JOURNAL OF SOLID STATE CHEMISTRY **18**, 57-62 (1976)

Kinetics and Mechanism of Reaction between Mercuric Bromoiodide and Silver Iodide in Solid State

M. AIJAZ BEG AND SAIFUDDIN MUMTAZ ANSARI

Department of Chemistry, Aligarh Muslim University, Aligarh, 202001 India

Received October 23, 1975; in revised form January 5, 1976

Kinetics and the mechanism of the reaction between mercuric bromoidide and silver iodide in solid state were studied by X-ray, chemical analysis, thermal, and electrical conductivity measurements. HgBrI and AgI react in the molar ratio 1:3 to give AgBr and Ag_2HgI_4. The data for the lateral diffusion fit best in the equation $X_t^n = kt$. It has been established that the reaction proceeds via a vapor phase diffusion-controlled mechanism through counterdiffusion of Ag^+ and Hg^{2+}. There also seems to be some evidence for the formation of solid solutions between reactant and product phases.

Introduction

Due to the complexity of the problem, the study of solid-state reactions is limited to cases where only one product is formed (addition type) or where the reaction proceeds with the evolution of a gas. In the former case, the thickness of the product layer reads the kinetics and in the latter the amount of gas evolved is used to calculate the fraction of reaction completed. The study of a solid-state reaction where more than one product is formed without evolution of a gas is a real problem and references to such reactions are thus rare.

The existence of mixed halides of mercury (*1*) and the formation of Ag_2HgI_4 from AgI and HgI_2 (*2*) tempted us to investigate the reaction of AgI with other mercury halides, with the hope of getting mixed halide complexes. AgI gives mixed halide complexes with $HgCl_2$ and an even more novel reaction with $HgBr_2$. These results will be described in communications to follow. The present paper describes the kinetics and mechanism of the solid-state reaction between HgBrI and AgI, where Ag_2HgI_4 and AgBr are the products. The reaction is vapor phase diffusion controlled and has been explained in terms of counterdiffusion of Ag^+ and Hg^{2+}. Formation of solid solution in the following systems has been noted: AgBr—AgI, AgBr–Ag_2HgI_4, and HgBrI—Ag_2HgI_4.

Experimental Section

Materials. HgBrI was prepared (*3*) by Oppenheim's method. Equimolar solutions of $HgBr_2$ and HgI_2 in acetone were mixed. On standing, crystals of HgBrI were obtained. X-ray pattern and melting point showed it to be single-phase HgBrI. Its *d* values compared well with those of orthorhombic HgBrI prepared by Rastogi and Dubey (*4*). AgI was prepared (*5*) by mixing, in the dark, hot aqueous solutions of $AgNO_3$ and KI. The X-ray pattern showed it to be of gamma-form. Ag_2HgI_4 was prepared by mixing equivalent amounts of solid HgI_2 and AgI (each above 300-mesh size). The X-ray analysis showed it to be single-phase β-Ag_2HgI_4. All its *d* values are the same as reported in ASTM Card 3-0949. But I/I_o values are different from the reported ones. The intensity ratios reported in ASTM Card were obtained visually whereas ours were recorded by diffractometer. (The values reported in ASTM have not yet been internationally accepted.)

Printed in Great Britain

Rate measurements. The kinetics of the reaction in the solid state were studied by placing HgBrI over AgI (each above 300 mesh) in a vertical Pyrex glass tube of 0.5 cm internal diameter. An approx. 10-cm long tube of uniform bore was chosen. One end was sealed by fusion and a fixed weight of AgI was introduced into the tube through its open end. The capillary was then held vertical and the AgI powder was gently pressed just by placing a 20-cm long glass rod of about 0.5 cm external diameter into the reaction tube. The reaction tube containing AgI and a weighed amount of HgBrI on a tissue paper were kept in an air oven thermostatically controlled to ±0.5°C. After about 20 min. HgBrI was placed over the AgI layer in the reaction tube. To press the HgBrI powder, the same glass rod was placed gently over HgBrI and then removed immediately after. The placement of the glass rod in the reaction tube and its removal thereafter was manipulated from outside through a hole in the oven. As a change in the reaction kinetics in powdered solids is likely to occur due to pressure changes, mainly owing to its action on elementary processes such as sintering, recrystallization and diffusion, etc., the same quantity of the reactants was always used. The progress of the reaction was followed by measuring the total thickness of the product layer formed at the interface by a traveling microscope having a calibrated scale in its eyepiece. Each experiment was run in triplicate and the average values of different sets whose average is reported (Table I) was quite satisfactory.

