JOURNAL OF SOLID STATE CHEMISTRY **105**, 346–353 (1993)

A Comparative Study of the Kinetics and Mechanism of Solid–Solid Reaction between AgI and Some Mixed Mercury Halides

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Received July 10, 1992; in revised form November 24, 1992; accepted November 24, 1992

The reaction of AgI with mercuric chlorobromide and mercuric chloroiodide in solid state was studied by X-ray diffraction, chemical analysis, and electrical conductivity measurements. The kinetics of the reaction has been studied by a visual technique. The data for the lateral diffusion best fit the equation $X^n = kt$. Both of the reactions are diffusion controlled and proceed via vapor phase diffusion of the mixed mercury halides. The reaction with HgClI is somewhat simple that with HgClBr is a complex one. © 1993 Academic Press, Inc.

Introduction

The growing application of solid state devices in modern technologies lays vital emphasis on syntheses of newer materials with unusual combinations of properties on one hand and development of a structure–property relationship on the other. The majority of inorganic materials are nonmolecular in nature and their reactivity is highly structure dependent. Of all the methods that are used to synthesize materials, the solid–solid reaction is the most important one.

AgI reacts with HgI_2 (*1*) in solid state yielding highly conducting Ag_2HgI_4. Its reactions with $HgBr_2$ and $HgCl_2$ are quite complex and follow altogether different paths (*2, 3*). Formation of mixed mercury halides from equimolar mixtures of mercury halides in solid state is reported (*4–6*) but no effort seems to have been made so far to understand the mechanism of the interaction of mixed mercury halides with other compounds.

Following our studies on the reactivity of copper(I) and silver(I) halides with mercury halides (*2, 3, 7, 8*). This paper presents a study on the kinetics and mechanism of the reactions of AgI with mercury chlorobromide and mercury chloroiodide in solid state. Both of the reactions are multistep and proceed through the formation of Ag_2HgI_4.

Experimental

$HgBr_2$ (E. Merck), $HgCl_2$ (E. Merck), and HgI_2 (B.D.H. AR) were used. AgI was prepared by the method reported by Mehdi and Ansari (*10*).

Electrical resistivity measurements were made in darkness, on samples that had been compressed into pellets (about 0.2×10^{-2} m thick and 0.31×10^{-4} m^2 in surface area) in molar ratios 1 : 4, 1 : 3, 1 : 2, 1 : 1, and 2 : 1 of mixed mercury halides to silver iodide, using a Teflon conductivity cell with platinum electrodes as described elsewhere (*2*) by LCR Bridge (Gen. Rad. Model 1659). Samples were exposed to light for a brief period only during the data recording. It was observed that under our experimental conditions, conductivity of the silver halide practically remained uneffected during this period. The results are plotted against time for various molar mixtures (Figs. 1 and 3).

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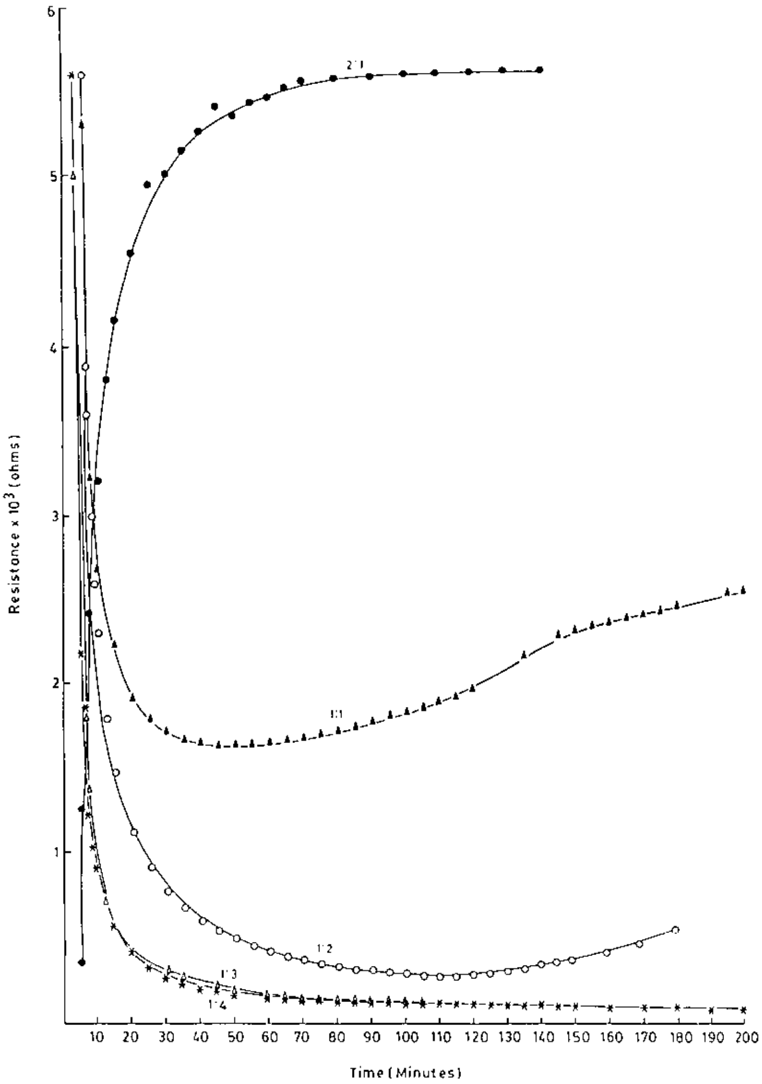

