JOURNAL OF SOLID STATE CHEMISTRY **105**, 130–135 (1993)

Solid State Reaction between CuI and HgClBr: Relevance of Electrical Resistivity Measurements in the Study of Solid–Solid Reactions

SABA BEG AND AFAQ AHMAD

Department of Chemistry, Aligarh Muslim University, Aligarh 202002, India

Received June 25, 1992; in revised form October 30, 1992; accepted November 4, 1992

The reaction between CuI and HgClBr in the solid state has been studied by resistivity measurements, X-ray diffraction, and chemical analysis. The reaction occurs differently at different molar ratios. The kinetics of the reaction has been studied by a visual technique. The reaction follows the usual rate law, $X^n = kt$. The k's show the Arrhenius dependence. The activation energy, 43.30 ± 0.53 kJ/mol, calculated by least-squares fitting, suggests that the reaction is diffusion controlled and proceeds via vapor phase diffusion of HgClBr. © 1993 Academic Press, Inc.

Introduction

Solid state reactions are of practical interest especially in the preparation of spinels, ceramics, catalysts, and pharmaceutical materials (*1–3*). From time to time, studies have been made to understand the mechanisms and reactivity of such reactions. In solid state reactions, breaking and reforming of chemical bonds in the solid is essentially a geometrical reshuffling of lattice elements.

In previous papers (*4–8*), a comprehensive picture of the initial surface reaction followed by diffusion of reactants through the product layer has been obtained, including information about the mode of diffusion. In order to have more information about the mechanism of reaction between copper halides and mixed mercury halides additional data are required. In the present paper, we have studied the reaction between CuI and HgClBr to understand the reactivity of copper(I) iodide toward HgClBr.

Experimental

$HgBr_2$ (E. Merck), $HgCl_2$, $CuSO_4$, and KI, of BDH quality, were used as such. CuI was prepared following the technique reported earlier (*4*). HgClBr was prepared by the method reported by Ansari and Mehdi (*9*).

Electrical conductivity measurements were made on compressed samples using a Teflon conductivity cell. Powdered CuI and HgClBr (each above 200 mesh size), in different molar ratios, were thoroughly mixed, poured into a die, and pressed into discs about 0.2×10^{-2} m thick and 0.31×10^{-4} m^2 in surface area by applying 4000 lb pressure with a hydraulic press (Carver Laboratory Press, Model C, Fred S. Carver, Inc., U.S.A.). Resistance measurements were made at 80°C by keeping the compressed discs between platinum electrodes using an LCR conductivity bridge (Gen Rad Model 1659 USA). The results are plotted against time for various molar mixtures (Fig. 1).

The kinetics of the reaction between CuI and HgClBr was studied using a visual technique described elsewhere (*10*). A weighed amount of HgClBr was placed over a weighed amount of CuI in a glass capillary of uniform bore. The reaction capillary was placed in an air thermostat maintained to

