of the cracks shown are seen in Fig. 2b. The contact zone is shown in Fig. 2c.

From these, and other microscopic observations, we reach the following conclusions that are relevant to the consideration of the reaction mechanism. Cleavage cracks, propagating in a chrome alum crystal, advance without change of orientation as the reaction interface progressively moves through the reactant. The texture of the coherent blocks of product gave roughened replicated surfaces, evidence of recrystallization. The product is probably composed of small particles (< 0.2 μm) together with associated pore development. The detailed structure of this assemblage was below the limits of resolution or of replication. The abrupt change in texture (Fig. 2) coincides with the limit of intranuclear crack development (channels of

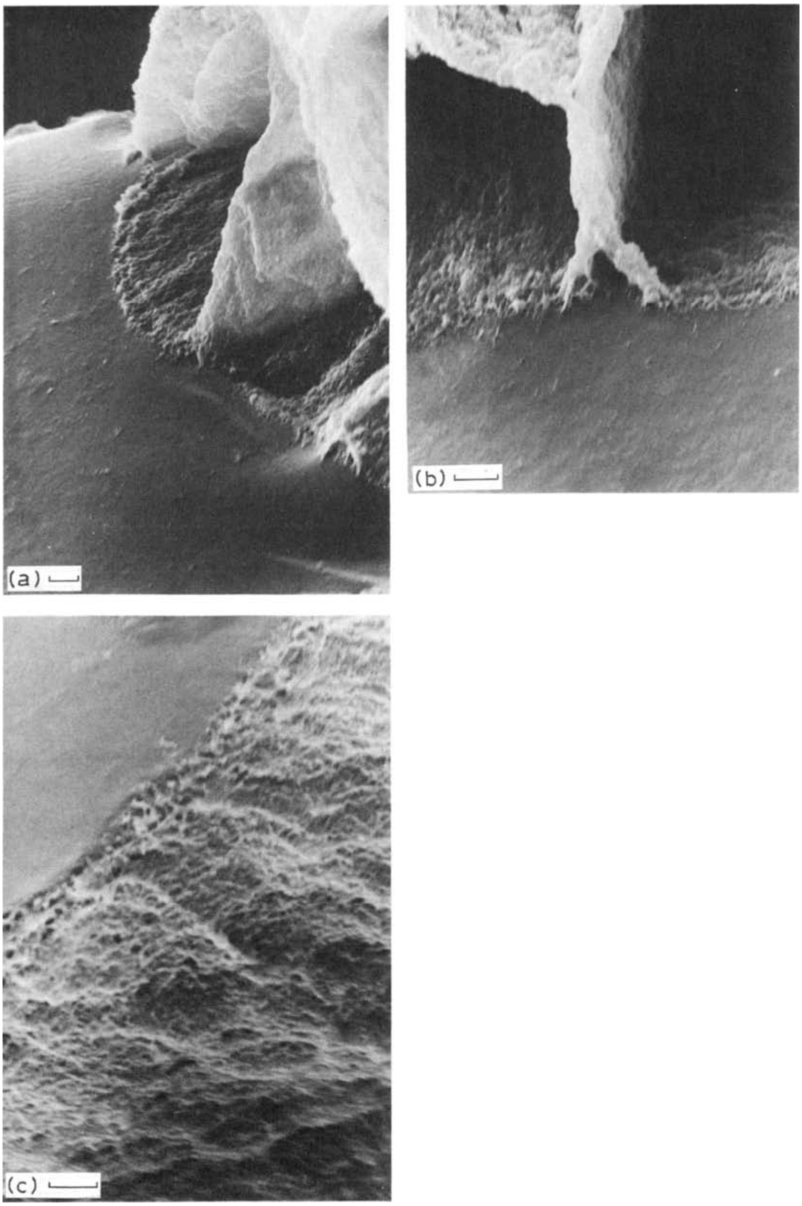

Fig. 2. Scanning electron micrographs of cleavage sections of the peripheries of chrome alum dehydration nuclei, seen from different perspectives. Scale bars all 1.0 μm. (a) The roughened texture of the cleaved product surface contrasts with the smoother face exposed on fracture of the reactant. The intranuclear crack system is seen to extend to the reaction interface. (b) The product surface exposed is again rougher than that of the reactant. The replicated intranuclear crack divides at top and bottom. (c) The cleaved reactant is smooth, the product is rough. No crack or pore system can be associated with the interface and the sizes of particles or holes in the product are below the limits of resolution of the method (< 0.2 μm).