TABLE I

Dependence of Parameters of Equation $X_t^n = kt$ on Temperature for AgI–HgBrI Reaction

Temperature (°C ± 0.5)	k (cm hr)	n
68	1.334×10^{-6}	2.5
78	4.217×10^{-6}	
88	8.414×10^{-6}	
99	21.130×10^{-6}	
111	47.320×10^{-6}	

Soon after the placement of the HgBrI powder over the AgI in the tube, a red boundary formed at the interface and this grew with time on the AgI side. After some time a yellow product started to develop between the HgBrI and the red product and a gap developed between the HgBrI and the yellow product. On cooling to room temperature the red product turned yellow. Ag_2HgI_4 is red above 50.7°C and yellow below 50.7°C (*6*). The kinetics were likewise studied at different temperatures.

Later, experiments were run with an air gap between AgI and HgBrI at the start itself. The reaction proceeded smoothly to give the same products.

Analysis of the product layers. A reaction tube having two distinct layers of the product was broken and the two product layers were collected separately. The X-ray and chemical analyses of the two materials showed them to be single-phase AgBr and Ag_2HgI_4.

X-ray studies. Powdered (above 300 mesh) AgI and HgBrI were mixed thoroughly in a mortar in different molar ratios. One part of each mixture was heated for about 24 hr in an air oven, maintained at 90 ± 0.5°C. The reaction mixtures maintained at room temperature (about 30°C) and at a higher temperature (90°C) were analyzed by a "Norelco" Geiger Counter X-ray diffractometer (pw 1010 Philips) by Cu*Kα* radiation applying 32 kV at 12 mA with a Ni-filter. X-ray photographs were obtained using a Debye–Scherrer Camera (diam, 11.46 cm).

The compounds present were identified by calculating the *d* values and the intensities of

TABLE II

Compounds Present in Different Molar Ratio Mixtures of HgBrI and AgI

Mixture	Molar ratios of HgBrI:AgI	Compounds identified in mixtures maintained at room temperature and at 90°C
a	1:4	AgI, Ag_2HgI_4, AgBr
b	1:3	Ag_2HgI_4, AgBr
c	1:2	HgBrI, Ag_2HgI_4, AgBr

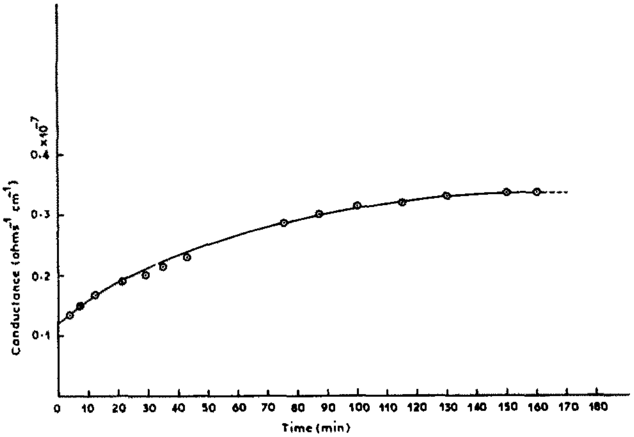

FIG. 1. Variation of conductance with time for the reaction between HgBrI and AgI (1:3 molar) at 30°C. Applied voltage, 0.2 V; frequency, 2×10^3 Hz.

the lines and comparing them with the standard values of the expected compounds. The compounds obtained in different mixtures are given in Table II.