0022-4596/93 $5.00

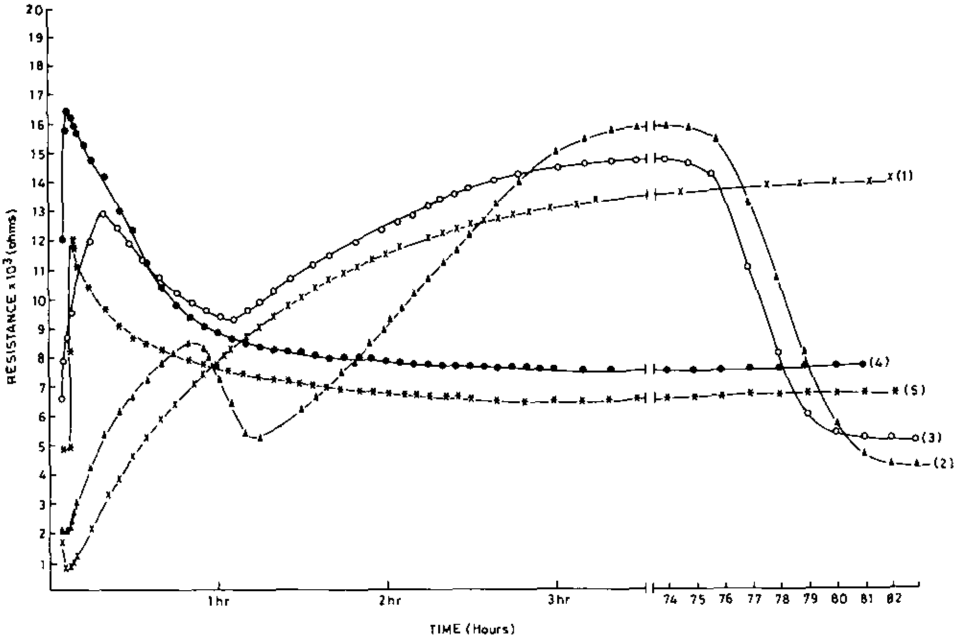

FIG. 1. Resistivity change at 80°C as a function of time for CuI and HgClBr mixed in the molar ratios (1) 4 : 1 (×), (2) 3 : 1 (▲), (3) 2 : 1 (○), (4) 1 : 1 (●), (5) 1 : 2 (*).

±0.5°C. The progress of the reaction was followed by measuring the total thickness of the product layers formed at the interface by a calibrated travelling microscope. The results are given in Table I. To check for the reproducibility of our results, five reactions were run at the same temperature. The agreement between the corresponding values of different sets was well within the limits of experimental error.

The X-ray diffractograms of powdered CuI and HgClBr, mixed in different molar ratios, were recorded by a Norelco Geiger X-ray diffractometer (PW 1010 Philips) using Cu$K\alpha$ radiation and a Ni filter. The reactants in different molar ratios were mixed in an agate mortar and kept at 80°C in an air thermostat for over 3 days to ensure complete reaction. The diffractograms of these mixtures were recorded at room temperature. Compounds present in different mixtures were identified by calculating their *d*-

TABLE I

Temperature (°C ± 0.5)	k (cm/hr)	Standard deviation	Relative standard deviation	n
50	3.26×10^{-4}	1.241×10^{-5}	3.307×10^{-2}	2.27
60	3.592×10^{-4}	1.934×10^{-5}	4.480×10^{-2}	2.35
70	6.477×10^{-4}	5.519×10^{-5}	6.75×10^{-2}	2.48
80	1.006×10^{-3}	6.795×10^{-5}	4.159×10^{-2}	2.40
90	3.082×10^{-3}	1.500×10^{-4}	3.594×10^{-2}	2.30
100	2.20×10^{-2}	1.355×10^{-3}	5.28×10^{-2}	2.48

TABLE II

COMPOUNDS IDENTIFIED BY X-RAY ANALYSIS AFTER HEATING THE MIXTURE AT 80°C FOR 3 DAYS AND THEN COOLING TO ROOM TEMPERATURE

Molar ratio of CuI : HgClBr	Compounds present
4 : 1	Cu_2HgI_4, CuCl, CuBr
3 : 1	Cu_2HgI_4, CuCl, CuBr, HgI_2
2 : 1	Cu_2HgI_4, CuCl, CuBr, HgI_2, $HgCl_2$
1 : 1	CuCl, CuBr, HgI_2, $HgCl_2$, HgBrI
1 : 2	HgClBr, CuCl, CuBr, HgI_2, $HgCl_2$, HgBrI, $HgBr_2$

values and intensities and comparing them with the known *d*-values of the expected compounds. Compounds identified in different mixtures of the reactions are given in Table II.

Results and Discussion

X-ray diffraction analysis (Table II) of 4 : 1 molar mixtures of CuI and HgClBr heated at 80°C for 3 days and then cooled to room temperature indicated the presence of CuCl, CuBr, and β-Cu_2HgI_4. This suggests the following reaction:

$$4CuI + HgClBr = CuCl + CuBr + Cu_2HgI_4. \quad (1)$$

However, in addition to the above products, HgI_2 was also detected in 4 : 1 molar samples analysed only after 1 hr of heating. In a kinetic experiment, described later, when a small amount of CuI was in contact with an excess of HgClBr and the reaction was allowed to proceed till the whole of the CuI was consumed, a red layer, identified as HgI_2, was formed on the CuI side. This evidences beyond doubt that the reaction takes place via the formation of HgI_2.