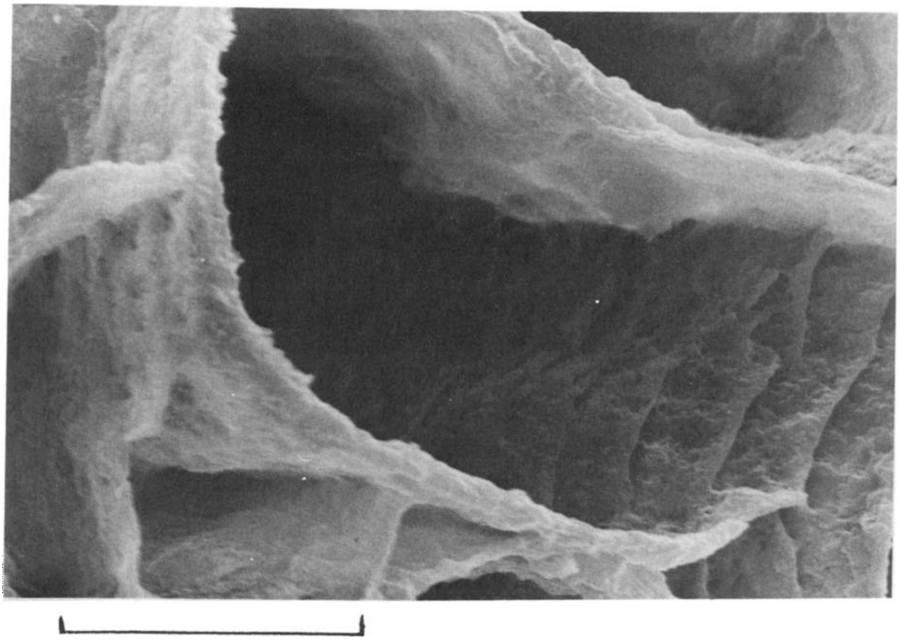

Fig. 3. Scanning electron micrograph showing the surface texture of a replica of an intranuclear crack. The irregular ridges may result from tributary, finer cracks penetrating the product or may record slip movements of the product block relative to the reactant during the growth process. Scale bar, 10 μm.

escape for the volatilized water product) and is identified as the reactant–product contact. This interface gave no evidence of the existence of an associated crack or pore disposition or, indeed, the generation of any recognizable characteristic features. It is evident from these photographs that the product adheres strongly, and coherently, to the reactant across the interface, and post-reaction crystal cleavage propagates across the discontinuity without deviation.

A part of the volume disparity between that of the original reactant and the smaller occupancy by the dehydrated products was represented by the intranuclear crack system, described previously [1]. These channels afford escape routes for the volatile reaction product and the following additional observations may be made concerning their textures. Cracks extended to the reaction interface and the leading face of these advancing extremities were approximately flat. The surfaces of these intranuclear channels were not strictly smooth or planar but included aligned small-angle cracks (slip-surfaces?) spaced irregularly (Fig. 3), but usually these did not develop as individual cracks.

Similar experiments were made using $KAl(SO_4)_2 \cdot 12H_2O$, but observations were less meaningful. The intranuclear channels of nuclei in this reactant were narrower so that replicas were permeated by holes and consequently collapsed because the structures were mechanically weaker. There was evidence that the intranuclear crack structures within this salt were similar to those described for chrome alum but the larger number of smaller channels made acceptable replication impossible by the present technique. From the observations made, however, it seems probable that both compounds behave similarly.