Thermal studies. A weighed amount (17.609 g) of AgI was taken in a small Dewer flask. A $\frac{1}{3}$ M equivalent of HgBrI (10.185 g) was weighed on a tissue paper and poured into the Dewer flask colorimeter. The mixture was stirred thoroughly and the rise in temperature was noted.

Conductivity measurements. HgBrI and AgI (molar ratio, 1:3) were thoroughly mixed with each other. This mixture was immediately poured into a die and pressed into a disk. This disk was then fixed between platinum electrodes (applied voltage 0.2 V and frequency 2×10^3 Hz) and the change in conductance with time at room temperature was determined (Fig. 1).

Discussion

For a comprehensive understanding of the process the following aspects are important to consider: (i) mechanism of chemical interaction, (ii) miscibility of reactant and product phases, and (iii) mechanism of lateral diffusion when the reactants were kept in contact and when they were separated by an air gap.

Mechanism of chemical interaction. The X-ray diffraction measurements (Table II) showed that in the solid state HgBrI and AgI react in the molar ratio 1:3.

$$\mathrm{HgBrI} + 3\mathrm{AgI} \rightarrow \mathrm{Ag_2HgI_4} + \mathrm{AgBr}. \quad (1)$$

It was observed that as soon as the reactants were mixed (at room temperature) a red color formed which gradually changed to yellow. The red color is probably the indication of the transitory formation of $\mathrm{HgI_2}$, which immediately reacted with AgI to give the addition product $\mathrm{Ag_2HgI_4}$:

$$\mathrm{HgBrI} + \mathrm{AgI} \rightarrow \mathrm{HgI_2} + \mathrm{AgBr}, \quad (1a)$$

$$\begin{array}{l} \mathrm{HgI_2} + 2\mathrm{AgI} \rightarrow \mathrm{Ag_2HgI_4} \\ \hline \mathrm{HgBrI} + 3\mathrm{AgI} \rightarrow \mathrm{Ag_2HgI_4} + \mathrm{AgBr} \end{array} . \quad (1b)$$

Thermal and conductance measurements show only one inflection and thus offer no evidence for a two-step reaction. The X-ray patterns of stoichiometric as well as nonstoichiometric mixtures had no line for $\mathrm{HgI_2}$. This is understandable if step (1b) is much faster than step (1a). Although, exchange reactions (*7*) are usually fast, step (1a) will be slow because the ionic sizes of $\mathrm{Ag^+}$ and $\mathrm{Hg^{2+}}$ are very close to each other. Step (1b) is known to be fast (*2*) even at low temperatures. This explains why thermal and conductance measurements fail to provide evidence for step (1a), if it occurs at all.

Miscibility of reactant and product phases. During the X-ray analysis of products obtained in different molar mixtures of reactants

(Table II), it was noted that Ag_2HgI_4 is soluble in AgBr and HgBrI, whereas both AgBr and HgBrI seemed to be only slightly soluble in Ag_2HgI_4. AgBr and AgI, to some extent, seemed miscible with each other. Miscibility has been checked by measuring the deviation in *d* values of the components with their respective standard *d* values. The miscibility of AgI and AgBr is understandable in terms of the cubic structure of either. AgBr dissolves in Ag_2HgI_4 because AgBr has vacant cationic sites in the tetrahedral structure of Ag_2HgI_4 due to the exchange equilibrium between Ag^+ and Hg^{2+}. The miscibility of HgBrI and Ag_2HgI_4 was further checked by heating a mixture of Ag_2HgI_4 and HgBrI in 1:2 molar ratio, for about 24 hr at 90°C. The X-ray pattern of the mixture revealed that the *d* values of HgBrI had increased whereas those of Ag_2HgI_4 had slightly decreased. HgI_2 and $HgBr_2$, when fused in different molar ratios, give a series of mixed crystals (*8*) where HgBrI is intermediary. In HgI_2, in solid state, the equilibrium always exists (*6*). $2HgI_2 \rightleftharpoons Hg\ [HgI_2 \cdot 2I]$. The presence of $[HgI_2 \cdot 2I]^{2-}$ (from Ag_2HgI_4) in the vicinity of HgBrI would make HgBrI tend toward a member of mixed crystals of the series and consequently increase the *d* values of HgBrI.