Electrical resistivity measurements (Fig. 1.1) on a 4 : 1 molar mixture of CuI and HgClBr show a sharp decrease, followed by a continuous rise in resistivity leading to a constant value. The presence of a minimum in the time–resistivity curve in the initial stages clearly suggests that the reaction represented by Eq. (1) passes through the formation of some intermediate product, which is immediately consumed to give a material of high resistivity. Since CuI is known to react fast (*4*) with HgI_2 to produce Cu_2HgI_4, which has very low resistance, it seems reasonable to presume that in the first step HgI_2 is formed rapidly through a simple exchange mechanism, followed by its conversion into Cu_2HgI_4.

The reaction can therefore be represented as

$$2CuI + HgClBr = CuCl + CuBr + HgI_2 \quad (1a)$$

$$2CuI + HgI_2 = Cu_2HgI_4 \quad (1b)$$

$$4CuI + HgClBr = Cu_2HgI_4 + CuCl + CuBr \quad (1)$$

This explains the initial fall in resistance but not the increase thereafter.

X-ray diffraction analysis of the 3 : 1 molar mixture of CuI and HgClBr showed the presence of HgI_2 in addition to CuCl, CuBr, and Cu_2HgI_4.

The electrical resistivity (Fig. 1.2) of a pellet made out of 3 : 1 molar mixture first increased, then decreased, followed by a rise and a final rapid fall. The information, just described, about the reaction sequence in a 4 : 1 molar mixture, coupled with resistivity measurements and the results of X-ray analysis of the 3 : 1 molar mixture, is suggestive of the following reaction mechanism:

$$2CuI + HgCl\,Br = CuCl + CuBr + HgI_2 \quad (2a)$$

$$2CuI + HgI_2 = Cu_2HgI_4 \quad (2b)$$

$$Cu_2HgI_4 + HgClBr = CuBr + CuCl + 2HgI_2 \quad (2c)$$

$$2CuI + HgI_2 = Cu_2HgI_4 \quad (2d)$$

$$6CuI + 2HgClBr = 2CuCl + 2CuBr + Cu_2HgI_4 + HgI_2 \quad (2)$$

Step (2a), being a simple exchange reaction, is very fast. The initial increase in resistivity pertains to the formation of highly resistive HgI_2 through step (2a); thereafter the decrease in resistivity is due to the formation of less resistive Cu_2HgI_4 through step (2b). The reaction of Cu_2HgI_4, formed in step (2b), with unreacted HgClBr produces the more resistive HgI_2, leading to the second rise in the time resistivity curve (Fig. 1.3).

Step (2c) was separately confirmed by heating an equimolar mixture of Cu_2HgI_4 and HgClBr. X-ray analysis of the product revealed it to be CuCl, CuBr, and HgI_2. The *d*-values of CuBr and CuCl do not match well with their standard *d*-values (*11*), probably due to the formation of a solid solution between CuBr and CuCl. The second rise and the final fall in resistivity are respectively due to steps (2c) and (2d).

Though the results of electrical resistivity measurements (Fig. 1.3) for a 2 : 1 molar mixture is similar to that obtained for a 3 : 1 molar mixture, the X-ray diffraction analysis of the products of this mixture points towards a different mechanism. This is probably due to the larger proportion of HgClBr in this mixture. The following interesting observation was made while we were trying to check reaction (3c) by placing the two reactants Cu_2HgI_4 and HgClBr side by side in a reaction capillary. Two thin layers, white and red, were formed. The red layer soon started dwindling and disappeared altogether, giving rise to a light yellow layer. The white and the yellow layers continued to grow with time. As the product layers were formed in between the reactants, the disappearance of red HgI_2 is presumed to be due to its secondary reaction with the incoming HgClBr. To check this hypothesis, HgI_2 was mixed with a double molar amount of HgClBr. The mixture was heated at 80°C and analyzed. $HgCl_2$ and HgBrI were the products. This reaction is therefore presumed to be

$$\begin{array}{l} HgI_2 + HgClBr = HgClI + HgBrI \\ HgClI + HgClBr = HgCl_2 + HgBrI \\ \hline HgI_2 + 2HgClBr = HgCl_2 + 2HgBrI \end{array}$$

