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

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Kinetics and mechanism of the reaction between mercuric bromide and silver iodide were studied in the solid state. It has been established that $HgBr_2$ reacts via the gaseous state and that the reaction proceeds through counter diffusion of Ag^+ and Hg^{2+}. Thermal and conductivity measurements indicate that the reaction is multistep. X-ray and chemical analyses show that $HgBr_2$ and AgI mixed in different molar ratios give rise to different products. The data for the lateral diffusion fitted the equation $X_i^n = kt$, where X_i is the thickness of the product layer at time t, and n and k are constants. Evidence for the formation of solid solutions between reactant and product phases is reported.

Introduction

The authors have recently reported (*1*) that HgBrI and AgI in the solid state give rise to AgBr and Ag_2HgI_4 through counterdiffusion of Ag^+ and Hg^{2+}, as Koch and Wagner (*2*) observed for the HgI_2–AgI reaction.

This paper presents the kinetics and mechanism of the reaction between $HgBr_2$ and AgI in the solid state. It has been observed that at room temperature, an equimolar mixture of $HgBr_2$ and AgI developed an orange-yellow color which, on standing, first turned red and finally yellow. Our results show that the reaction is multistep. Ag_2HgI_4 and HgI_2 were formed as intermediates and HgBrI and AgBr were the end products when the reactants were mixed in equimolar proportions. Mixtures of other molar ratios give rise to other products. Ag_2HgI_4 forms solid solutions with AgBr and HgBrI.

Experimental Section

Materials. $HgBr_2$ and HgI_2 (E. Merck grade) were used without further purification. Ag_2HgI_4, AgI, and HgBrI were prepared as described earlier (*1*).

Rate measurements. The kinetics of the reaction were studied by placing $HgBr_2$ over AgI (both above 300-mesh size) in a thin tube as before (*1*).

Soon after placing the $HgBr_2$ powder over AgI in the tube a red boundary formed at the interface and this grew with time on the AgI side. After some time a greenish yellow product started to develop between $HgBr_2$ and the red product and a gap developed between $HgBr_2$ and the greenish yellow product. On cooling to room temperature (30°C), the red product turned yellow (Ag_2HgI_4 is red above 50.7°C and yellow below 50.7°C) (*3*). To our surprise, in one of the reaction tubes which was examined after several days, AgI had completely disappeared and a third product, which was red in color, had appeared at the end.

It was later discovered that whenever the reaction was performed this way with a proportionately smaller amount of AgI, the red product was always formed. The kinetics were likewise studied at different temperatures.

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TABLE I

COMPOUNDS PRESENT IN $HgBr_2$–AgI REACTION MIXTURES AFTER COMPLETION OF THE REACTION

Mixture	Molar ratios of $HgBr_2$ and AgI	Compounds identified in mixture	
		Maintained at 30°C	Maintained at 90°C
a	1:4	AgBr, Ag_2HgI_4	AgBr, Ag_2HgI_4
b	1:3	AgBr, Ag_2HgI_4, HgI_2	AgBr, Ag_2HgI_4, HgBrI
c	1:2	AgBr, HgI_2	AgBr, Ag_2HgI_4, HgBrI
d	1:1	AgBr, HgBrI	AgBr, HgBrI

Later, lateral diffusion experiments were run, keeping an air gap between AgI and $HgBr_2$ at the start itself. The reaction proceeded smoothly to give the first two products. However, no attempt was made in this case to see the formation of the third red product.

Analysis of the product layers. X-ray and chemical analyses of the three distinct layers of the product showed them to be AgBr, Ag_2HgI_4, and HgI_2.

X-ray,[1] thermal, and conductivity[2] measurements of mixtures having different molar ratios of $HgBr_2$ and AgI were carried out as before (*1*) and the results are reported in Table I and Figs. 1 and 2, respectively.

Results and Discussion

Mechanism of chemical interaction. It is evident from Table I that $HgBr_2$ and AgI react differently in different molar mixtures as well as at different temperatures.