Discussion

Examination of the replicated intranuclear crack structure showed that these roughened but close to parallel-walled channels were ca. 0.3 μm wide. During growth of the approximately hemispherical nuclei such cracks diverged outward from a central focus so that the diameters of these often hexagonal-section blocks of product increased as the interface advanced. However, at a limiting diameter of around 50 μm this dimension could increase no further and cracks bifurcated, thus generating a new coherent assemblage of product. This maintained an effective maximum distance from the crack to the furthest point of the interface zone, located at the centre of each coherent contact area. No tributary system of pores providing channels for water transport along or away from the interface could be discerned. Since the product texture was unresolved, it must be assumed that these coherent product assemblages were porous to water movement, at least initially and in the vicinity of the interface. Previous calculations concerned with the ease of water escape through internuclear channels [1] indicated that perhaps half of the saturated water vapour pressure was maintained at the innermost extremities of the crack system. The present work shows that the paths connecting the interface to escape channels are even narrower, below the limits of replication (< 0.1 μm) and may similarly be expected to retain a significant effective pressure of water vapour. This pore structure may have contributed to the roughened appearance of the replica, but the residual product, from surface area measurements [1], did not contain a significant amount of zeolite material. These observations, therefore, are entirely consistent with the previous mechanistic conclusion that water elimination at the reaction interface is accompanied by product recrystallization in a maintained atmosphere of water vapour somewhat below saturation.

The present demonstration that crack development does not propagate into the reactant beyond the interface represents a difference from the mechanism described previously (illustrated by fig 20 of ref. 1). We found no evidence that the reactant fragmented in advance of the interface and the main intranuclear channels terminated in approximately flat surfaces at the plane of reactant–product contact. Clearly recrystallization at the interface must induce local strain but it is now clear that this is restricted to the immediate vicinity of the site of chemical change and less extensive than was concluded previously.

The present evidence of strong coherent interfacial contact between reactant and product contrasts with behaviour observed under specialized conditions when growth dehydration nuclei are exposed to ammonia [7]. Ammonia evidently displaces water in unreacted salt and this can, in suitable circumstances, result in separation of phases at the interface, as shown in fig. 3 of ref. 7. Again this is consistent with the occurrence of the water release steps within a well-defined, limited reaction zone.

ALUM DEHYDRATION IN CONCENTRATED SULPHURIC ACID

The important feature of the dehydration mechanism proposed previously [1], and further considered above, was that the nucleus structure provided an environment within which water promoted residual product recrystallization. It follows, therefore, that contact of the alum surface with a liquid which was both a dehydrating agent and also a solvent for the reactant would change the behaviour. Under these conditions it would be expected that the induction period to nucleus generation would be eliminated and the reaction interface would be rapidly initiated, comprehensively and immediately across the entire reactant surface. Sulphuric acid possesses the appropriate properties and indeed exhibited the behaviour anticipated.

Experimental

The concentrated sulphuric acid used in each experiment was presaturated with the appropriate alum. Large, perfect single crystals were investigated and immediately after immersion in the dehydrating medium were examined by an optical microscope. Retention of acid within the product layer, and consequent continuation of chemical change, precluded the use of deferred observations, as, for example, in the scanning electron microscope. Observations were of two types. In one series of experiments freshly cleaved faces were observed microscopically immediately after drops of acid had been placed on them. In the alternative series the crystal was placed in excess acid for a known time before being withdrawn for examination. As much acid as possible was washed away using acetone. The crystal was then cleaved and sections across reacted zones observed microscopically.

RESULTS

$KAl(SO_4)_2 \cdot 12H_2O$

As soon as the reactant $KAl(SO_4)_2 \cdot 12H_2O$ face was covered with alum-saturated sulphuric acid, the entire surface so immersed underwent marked retexturing to form a recrystallized boundary layer. Such onset of reaction was more extensive and more rapid than the reaction in vacuum [1] at the same temperature. Cleaved sections of crystals that had been immersed in excess acid possessed a coherent outer product layer and an interface which advanced inwards from the original crystal surface. Continuation of reaction during observation and the migration of acid across newly exposed faces made it difficult to identify and to locate precisely the reactant–product boundary.

