Mosaic Structures in Uncatalyzed BZ Oscillators

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It has been shown that mosaic structures formed in \( \text{BrO}_3^- + \text{phenol} + \text{H}_2\text{SO}_4 \) uncatalysed oscillatory reaction system are simply agglomeration of fine grains of solid solution of tribromophenol and \( p \)-benzoquinone.

In uncatalyzed BZ oscillatory reaction system, specific type of structures called mosaic structures have been observed, e.g. in phenol-bromate-\( \text{H}_2\text{SO}_4 \) (ref. 1) and ferroin-bromate-\( \text{H}_2\text{SO}_4 \) (ref. 2) systems. Mosaic structures with sharp boundaries appear in a layer thickness of more than 1 mm some minutes after spreading the mixture in a petri dish. The boundaries become more and more diffuse with time and finally either the solution turns homogeneous or a precipitate separates. However, the nature and mechanism of development of such structures are obscure. The present investigation has been undertaken with a view to understanding the nature and mechanism of formation of such structures in uncatalyzed BZ oscillators and for our purpose we have chosen the phenol-bromate-\( \text{H}_2\text{SO}_4 \) system.

Materials and Methods

Phenol (BDH), \( \text{KBrO}_3 \) (Thamos Baker), \( p \)-benzoquinone (BDH), \( \text{H}_2\text{SO}_4 \) (E Merck), \( n \)-butanol (CDH), ethanol (E Merck) and (\( \text{NH}_4 \))\(_2\) \( \text{CO}_3 \) (BDH) were used as such.

Mosaic structures

One dimensional study of these structures was made. The reactants \( \text{H}_2\text{SO}_4 \) (2.0\( M \)), \( \text{KBrO}_3 \) (0.05\( M \)) and phenol (0.026\( M \)) were taken in a tube (length = 30 cm; int. diam = 5 mm). On mixing phenol and bromate, a clear solution was obtained, which became dark yellow after 5 min while precipitation started after 35 min. Mosaic structures were formed on the walls of the tube after 3 hr.

Results

Chemical nature of mosaic structures

The solution was decanted and the mosaic precipitate scrapped and dried, m.p. 104.8-110.0°. Since the melting occurred in a temperature range, the structure was thought to be a mixture. TLC studies using \( n \)-butanol-ethanol-3\( N \)(\( \text{NH}_4 \))\(_2\) \( \text{CO}_3 \) buffer (40:11:19, v/v) as the solvent and the iodine chamber as the spraying agent indicated only two spots, one of which was due to \( p \)-benzoquinone (\( p \)-BQ) and the other due to tribromophenol (TBP). In order to confirm the presence of these two products, the constituents of the mosaic precipitate were separated by sublimation and the sublimate collected. The m.p. of the sublimate (115.9°) corresponded to that of \( p \)-BQ. The residue also had a sharp m.p. (94.2°) which corresponded to that of TBP.

Composition of mosaic structure

Since the range of temperature in which the melting of mosaic structure occurred was between the melting points of \( p \)-BQ and TBP, it was suspected that this mosaic structure might be a solid solution of the two components particularly because these have similar structures. In order to test this point phase-diagram of \( p \)-benzoquinone + tribromophenol was investigated by the thaw-melt method as described by Rastogi and Varma. For this purpose, TBP was prepared by the direct bromination of phenol. The phase-diagram was plotted and is shown in Fig. 1, where melting and thaw points have been plotted against composition. It does show that the two components form a solid solution.
From the phase-diagram, the molar ratio of the two components, viz $p$-BQ and TBP in the mosaic structure was found to be 2:3.

**Microphotographic studies**

In order to study the nature of mosaic structure, microphotographs of crystals of $p$BQ and TBP were taken along with those of a sample of mosaic structure and the solid solution of corresponding composition (Plate I). Microphotograph of the mosaic structure (Fig. C) and the solid solution (Fig. D) show striking similarity indicating that the two are identical.

**X-ray diffraction studies on mosaic structures**

After the formation of mosaic structure on the walls of the test tube, the reactant mixture was decanted and the mosaic structure scratched out. X-ray diffraction pattern of a specimen of this material was taken with the help of CuK$\alpha$ radiation monochromatized using curved crystal graphite monochromator. The diffractogram showed that the material had an amorphous structure whereas the same for $p$BQ and TBP showed that the two species were crystalline in nature.

**Mechanism of precipitation**

Mosaic structure are not formed in a tube which has been freshly cleaned by steaming. However, if the steamed tube is exposed to atmosphere for several hours, mosaic structures are observed to have been formed.

**Discussion**

The above results show that mosaic structures in phenol-bromate system are formed due to precipitation of a solid solution of $p$BQ and TBP in the molar ratio 2:3. These are not examples of symmetry-breaking instability in the usual sense. In a way, these appear to belong to the case of patterned precipitation discussed by Fennin et al. X-ray diffraction pattern of
the precipitated material shows that it is amorphous in nature. This is not surprising since in the process of formation of mosaic structure \( pBQ \) and TBP crystal nuclei are formed one after the other. These grow to a certain size after which the nucleus of the other species is formed. This periodic nucleation gives rise to a structure which behaves like a solid solution containing very fine grains. That is why the material is found to be amorphous by X-rays.

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References