A 1:4 molar mixture of $HgBr_2$ and AgI maintained at room temperature or at 90°C for about 24 hr after mixing showed the presence of only Ag_2HgI_4 and AgBr.

$$HgBr_2 + 4AgI \rightarrow Ag_2HgI_4 + 2AgBr. \quad (1)$$

Thermal (Fig. 1, 1) as well as conductivity measurements (Fig. 2, 1) taken with a 1:4

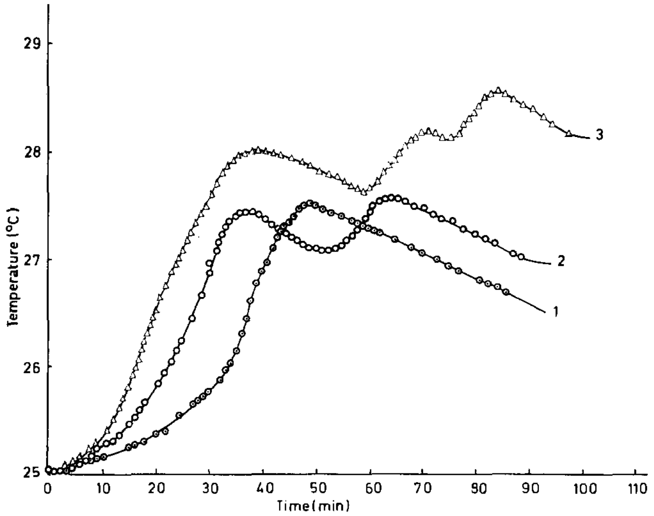

FIG. 1. Temperature rise as a function of time for the reaction between $HgBr_2$ and AgI at molar ratios of: (1) 1:4, (2) 1:2, and (3) 1:1.

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[1] The reaction mixtures maintained at 30 and at 90°C were analyzed using a Norelco geiger counter X-ray diffractometer by Cu$K\alpha$ radiation with an Ni filter, applying 32 kV at 12 mA.

[2] Conductivity measurements were made by a current ratio I.C. bridge.

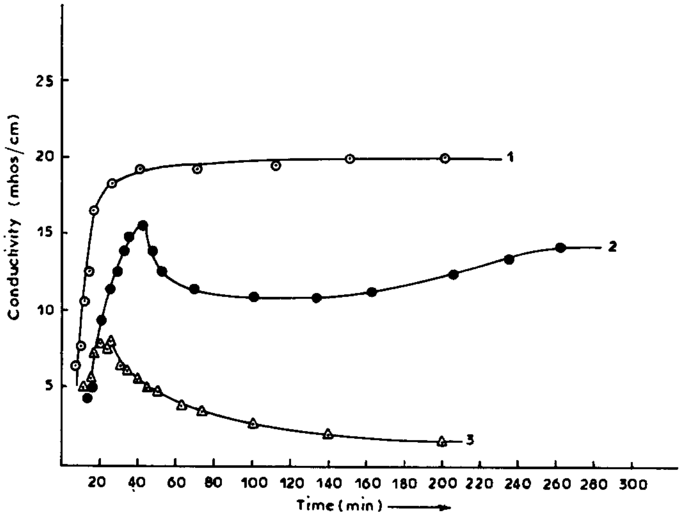

FIG. 2. Conductivity change as a function of time for the reaction between $HgBr_2$ and AgI at 90°C. Molar ratios of $HgBr_2$:AgI are (1) 1:4, (2) 1:2, and (3) 1:1. Applied voltage, 0.2 V (rms); frequency, 2×10^3 Hz.

molar mixture of $HgBr_2$ and AgI give no evidence for the existence of any substep of reaction (1). The steep rise, in either case, shows that reaction (1) is very fast even at room temperature.