$KCr(SO_4)_2 \cdot 12H_2O$

This reactant apparently behaved identically to $KAl(SO_4)_2 \cdot 12H_2O$. Observations were, however, slightly more difficult since the dissolved chromium rendered the liquid phase less transparent.

Discussion

The occurrence of rapid initiation of reaction across the total surface covered by concentrated sulphuric acid, at 285 K, contrasts with the slower, linear rate of production of discrete nuclei characteristic [1] of the reaction in vacuum. Under both conditions alum is dehydrated. However, when the dehydration medium is also a solvent, the liquid phase provides the surface mobility necessary for reaction to be initiated comprehensively and immediately across all crystal faces and to be propagated below the original surface. This contrasts with the generation of a small number of individual and separate nuclei that is observed during reactions in vacuum where propagation is deferred until specialized nucleus textures are established, capable of promoting the advance of the active zone of chemical change. Thus, the observed differences in behaviour are entirely consistent with the view [1] that the essential step in product retexturing is promoted by the presence of a fluid solvent.

It should also be remembered that the reaction products may be different in the acid since acid salts may be formed and the lower hydrates could be different. Investigation of the product texture here by replication procedures [6] was impracticable because sulphuric acid was retained in the fine pores. The product was adherent and the slow rate of later interface advance, compared with vacuum dehydration, is ascribed to diffusion control for removal of water across a thick layer of product.

CONCLUSIONS

One principal objective of the present work was to emphasize the value of including microscopic observational evidence in discussions concerning the mechanisms of chemical changes proceeding in crystalline reactants. Such observational evidence is complementary to kinetic data but is not always provided in confirmation of published conclusions concerning the development of interface geometry based on the interpretation of rate measurements. Here we have drawn attention to the significance of textural information in understanding the chemistry of this reaction. We have also carefully selected conditions to maximize benefit from our application of microscopic methods to the specific system of interest.

The observation that pores within the zone of active water elimination, during vacuum dehydrations, are small (considered to be < 0.1 μm diameter, Fig. 2) is evidence that after reaction there was temporarily maintained a close contact between both products, volatile and residual. It has already been shown that exposure to water facilitates the reorganization of dehydrated alum ("orange peel" texture [1]). Such promotion of structural change here evidently results in loss of interfacial strain and this is interpreted as evidence of product recrystallization. On cleavage, the nucleus boundary is traversed by the propagating crack without inflicting local damage at the reactant–product contact. Also, under normal growth conditions, stress cracks are not developed in advance of the progressing reaction zone. It must be concluded that the lattice of the intranuclear product material retains structural contact with the reactant during and following dehydration. The local availability of high concentrations of water within narrow pores is believed to enhance component mobilities of the residual products, bearing formal similarities to crystal growth. The continuation, without deviation, of cleavage crack surfaces across the residual products may be evidence of a topotactic relation between the reactant alum crystal and its, as yet incompletely characterized [1], solid products.

The significant observation from the microscopic examinations of dehydrations in sulphuric acid is the instantaneous appearance and growth of solid product across the entire crystal surfaces. This contrasts with the remarkably rare development of nuclei in vacuum, where the number of such nuclei is miniscule compared with the total number of surface sites. This difference in behaviour is explained by the enhanced mobilities of reactant constituents in the fluid medium, immediately available on crystal immersion, which is in contrast with the reaction in vacuum where product formation can be developed at only a very few very highly specialized crystal surface sites. We regard the fluid (reactant) medium as providing a similar mobility of lattice components to that inferred as being active within the advancing interface of vacuum-grown nuclei.

We conclude that the effective barrier, or rate-controlling parameter, in alum dehydration is product recrystallization. This essential step is promoted by the presence of fluid (behaving as a solvent) either as product water temporarily retained at the active interface or as a dehydrating solvent medium such as sulphuric acid.

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