Mechanism of lateral diffusion. In the lateral diffusion experiments, the red boundary, formed at the interface soon after placement of the reactants in the tube, grew only on the AgI side. This shows that it is only the HgBrI that moves towards the AgI side through the product. The initiation of reaction by migration of HgBrI into AgI will maintain the condition of excess of AgI in the reaction zone and will thus account for the formation of red product (α-Ag_2HgI_4). The lateral diffusion reaction proceeded well even when the reactants were placed about 0.25 cm apart. This shows that solid HgBrI reacts here via the gaseous state.

At the reaction zone, HgBrI vapor surrounds each AgI grain and reacts through counter diffusion of Ag^+ and Hg^{2+} with the simultaneous separation of AgBr and Ag_2HgI_4. On the addition of divalent metal halides in silver halides (*9*, *10*), the divalent cations go to occupy the cationic positions creating an equal number of cationic vacancies due to its double charge. Ag^+ ions move by jumping from normal positions to adjacent cationic vacancies and the same is true for the divalent cations. This explains the diffusion of Hg^{2+} and of Ag^+ through AgBr layer in the present case. The transport of ions through the product layers, around AgI grain, is shown in Fig. 2 and the reactions occurring at phase boundaries are presented below.

Reaction at interface 1 (Fig. 2):

$$HgBrI + 2Ag^+ \rightarrow AgBr + AgI + Hg^{2+}.$$

Reaction at interface 3 (Fig. 2):

$$\begin{array}{l} 4AgI + Hg^{2+} \rightarrow Ag_2HgI_4 + 2Ag^+ \\ \hline HgBrI + 3AgI \rightarrow Ag_2HgI_4 + AgBr \end{array}.$$

The AgI formed at interface 1 is immediately consumed. These two products then separate out to give two different layers, yellow and red (above 50.7°C), in the reaction tube. The analyses of the product layers support the above scheme.

The various types of diffusion involved in solid-state reactions are bulk diffusion, surface diffusion, lattice diffusion, grain boundary migration, and vapor-phase diffusion. The reaction between HgBrI and AgI is diffusion controlled via vapor phase. It is clear from Fig. 3 that the rate of reaction decreases with increase in time and therefore also with an increase in X_i, the thickness of the product. The initial rapid increase in the thickness of the product is due to the fact that the chemical reaction is much faster than the diffusion process. As the product thickness increases, reactions take more time to diffuse through and the reaction rate thus falls continuously.

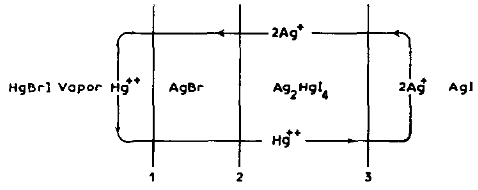

FIG. 2. Representation of counter diffusion of Ag^+ and Hg^{2+} through product phases for the reaction between HgBrI and AgI.

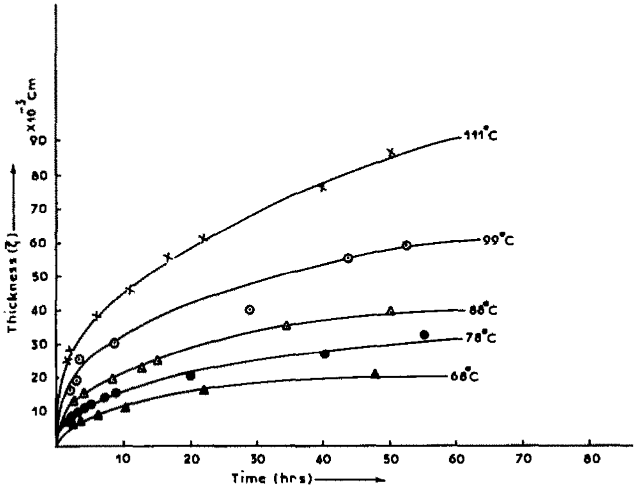

FIG. 3. Kinetic data for the reaction between HgBrI and AgI at various temperatures.