It was observed that the light yellow color of a 1:2 molar mixture of $HgBr_2$ and AgI changed rapidly to orange-yellow and then slowly to red. X-ray analysis of this mixture, maintained at room temperature (30°C) for about 24 hr, showed only the presence of HgI_2 and AgBr.

$$HgBr_2 + 2AgI \rightarrow HgI_2 + 2AgBr. \quad (2)$$

The sharp initial rise in temperature (Fig. 1, 2) and the initial color change noted on mixing $HgBr_2$ and AgI suggest that reaction (2) proceeds through the intermediate formation of Ag_2HgI_4.

$$HgBr_2 + 4AgI \rightarrow Ag_2HgI_4 + 2AgBr \quad (2a)$$

$$HgBr_2 + Ag_2HgI_4 \rightarrow 2HgI_2 + 2AgBr \quad (2b)$$

$$\overline{2HgBr_2 + 4AgI \rightarrow 2HgI_2 + 4AgBr}$$

In support of this mechanism, step (2b) was confirmed separately by mixing $HgBr_2$ and Ag_2HgI_4 in equimolar proportions and taking the X-ray pattern of this mixture (kept at 30°C) after 24 hr. The pattern indicated complete conversion into HgI_2 and AgBr.

X-ray analysis of the same mixture (1:2 molar) of $HgBr_2$ and AgI, maintained at 90°C for about 24 hr, showed the presence of HgBrI, Ag_2HgI_4, and AgBr, but not of HgI_2 or of any of the reactants. This is probably because at higher temperature, the product, HgI_2, formed in step (2b) is quantitatively consumed by AgBr to give HgBrI and Ag_2HgI_4. To confirm this conjecture, HgI_2 and AgBr were mixed in a 1:2 molar ratio and kept at 90°C for about 24 hr. Its X-ray pattern was similar to that of the product of a 1:2 molar mixture of $HgBr_2$ and AgI (maintained at 90°C for about 24 hr). Thus, the mechanism of the $HgBr_2$–AgI reaction when taken in a 1:2 molar ratio and maintained at 90°C can be postulated as follows:

$$3(HgBr_2 + 4AgI \rightarrow Ag_2HgI_4 + 2AgBr) \quad (3a)$$

$$3(HgBr_2 + Ag_2HgI_4 \rightarrow 2HgI_2 + 2AgBr) \quad (3b)$$

$$2(3HgI_2 + 2AgBr \rightarrow 2HgBrI + Ag_2HgI_4) \quad (3c)$$

$$\overline{6HgBr_2 + 12AgI \rightarrow 4HgBrI + 2Ag_2HgI_4 + 8AgBr} \quad (3)$$

The plot of conductivity versus time (Fig. 2, 2) for a 1:2 molar mixture of $HgBr_2$ and AgI maintained at 90°C clearly shows that the reaction is multistep. The first rapid increase in conductivity is due to the formation of the highly conducting material, Ag_2HgI_4, and the decrease thereafter is due to its disappearance through reaction (3b). The second increase in conductivity points toward the regeneration of this conducting material through step (3c). Thus, in conclusion, it can be said that the X-ray analysis of a 1:2 molar mixture of $HgBr_2$ and AgI showed that at 90°C, HgBrI, Ag_2HgI_4, and AgBr were formed, whereas at room temperature, the same mixture gave rise to HgI_2 and AgBr.

The X-ray analysis of a 1:3 molar mixture of $HgBr_2$ and AgI showed that at room temperature, HgI_2, Ag_2HgI_4, and AgBr were formed, whereas at 90°C, HgBrI, Ag_2HgI_4, and AgBr were the products. The overall reactions may be the following: at room temperature,

$$\begin{aligned}&2HgBr_2 + 6AgI\\ &\quad \rightarrow HgI_2 + Ag_2HgI_4 + 4AgBr; \qquad (4)\end{aligned}$$

and at high temperature,

$$\begin{aligned}&3HgBr_2 + 9AgI\\ &\quad \rightarrow HgBrI + 2Ag_2HgI_4 + 5AgBr. \qquad (5)\end{aligned}$$

The steps involved here seem to be the same as those in a 1:2 molar mixture. At room temperature, the results of X-ray analysis of 1:2 and 1:3 molar mixtures are different simply because in a 1:3 molar mixture, some Ag_2HgI_4 is left unreacted, whereas in a 1:2 molar mixture it is completely consumed by the subsequent step. At 90°C, although the end products of the 1:2 and 1:3 molar mixtures were the same, the I/I_0 values of the Ag_2HgI_4 and AgBr lines were higher for a 1:3 molar mixture, whereas those for HgBrI lines were higher in a 1:2 molar mixture. This clearly shows that the products of the two reaction mixtures have different molar ratios and explains the difference in the molar ratios of the products of reactions (3) and (5).