FIG. 1. Resistivity change as a function of time for the reaction between HgClBr and AgI in different molar ratios.

TABLE I

DEPENDENCE OF PARAMETERS OF EQUATION $X^n = kt$ ON TEMPERATURE FOR HgClBr–AgI REACTION

Temperature (°C ± 0.05)	k (cm/hr)	Standard deviation	Relative standard deviation	n
50	7.533×10^{-4}	3.505×10^{-4}	3.460×10^{-2}	2.00
60	1.036×10^{-3}	3.065×10^{-4}	2.186×10^{-2}	2.04
80	4.72×10^{-3}	2.170×10^{-4}	3.326×10^{-2}	1.95
100	1.15×10^{-2}	5.512×10^{-4}	3.383×10^{-2}	1.92
105	1.679×10^{-2}	6.612×10^{-4}	3.004×10^{-2}	1.93
110	2.088×10^{-2}	8.943×10^{-4}	3.367×10^{-2}	1.89

TABLE II

DEPENDENCE OF PARAMETERS OF EQUATION $X^n = kt$ ON TEMPERATURE FOR HgClI–AgI REACTION

Temperature (°C ± 0.05)	k (cm/hr)	Standard deviation	Relative standard deviation	n
50	8.07×10^{-4}	5.42×10^{-4}	3.51×10^{-2}	2.23
60	9.86×10^{-4}	1.178×10^{-4}	7.532×10^{-2}	2.36
70	3.55×10^{-3}	6.812×10^{-5}	1.667×10^{-2}	2.01
90	1.157×10^{-2}	4.76×10^{-4}	3.66×10^{-2}	1.86
100	1.435×10^{-2}	8.75×10^{-4}	3.979×10^{-2}	1.93
110	2.111×10^{-2}	1.496×10^{-3}	5.28×10^{-2}	1.94

The kinetics of the two reactions were studied using the visual technique described elsewhere (*11*). The results are shown in Tables I and II.

The X-ray diffractograms of powdered materials were recorded on a Norelco Geiger X-ray diffractometer (PW 1010 Philips) using Cu$K\alpha$ radiation and a Ni filter. Reactants mixed in different molar ratios were kept in an air thermostat maintained at 80°C for over 3 days. The diffractograms of these mixtures were then recorded at room temperature. Compounds present in different mixtures were identified by comparing their *d*-values with those of expected compounds. The results are listed in Tables III and IV. The decomposition temperature of Ag_2HgI_4 is 158°C and the studies were limited to 80°C. However, kinetic experiments were extended up to 110°C.

Results and Discussion

For a comprehensive understanding of the process, the mechanism of chemical interaction and that of lateral diffusion, when the reactants were kept in contact and also when separated by an air gap, are considered.

Mechanism of Chemical Interaction

HgClBr–AgI reaction. X-ray diffraction patterns of different molar ratio mixtures suggest that the reaction is taking place at a 1 : 4 molar ratio.

