Notes

Kinetics of Solid State Reaction between Copper & Bromine Vapours

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Kinetics of the reaction between copper (plates) and bromine (vapour) has been studied in the temperature range 30-50°. The kinetic data follow a parabolic equation. The reaction product has been identified as γ-CuBr by chemical analysis and X-ray diffraction studies.

In the tarnishing reactions when the product layer is coherent and thick (above 1000 Å) generally a parabolic equation is found to fit the kinetic data[1,2]. This is attributed to the diffusion of reacting species under a concentration gradient. In some cases, however, deviations have also been found, which are due to periodic cracking of the product film[3,4].

Studies of the reaction between silver metal and bromine (vapour) show that the kinetic data follow a parabolic equation where quite thick product film is formed[5]. In the present note kinetics of the reaction between copper (plates) and bromine (vapour) have been studied at various temperatures. The product was analysed by chemical and X-ray diffraction analyses.

Copper (plates) of equal size (each 4·00 cm²) were cut from copper metal foil (AR), a hole was drilled in each plate near the one end to facilitate suspension and rubbed with emery powder by keeping the plates dipped in benzene (AR) so as to absorb any heat generated due to abrading and ultimately to prevent any cold work on the metal plates. Closed reaction vessels made of pyrex glass and provided with standard joints and platinum wire hangers (provided at the top of the vessel to suspend the metal plates inside the vessel) were taken, each filled with 10 g of bromine (liquid) and placed in a thermostat kept at constant temperature (±0·1°). The copper plates were taken out of benzene, and weighed. The plates were suspended in the vessels so that the plates while not in contact with liquid bromine are in an atmosphere of bromine vapour at saturated pressure at the temperature of the experiment. Each plate was removed after certain intervals of time and weighed. The increase in weight gave the weight of bromine reacted which is proportional to the thickness of the product layer. The reaction product analysed for CuBr. The identity of the product as γ-CuBr was further confirmed by X-ray diffraction studies of the product using CuK$_\alpha$ radiation (Table 1).

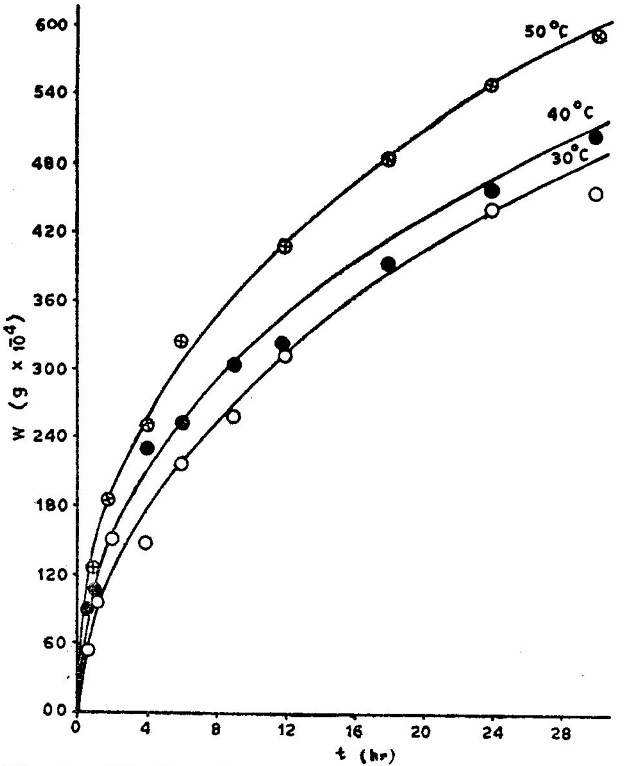

Fig. 1 — Kinetics of bromination of copper (plates) by bromine (vapour) at different temperatures

Plots of *w*, weight of bromine reacted against time, *t*, are given in Fig. 1. The following equation is found to fit the kinetic data of the reaction

$$w^2 = Kt + C \qquad \ldots(1)$$

where K and C are constants. The applicability of the equation is shown in Fig. 2 where w^2 is plotted against time t. Parameters of the equation are given in Table 2.

Table 1 — X-ray Diffraction Data of the Reaction Product and the Known Data of γ-CuBr

d (Å)		*d* (Å)	
Expl.	Known	Expl.	Known
3·218	3·285	0·962	0·962
1·956	2·012	0·949	0·948
1·695	1·716	0·899	0·899
1·406	1·423	0·868	0·868
1·295	1·306	0·820	0·821
1·153	1·162	0·797	0·796
1·084	1·095	0·790	0·789
1·005	1·006		

Table 2 — Parameters of Eq. (1) for the Reaction Between Copper and Bromine (Vapour) at Different Temperatures

Temp. °C	$K \times 10^5$ (g²/hr)	$C \times 10^5$ (g²)
30	6·92	4·50
40	8·09	6·05
50	12·30	7·00