In an equimolar mixture, the conductivity first rises steeply and then falls slowly (Fig. 2, 3), thereby indicating the multiplicity of the steps. X-ray diffraction patterns of an equimolar mixture of $HgBr_2$ and AgI maintained at room temperature (30°C) or at 90°C for 3 days show that HgBrI and AgBr were the end products in either case. The steps involved were confirmed by taking X-ray patterns at different time intervals. At room temperature, the X-ray pattern of the mixture, taken after about 5 hr, when the color of the mixture had changed to orange-yellow, showed lines for Ag_2HgI_4, AgBr, and $HgBr_2$ but not for AgI. The X-ray pattern, taken after about 30 hr when the color of the mixture had changed to red, showed the presence of HgI_2, AgBr, and $HgBr_2$. The last pattern, which was taken after 3 days when the color of the mixture had finally turned yellow, showed the presence of only HgBrI and AgBr and of nothing else. In light of the above, the reaction sequence occurring in the equimolar mixture can be written as

$$\begin{array}{lll}HgBr_2 + 4AgI & & \\ \quad \rightarrow Ag_2HgI_4 + 2AgBr & \text{Fast} & (6a)\\ HgBr + Ag_2HgI_4 & & \\ \quad \rightarrow 2HgI_2 + 2AgBr & \text{Moderate} & (6b)\\ 2HgBr_2 + 2HgI_2 & & \\ \quad \rightarrow 4HgBrI & \text{Slow} & (6c)\\ \hline 4HgBr_2 + 4AgI & & \\ \quad \rightarrow 4HgBrI + 4AgBr & & (6)\end{array}$$

It is interesting to point out that experiments performed (X-ray pattern of equimolar mixture of $HgBr_2$ and HgI_2) to check step (6c) indicated that it occurred at 90°C but not at room temperature. Further, as according to reaction (3c), HgI_2 and AgBr yield HgBrI and Ag_2HgI_4 at 90°C, an alternative way of explaining the formation of HgBrI at higher temperatures would be

$$\begin{array}{rcl}3HgI_2 + 2AgBr & \rightarrow & 2HgBrI + Ag_2HgI_4\\ HgBr_2 + Ag_2HgI_4 & \rightarrow & 2HgI_2 + 2AgBr\\ \hline HgBr_2 + HgI_2 & \rightarrow & 2HgBrI\end{array}$$

From the present work it seems difficult to decide which of the two mechanisms is operative in this case.

It was surprising to note that the X-ray pattern of an equimolar mixture of $HgBr_2$ and HgI_2 maintained at room temperature had lines for HgBrI only when AgBr was present in the mixture. No attempt, other than the following conductivity measurement, was made to understand the catalytic influence of AgBr on the reaction:

$$HgBr_2 + HgI_2 \rightarrow 2HgBrI.$$

At 30°C, a 1:2 molar mixture of $HgBr_2$ and AgBr showed a change in conductivity from 3×10^{-9} to 2×10^{-8} ohms^{-1} cm^{-1} in 4 hr, whereas no change in conductivity was noted for a 1:1 molar mixture of HgI_2 and AgBr. In analogy with the formation of highly conducting Ag_2HgI_4 from AgI and HgI_2, the increase in conductivity in the $HgBr_2$–AgBr mixture may be assumed to be due to the formation of Ag_2HgBr_4 (*3*). If this presumption is true, the reaction sequence in an equimolar mixture of $HgBr_2$ and AgI at room temperature (30°C) may be

$$\begin{array}{rcl}
HgBr_2 + 4AgI & \rightarrow & Ag_2HgI_4 + 2AgBr \\
HgBr_2 + Ag_2HgI_4 & \rightarrow & 2HgI_2 + 2AgBr \\
2HgBr_2 + 4AgBr & \rightarrow & 2Ag_2HgBr_4 \\
2HgI_2 + 2Ag_2HgBr_4 & \rightarrow & 4HgBrI + 4AgBr \\
\hline
4HgBr_2 + 4AgI & \rightarrow & 4HgBrI + 4AgBr
\end{array}$$