It was observed that as soon as HgClBr and AgI were mixed in the molar ratio 1 : 4 at room temperature, a red color appeared which gradually transformed into yellow. The process, though slow at room temperature, became increasingly faster with rise

TABLE III

COMPOUNDS PRESENT IN DIFFERENT MOLAR MIXTURES OF HgClBr AND AgI

Molar ratio HgClBr : AgI	Compounds identified after heating the mixture at 80°C for 3 days and thereafter cooling to room temperature
1 : 4	Ag_2HgI_4, AgCl, and AgBr
1 : 3	Ag_2HgI_4, AgCl, AgBr, and HgI_2
1 : 2	AgCl, AgBr, and HgI_2
1 : 1	AgCl, AgBr, HgBrI, $HgCl_2$, and HgI_2
2 : 1	AgCl, AgBr, $HgCl_2$, HgI_2, HgBrI, and HgClBr

TABLE IV

COMPOUNDS PRESENT IN DIFFERENT MOLAR MIXTURES OF HgClI AND AgI

Molar ratio HgClI : AgI	Compounds identified after heating the mixture at 80°C for 3 days and thereafter cooling to room temperature
1 : 4	AgCl and Ag_2HgI_4 + AgI
1 : 3	AgCl and Ag_2HgI_4
1 : 2	AgCl, $HgCl_2$, HgI_2, and Ag_2HgI_4
1 : 1	AgCl, $HgCl_2$, HgI_2, and Ag_2HgI_4
2 : 1	AgCl, $HgCl_2$, HgI_2, and Ag_2HgI_4

in temperature. However, when this molar mixture was kept above 55°C the red color did not change into yellow (β-Ag_2HgI_4 is yellow below 50.7°C and the α-form is red above this temperature (*12*).

The time-resistivity curve (Fig. 1) first falls very steeply and then tapers off slowly. Though there is no evidence of HgI_2 in the X-ray pattern of the (1 : 4) mixture its presence is indicated in other molar mixtures (Table III). The transitory appearance of the red color is due to HgI_2 which is first produced and then consumed rapidly by the AgI present in the mixture, producing Ag_2HgI_4 (*1*) even at low temperatures. Evidence of the formation of HgI_2 was obtained when the lateral diffusion experiment, carried out at 80°C, was continued until all the AgI was consumed, a red layer of HgI_2 was formed on the AgI side of the reactants. Ag_2HgI_4 is red above 50.7°C and the total product thickness of different layers was measured at 80°C. The reaction is thus presumed to proceed through the transitory formation of HgI_2 as follows:

$$HgClBr + 2AgI = AgCl + AgBr + HgI_2 \tag{1a}$$

$$HgI_2 + 2AgI = Ag_2HgI_4 \tag{1b}$$

$$HgClBr + 4AgI = AgCl + AgBr + Ag_2HgI_4. \tag{1}$$

Alternatively, HgI_2 formed as explained above may react with excess of HgClBr as follows:

$$HgClBr + HgI_2 = HgClI + HgBrI. \tag{1b'}$$

If HgI_2 is to be consumed by step (1b'), and not by the fast reaction (1b), the final color of the product must remain red because HgClI slowly disproportionates (*6*) at room temperature into $HgCl_2$ and HgI_2. But the X-ray diffractogram did not have lines for $HgCl_2$ and HgI_2. Therefore, HgI_2 is considered to be consumed by step (1b) and not by (1b'). HgBrI and HgClBr are stable while HgClI is unstable (*6*). This difference is probably due to difference in the ionic sizes.

The X-ray analysis of 1 : 3 molar mixture of HgClBr and AgI revealed the presence of Ag_2HgI_4, AgCl, AgBr, and HgI_2, which suggests the following stoichiometric reaction:

$$2HgClBr + 6AgI = Ag_2HgI_4 + 2AgCl + 2AgBr + HgI_2. \tag{2}$$

The time-resistivity curve (Fig. 1) for 1 : 3 molar mixture suggests that chemical interaction in 1 : 3 molar mixture is similar to that for 1 : 4 molar mixture. The presence of HgI_2 in the X-ray pattern Table III confirms the foregoing hypothesis. Since the amount of AgI, in 1 : 3 molar mixture is inadequate, HgI_2 produced in the first step is not consumed completely by the second step.