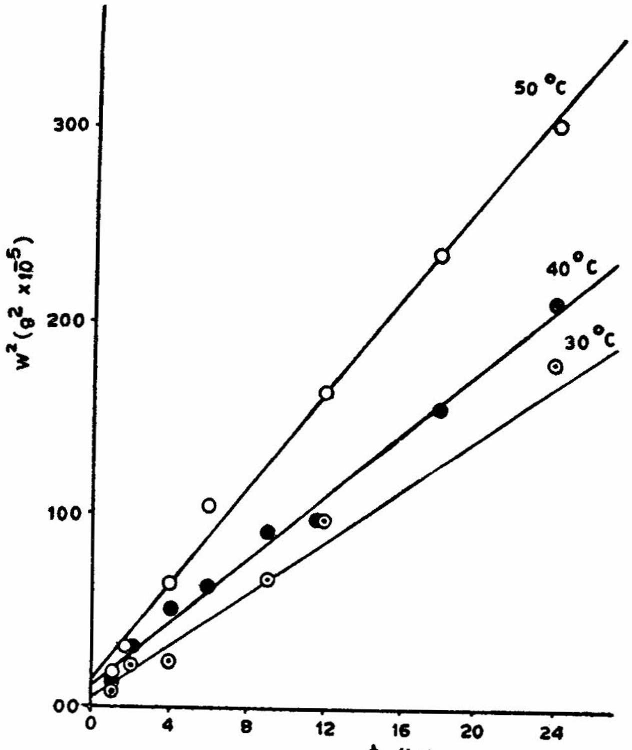

Fig. 2 — Plot of w^2 versus t at different temperatures for reaction between copper (plates) and bromine (vapour)

The average maximum thickness of the product film calculated from mass, theoretical density of the product Υ-CuBr and the dimensions of the metal plate comes out to be 0·0026 cm. The reaction is a diffusion-controlled process. The product film which is coherent and protective controls the diffusion process.

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IR Spectrum of Benzoic Acid-Naphthalene Eutectic

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In naphthalene-benzoic acid system, certain C-H in-plane and out-of-plane frequencies of naphthalene and also C$\overset{...}{-}$C bond stretching frequency of aromatic ring in benzoic acid are restricted, when the eutectic is formed. There, thus appears to be a definite orientation of naphthalene and benzoic acid with respect to each other in the eutectic mixture.

RASTOGI and Bassi[1] have made a comprehensive study of the growth characteristics and thermochemistry of eutectics formed between organic compounds. The growth kinetics and structure of the liquid eutectics have also been studied[2]. Savchenko[3] considers a eutectic to be formed by some sort of loose molecular or atomic interaction which does not involve the formation of a chemical compound, i.e. the formation of a eutectic leads to some merging of electron energy levels, but this is not accompanied by the formation of inter-atomic electrostatic bonds. Investigations have revealed that the mechanism of eutectic crystallization is quite complex. X-ray examination shows that a binary eutectic is a mixture of two kinds of crystals, favourably oriented with respect to each other[4]. Many eutectic composites have been reported by Hogan[5] to show a unique crystallographic orientations relationship both between constituent phases and their mating planes. After nucleation, many eutectics grow more or less perpendicular to the solidification front. Perfect lamellar grains have been found in lamellar Sn-Cd eutectic by Gruzleski and Winegard[6]. But in a number of systems, the eutectic grains do not exhibit a fixed crystal orientation with respect to external lines of reference[7]. IR reflectivity measurements of LiF-NaF lamellar eutectic by Proux and Racek[8] revealed that the difference in peaks may be due to interfacial phonones.

In view of these conflicting ideas, it was thought necessary to havs some information regarding the character of eutectic from IR spectroscopy.

Naphthalene (USSR) was purified by sublimation (m.p. 80·3°) and benzoic acid (m.p. 121·2°, BDH, Analar) was used as such. Accurately weighed naphthalene and benzoic acid were taken in a tube, which was then sealed to avoid evaporation. The material in the tube was melted and then suddenly chilled in ice cold water 4-5 times. Tube was broken and the solid mixture thus formed was taken in agate crucible and powdered.

The phase diagram of naphthalene-benzoic acid system was determined by thaw melt method. Eutectic was found to be formed at 0·6670 mole-fraction of naphthalene with its melting point at 69·10° (ref. 9).

IR spectra (KBr) of the composite cannot be exactly superimposed on the spectra of constituent materials, naphthalene and benzoic acid. In the region 770 to 1030 cm^{-1}, a general decrease in intensities of the bands of eutectic in comparison with the parent compounds has been observed, e.g. the bands at 770 (s), 955 (m) and 1005 (m) cm^{-1} were reduced in intensity and appeared at 775 (m), 950 (sh) and 1005 (sh) cm^{-1} in the eutectic. Similarly bands at 800 (m) and 925 (m) cm^{-1} of benzoic acid appeared at 800 (sh) and 930 (m) cm^{-1} in the eutectic. Moreover, 978 (w) cm^{-1} band of naphthalene, which is due to out-of-plane homocyclic C—H deformation[10] was altogether missing in the eutectic. In-plane bending of C-H bond band 1020 (m) cm^{-1} of benzoic acid was diminished in intensity and shifted to 1030 (w) cm^{-1} in the eutectic.

In-plane bending bands 1237 (w) and 1265 (m) cm^{-1}, which are due to homocyclic C-H bond in naphthalene, were totally missing from the spectrum