On the basis of these experiments and their results, the resistivity behavior and the product analysis of a 2 : 1 molar mixture, the following reaction sequence is proposed in the 2 : 1 molar mixture:

$$2CuI + HgClBr = CuCl + CuBr + HgI_2 \quad (3a)$$

$$2CuI + HgI_2 = Cu_2HgI_4 \quad (3b)$$

$$Cu_2HgI_4 + HgClBr = CuBr + CuCl + 2HgI_2 \quad (3c)$$

HgI_2 reacts partly with HgClBr and partly with CuI:

$$HgI_2 + HgClBr = HgClI + HgBrI \quad (3d)$$

$$2CuI + HgI_2 = Cu_2HgI_4 \quad (3e)$$

$$6CuI + 3HgClBr = 2CuBr + 2CuCl + Cu_2HgI_4 + HgBrI + HgClI \quad (3)$$

Reaction (3d) was checked as follows. HgI_2 and HgClBr, in equimolar proportion, when heated at 80°C, turned yellow. On standing at room temperature, this again turned red and was analyzed as HgBrI, $HgCl_2$, and HgI_2.

Steps (3a) and (3b) are in accordance with the reaction occurring in the 4 : 1 molar mixture. Step (3c) produces HgI_2 and (3d) produces HgBrI and HgClI, which have comparatively high resistivity and thus account for the second increase in the time–resistivity curve. Step (3e) results in the regeneration of Cu_2HgI_4 and accounts for the final fall in the time–resistivity curve of the mixture. Since HgClI is not stable at room temperature, on standing it decomposed into $HgCl_2$ and HgI_2 (*12*), which showed up in the X-ray analysis.

The products identified by X-ray analysis, in a 1 : 1 molar mixture of CuI and HgClBr are CuCl, CuBr, HgI_2, $HgCl_2$, and HgBrI. The time–resistivity curve is somewhat simpler and has only one maximum. The first step, as before, appears to be the fast exchange reaction giving CuCl, CuBr, and HgI_2. This step, being as fast as exchange reactions normally are, did not show up in the time–resistivity curve (due to the time lag in preparation of the pellet and measurement of the resistance). HgI_2 produced in this step is consumed simultaneously by CuI and HgClBr, as represented by (4b) and (4c). Both reactions are fast, but due to the greater initial concentration of HgClBr, the reaction represented by (4c) is likely to dominate initially, which is reflected by the initial rise in the time–resistivity curve (Fig. 1.4). After a substantial decrease in the concentration of HgClBr, accumulation of Cu_2HgI_4 through (4b) dominates over its consumption through (4d), resulting in a sharp fall in resistivity. Thus overall reaction is represented by

$$2CuI + HgClBr = CuCl + CuBr + HgI_2 \quad (4a)$$

$$2CuI + HgI_2 = Cu_2HgI_4 \quad (4b)$$

$$HgI_2 + HgClBr = HgClI + HgBrI \quad (4c)$$

$$Cu_2HgI_4 + 2HgClBr = CuCl + CuBr + 2HgI_2 \quad (4d)$$

$$4CuI + 4HgClBr = 2CuCl + 2CuBr + HgClI + HgBrI \quad (4)$$

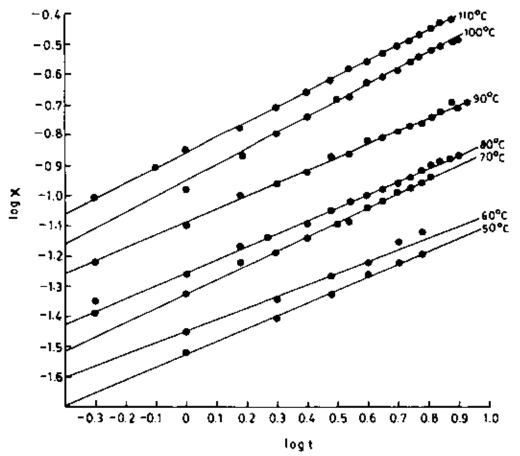

FIG. 2. Kinetic data for lateral diffusion and test for the equation $X^n = kt$ for the reaction between HgClBr and CuI.

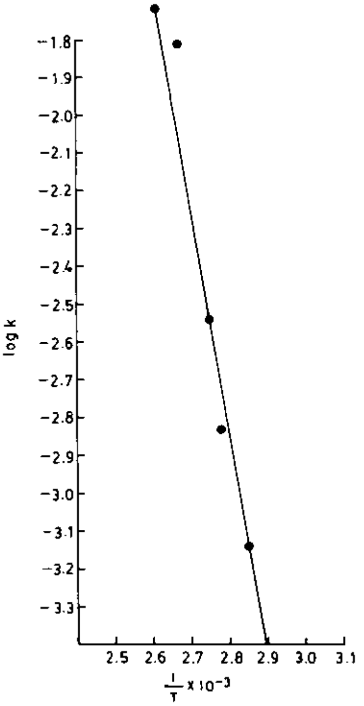

FIG. 3. Dependence of *k* on temperature for the reaction between HgClBr and CuI.