The X-ray analysis of 1 : 2 molar mixture of HgClBr and AgI showed the presence of AgCl, AgBr, and HgI_2. Its time-resistivity curve in initial stages is similar to those for 1 : 4 and 1 : 3 molar mixtures. The rapid fall in the resistivity and the similarity in the time-resistivity curve with earlier ones, suggest that Ag_2HgI_4 is formed in this case as well. But, this does not show up in X-ray analysis (Table III) of this mixture probably because it is being consumed by the unreacted HgClBr. The rapid step (3b) preceeds step (3c). In view of this, the following mechanism for 1 : 2 molar mixture is proposed:

$$\begin{aligned}
&\mathrm{HgClBr + 2AgI} &&= \mathrm{AgCl + AgBr + HgI_2} && \text{(3a)}\\
&\mathrm{HgI_2 + 2AgI} &&= \mathrm{Ag_2HgI_4} && \text{(3b)}\\
&\mathrm{HgClBr + Ag_2HgI_4} &&= \mathrm{AgCl + AgBr + 2HgI_2} && \text{(3c)}\\
\hline
&\mathrm{2HgClBr + 4AgI} &&= \mathrm{2AgCl + 2AgBr + 2HgI_2}. && \text{(3)}
\end{aligned}$$

Step (3c) was separately confirmed by mixing HgClBr and Ag_2HgI_4 in a 1 : 1 molar mixture and heating at 80°C. Its X-ray analysis revealed only the expected products.

The X-ray analysis of 1 : 1 molar mixture of HgClBr and AgI showed the presence of AgCl, AgBr, $HgCl_2$, HgI_2, and HgBrI (Table III). Its time-resistivity curve indicated that the resistance first decreased fast as in earlier cases, but, unlike the earlier ones, the resistance in this case increased in later stages to a fairly high value (Fig. 1). As is the case with all the preceeding molar mixtures, the first stage appears to be the formation of HgI_2 which is immediately consumed by AgI to form the highly conducting Ag_2HgI_4, well indicated by the initial rapid decrease in resistivity:

$$\begin{aligned}
&\mathrm{HgClBr + 2AgI} &&= \mathrm{AgCl + AgBr + HgI_2} && \text{(4a)}\\
&\mathrm{HgI_2 + 2AgI} &&= \mathrm{Ag_2HgI_4}. && \text{(4b)}
\end{aligned}$$

Ag_2HgI_4 formed in step (4b) combines with the unreacted HgClBr present in the reaction mixture:

$$\mathrm{3HgClBr + Ag_2HgI_4} \\ \mathrm{= AgCl + AgBr + 2HgBrI + 2HgClI}. \qquad \text{(4c)}$$

The later rise in resistivity (Fig. 1) in this mixture is in conformity with the predominance of step (4c) towards the end of the reaction. Hence the overall reaction can be represented as follows:

$$\begin{aligned}
&\mathrm{HgClBr + 2AgI} &&= \mathrm{AgCl + AgBr + HgI_2} && \text{(4a)}\\
&\mathrm{HgI_2 + 2AgI} &&= \mathrm{Ag_2HgI_4} && \text{(4b)}\\
&\mathrm{3HgClBr + Ag_2HgI_4} &&= \mathrm{AgCl + AgBr + 2HgBrI + 2HgClI} && \text{(4c)}\\
&\mathrm{2HgClI} &&= \mathrm{HgCl_2 + HgI_2} && \text{(4d)}\\
\hline
&\mathrm{4HgClBr + 4AgI} &&= \mathrm{2AgCl + 2AgBr + HgI_2 + HgCl_2 + 2HgBrI}. && \text{(4)}
\end{aligned}$$

The X-ray pattern of 2 : 1 molar mixture of HgClBr and AgI showed the presence of AgCl, AgBr, $HgCl_2$, HgI_2, HgBrI, and HgClBr (Table III). The time-resistivity curve (Fig. 1) is altogether different in this case. The resistance increased right from the beginning reaching a constant value in about an hour's time. However, as in other molar mixtures, the reaction in this case as well is considered to be going through the formation of Ag_2HgI_4. The rise in resistance from the beginning itself and the absence of Ag_2HgI_4 in the X-ray diffraction pattern of this mixture suggest that the rate of disappearance of Ag_2HgI_4 through step (4c) outweighs its accumulation rate through step (4b), due to the larger proportion of HgClBr in this mixture. This viewpoint was confirmed by the time-resistivity curve (Fig. 2) for a pellet made out of 3 : 1 molar mixture of HgClBr and Ag_2HgI_4. This pellet was initially red (Ag_2HgI_4 is red above 50°C), but turned yellow toward the end, and then very slowly turned red again on standing. This color change is in conformity with reactions (4c) and (4d). Reaction (4c) was also separately confirmed by heating HgClBr and Ag_2HgI_4 in 3 : 1 molar ratio and analyzing the product by X-ray.