Mechanism of lateral diffusion. In lateral diffusion experiments it was observed that immediately after mixing powdered $HgBr_2$ with AgI, a red boundary formed at the interface which with time grew on the AgI side and soon separated into greenish yellow and red layers. A gap developed simultaneously between $HgBr_2$ and the product layers. Later, when the experiment was repeated with an air gap between the reactants at the start itself, it proceeded likewise. This clearly demonstrates that $HgBr_2$ reacts via gaseous state. Gaseous $HgBr_2$ molecules like HgBrI react with the AgI grain at the interface via counterdiffusion of Ag^+ and Hg^{2+} through product layers. Growth of the thickness of the product layers follows the equation, $X_i^n = kt$ (Fig. 3), where X_i is the thickness of the product layers at time t and n and k are constants. The value of n in $X_i^n = kt$, varies from 3.2 to 2.2 in the temperature range 85.5–107°C and assumes a constant value of 2 in the temperature range 111–119°C. The variation in the value of n and the plot of log$k$ vs $1/T$ (Fig. 4) clearly shows that the process occurring at lower temperatures is different from the one that occurs at higher temperatures. The activation energies for the low- and high-temperature ranges are, respectively, 67.33 and 21.18 kcal/mole, and these activation energies suggest that at lower temperatures, the rate of the process is reaction controlled, whereas at higher temperatures, it is diffusion controlled. This simply implies that in the lower temperature range, diffusion is faster than the chemical reaction between $HgBr_2$ and AgI and as the

TABLE II

TEMPERATURE DEPENDENCE OF PARAMATERS OF THE EQUATION, $X_i^n = kt$, FOR THE $HgBr_2$–AgI REACTION

Temperature (°C ± 0.5)	k (cm/hr)	n
84.5	0.129×10^{-5}	3.10
88.0	0.275×10^{-5}	2.99
93.5	1.014×10^{-5}	2.79
99.5	6.668×10^{-5}	2.40
107.0	25.590×10^{-5}	2.19
111.0	59.730×10^{-5}	1.99
115.0	79.430×10^{-5}	2.00
119.0	100.000×10^{-5}	2.00

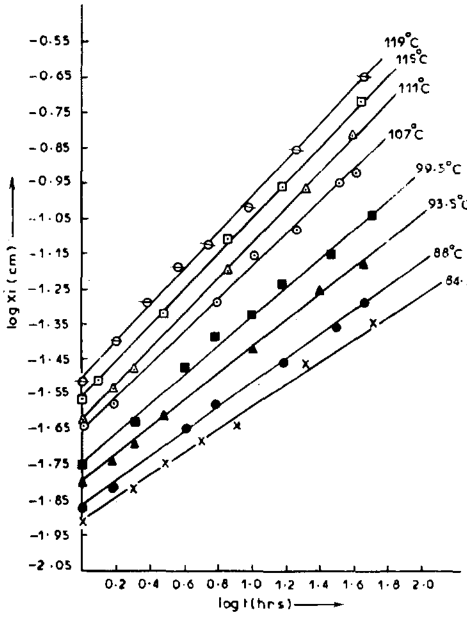

FIG. 3. Kinetic data for lateral diffusion and test of equation $x_i^n = kt$ for the reaction between $HgBr_2$ and AgI.