HgClI, unstable at room temperature, did not show up in the X-ray analysis as HgClI but as HgI_2 and $HgCl_2$.

Results of X-ray analysis (Table II) and electrical resistivity measurements (Fig. 1.5) with a 1 : 2 molar mixture of CuI and HgClBr suggest that the reaction in this case as well follows the same path as in the 1 : 1 molar mixture.

Mechanism of Lateral Diffusion

Soon after HgClBr was placed over CuI in the reaction capillary at 50°C, a red layer developed at the interface. The product layer grew with time toward the CuI side, which soon separated into red and light yellow layers. Later a gap developed between the light yellow product layer and HgClBr. When the experiment was repeated with air-gaps of varying length between the two reactants, the reaction proceeded in a similar way, giving the same kind of layers on the

CuI side as when the reactants were in contact. This shows that the mobile component is HgClBr and the air gap dimension did not affect the sequence of product layers. HgClBr reacts with CuI to produce CuCl, CuBr, and HgI_2. The latter then reacts with CuI to form colored Cu_2HgI_4. X-ray and chemical analyses of the different layers showed the following sequence of products in the reaction capillary:

$$CuI|Cu_2HgI_4, CuBr, CuCl|HgClBr.$$

The rate of growth of product layers decreased with time. Initially, the process was fast and reaction controlled. As the thickness of the product layers became significant HgClBr took more time to diffuse through the product layers. The process then became diffusion controlled and the rate of the reaction thus fell regularly with the growth of the product layers. The lateral diffusion data best fit (Fig. 2) the rate equation

$$X^n = kt, \qquad (5)$$

where X is the total thickness of the product layers at time t, k is a rate constant, and n is an exponent. The rate constant k follows the Arrhenius equation

$$k = A \exp(-E/RT). \qquad (6)$$

The activation energy evaluated from the log k versus $1/T$ plot (Fig. 3) made by the least-squares fit method was found to be 43.30 ± 0.53 kJ/mol. The rate constant measured with an initial air gap between the reactants decreased insignificantly with the increase in the length of the air gap. This simply implies that the rate constant does not vary with the increase in the length of the air gap. Hence, it is concluded that prior to diffusion, HgClBr exists in the vapor phase (*13*). The magnitude of the activation energy (*3*) coupled with the kinetic experiments with an initial air gap suggests that the reaction is diffusion controlled, taking place via the vapor phase.

Acknowledgment

The valuable assistance of Dr. Safia Mehdi, Scientist, X-Ray Division, IICT, Hyderabad, in X-ray diffraction studies is gratefully acknowledged.

References

1. J. A. HEDVALL, *J. Chem. Educ.* **30,** 638 (1953).
2. W. D. KINGERY, "Introduction to Ceramics," p. 67, Wiley, New York (1960).
3. R. P. RASTOGI, *J. Sci. Ind. Res.* **29,** 177 (1970).
4. M. A. BEG AND A. AHMAD, *Bull. Chem. Soc. Jpn.* **55,** 297 (1982).
5. M. A. BEG AND A. AHMAD, *Bull. Chem. Soc. Jpn.* **55,** 3607 (1982).
6. M. A. BEG, RAFIUDDIN, AND A. AHMAD, *J. Solid State Chem.* **80,** 94 (1989).
7. M. A. BEG AND S. M. ANSARI, *J. Solid State Chem.* **18,** 1 (1976).
8. M. A. BEG AND S. M. ANSARI, *J. Solid State Chem.* **23,** 409 (1978).
9. S. M. ANSARI AND S. MEHDI, *J. Solid State Chem.* **40,** 22 (1981).
10. R. P. RASTOGI AND B. L. DUBEY, *J. Am. Chem. Soc.* **89,** 200 (1967).
11. ASTM FILES 6-0292, 6-0344.
12. R. P. RASTOGI, B. L. DUBEY, AND N. D. AGARWAL, *J. Inorg. Nucl. Chem.* **37,** 1167 (1976).
13. B. L. DUBEY, AND N. TIWARI, *Bull. Chem. Soc. Jpn.* **65,** 495 (1992).