HgClI-AgI reaction. X-ray analysis of the

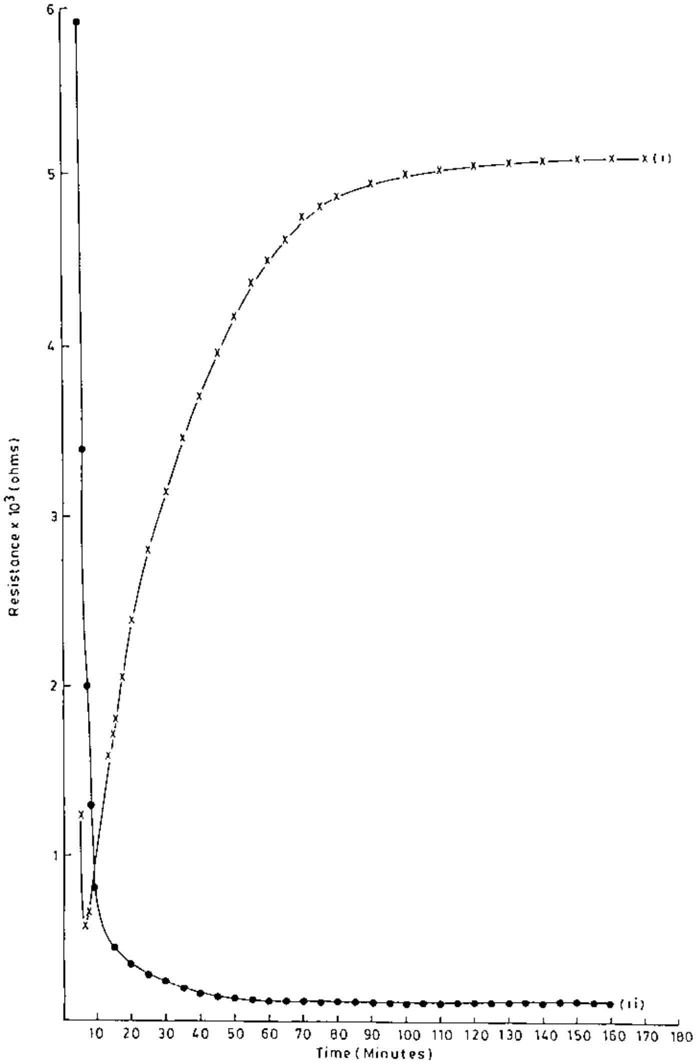

FIG. 2. Resistivity change as a function of time for the reaction between (i) HgClBr and Ag_2HgI_4 in the molar ratio 3 : 1 (ii) HgI_2 and AgI in the molar ratio 1 : 2.

products (Table IV) of 1 : 3 molar mixture of HgClI and AgI suggests the following stoichiometry:

$$\mathrm{HgClI + 3AgI = AgCl + Ag_2HgI_4}. \quad (5)$$

The time-resistivity curve (Fig. 3) was quite similar to that obtained for 1 : 3 molar mixture of HgClBr and AgI, and give no evidence for any substep of reaction (5). However, it was observed that as soon as the reactants were mixed at room temperature, a red color developed that gradually turned yellow as reported for the earlier reaction. The red color, in this case as well, is due to the formation of HgI_2, which immediately reacted with AgI to give the addition product Ag_2HgI4_4. The mechanism for this reaction therefore, appears as follows:

$$\mathrm{HgClI + AgI = AgCl + HgI_2} \quad (5a)$$

$$\mathrm{HgI_2 + 2AgI = Ag_2HgI_4} \quad (5b)$$

$$\mathrm{HgClI + 3AgI = AgCl + Ag_2HgI_4}. \quad (5)$$

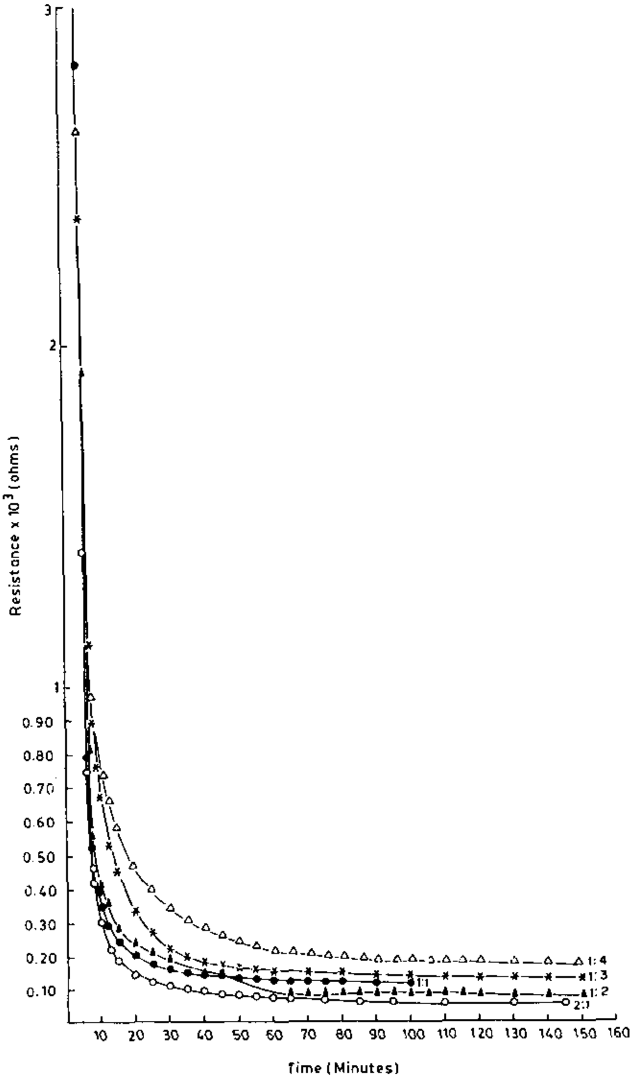

FIG. 3. Resistivity change as a function of time for the reaction between HgClI and AgI in different molar ratios.

The X-ray patterns of 1 : 2, 1 : 1, and 2 : 1 molar mixtures of HgClI and AgI (Table IV) showed the presence of HgI_2 and $HgCl_2$ in addition to AgCl and Ag_2HgI_4 in all the three mixtures. 1 : 4 molar mixture showed AgI in addition to the products of 1 : 3 molar mixture. The time-resistivity curves (Fig. 3) for these mixtures were also similar to the earlier ones. This indicates the same reaction sequence in all ratios studied. HgClI, being unstable at room temperature, disproportionated into HgI_2 and $HgCl_2$ (Table IV) on standing. However, the conductance and kinetic studies were carried out above 50°C, at which temperature the stability of HgClI is not questioned.

Mechanism of Lateral Diffusion

Soon after placing the mixed mercury halide over AgI in the reaction capillary, at 50°C, a red color layer developed at the interface. The red product layer grew with time towards the AgI side which later separated into red and yellow layers. Later, a gap developed between the yellow layer and the mixed mercury halide. When the experiment was repeated with an air-gap of varying lengths between the two reactants, the reaction proceeded similarly giving the same kind of layers on the AgI side. The air-gap did not affect the sequence of the layers. This shows that the mobile component is the mixed mercury halide. X-ray and chemical analyses of different layers showed the following sequence of the products in the capillary containing HbClBr and AgI:

$$\mathrm{AgI}|\mathrm{Ag_2HgI_4},\ \mathrm{AgBr} + \mathrm{AgCl}|\mathrm{HgClBr}$$

The product sequence in the capillary for HgClI-AgI reaction is

$$\mathrm{AgI}|\mathrm{Ag_2HgI_4},\ \mathrm{AgCl},\ \mathrm{HgI_2} + \mathrm{HgCl_2}|\mathrm{HgClI}$$

The rate of growth of product layers decreased with time in either case. Initially, the process is fast and reaction controlled. As the thickness of the product layers became significant, the mixed mercury halides took greater time to diffuse through the product layers. The lateral diffusion data, for either reaction best fit the rate equation

$$X^n = kt, \qquad (1)$$

where X is the total thickness of the product layers (in cm) at time t (in hr) and, k and n are constants. The rate constant, k follows the Arrhenius equation

$$k = A\ \exp(-E/RT). \qquad (2)$$

The activation energy evaluated from the $\log k$ versus $1/T$ plot made by a least-squares fit method was found to be 57.35 ± 0.14 kJ/mole for the reaction between AgI and HgClBr, and that for AgI–HgClI reaction was 111.84 ± 0.59 kJ/mole. The reaction rate constants measured with an initial air gap between the reactants decreased with the increase in the length of the air gap. The energies of activation suggest that the reactions are diffusion controlled, taking place via the vapor phase of HgClX (X = Br, I). The two systems are chemically similar but diffusing species are different in size. Hence, the difference in activation energies occurs.

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