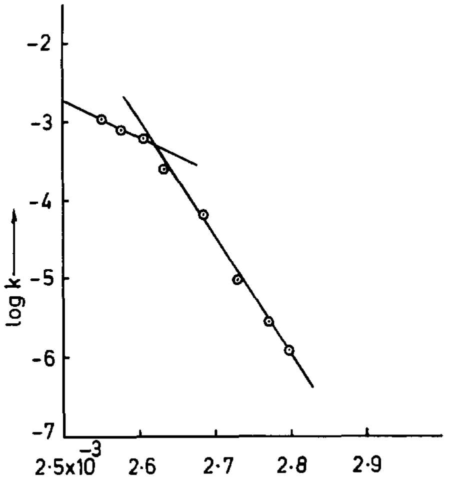

FIG. 4. Dependence of k on temperature for the reaction between $HgBr_2$ and AgI.

temperature is raised, a situation is reached where the chemical reaction becomes faster and consequently n decreases gradually with increasing temperature and attains a constant value of 2 at 111°C.

To see if there is any initial difference in the processes occurring in the two temperature ranges, the thickness of the product layers was plotted against time (Fig. 5), the slope at zero time of the product growth curve was calculated, and its logarithm was plotted against inverse temperature (Fig. 6). This plot is similar to the earlier log$k$ vs $1/T$ plot (Fig. 4). The activation energy of 9.48 kcal/mole in the lower temperature range in this case indicates that the process is grain boundary or surface diffusion controlled, whereas the activation energy of 41.45 kcal/mole for the second temperature range shows that in the higher temperature range this process is nucleation controlled at the start. Investigations, however, could not be extended to still higher temperatures because AgI, which is reported to have a transition temperature of 146°C, starts changing from cubic to hexagonal form at 120°C (*4*).

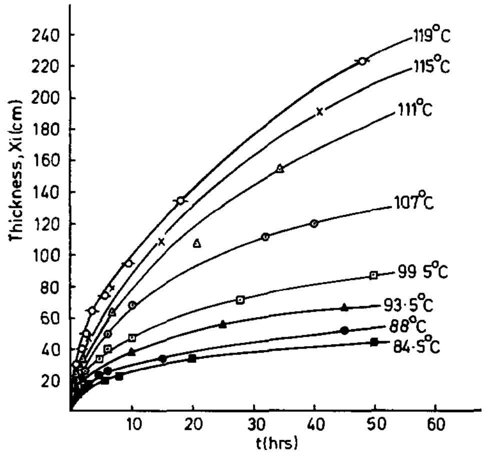

FIG. 5. Kinetic data for the reaction between $HgBr_2$ and AgI at various temperatures.

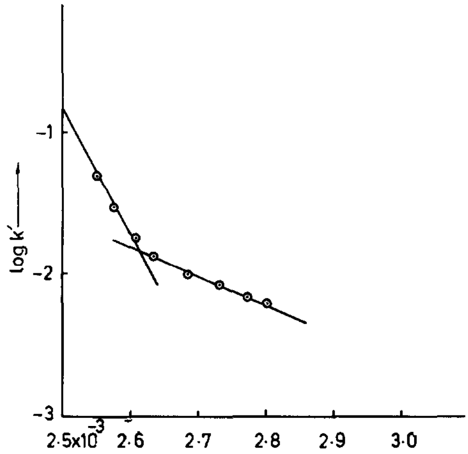

FIG. 6. Dependence of k', the initial rate constant, on temperature for the reaction between $HgBr_2$ and AgI.

It may be recalled that the formation of red HgI_2 in the lateral diffusion experiment between $HgBr_2$ and AgI could not be noticed till AgI remained in the reaction tube. Our failure to notice HgI_2 in the beginning was because, as soon as it was formed via the $HgBr_2$–Ag_2HgI_4 reaction, it was consumed by AgI, giving Ag_2HgI_4. This continued until AgI was there and afterward HgI_2 precipitated out to give the red layer. To confirm this conjecture, a separate lateral diffusion experiment between $HgBr_2$ and Ag_2HgI_4 was performed, which gave separate layers of AgBr and HgI_2 at the interface.

The formation of solid solutions in the systems AgBr–AgI, Ag_2HgI_4–AgBr, and

$HgBrI–Ag_2HgI_4$ noted during the study of the HgBrI–AgI reaction was again detected during X-ray analysis of the product in the present system.

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