For lateral diffusion, the kinetic data fit best (Fig. 4) in the equation

$$X_i^n = kt,$$

where X_i is the product thickness at time t, and k and n are constants. k is related to the diffusion constant and follows the Arrhenius equation (Fig. 5). The activation energy, measured from a log k versus inverse temperature plot, is 23.26 kcal.

The results described above were obtained at a constant pressure. It was, however, noted that the rate of this reaction was highly dependent upon the pressure with which the reactant powders were pressed in the reaction tube.

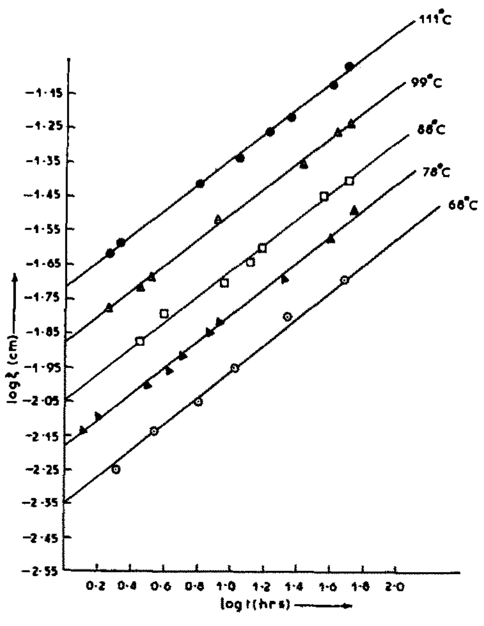

FIG. 4. Kinetic data for the lateral diffusion and the test of equation $X_i^n = kt$ for the reaction between HgBrI and AgI.

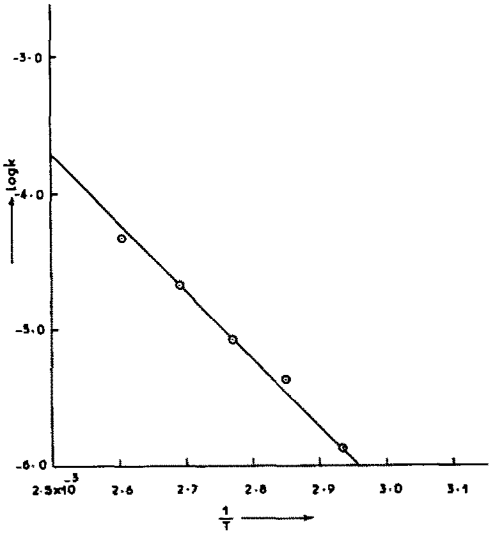

FIG. 5. Dependence of k on temperature for the reaction between HgBrI and AgI.

Acknowledgments

We are grateful to Dr. B. Rama Rao and Mir Raza Husain, Regional Research Laboratory, Hyderabad for generous help in X-ray measurements and to Prof. Wasiur Rahman for providing necessary facilities for work. One of us (S. M. Ansari) is also thankful to the Indian Council of Scientific and Industrial Research for fellowship.

References

1. R. P. Rastogi and B. L. Dubey, *J. Amer. Chem. Soc.* **89**, 200 (1967).
2. R. Koch and C. Wagner, *Z. Physik. Chem.* **B34**, 317 (1936).
3. A. Oppenheim, *Ber.* **2**, 571 (1869).
4. R. P. Rastogi and B. L. Dubey, *J. Inorg. Nucl. Chem.* **31**, 1530 (1969).
5. J. N. Bradley and P. D. Greene, *Trans. Faraday Soc.* **63**, 1023 (1967).
6. D. Grdenic, *Quart. Rev.* **19**, 303 (1965).
7. H. L. Link and L. J. Wood, *J. Amer. Chem. Soc.* **62**, 766 (1940).
8. W. Reinders, *Z. Physik. Chem.* **32**, 503 (1900).
9. A. L. G. Rees, "Chemistry of the Defect Solid State," p. 11, Wiley, New York (1954).
10. T. J. Gray, "The Defect Solid State", p. 91, Interscience, New York (1957).