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Studies on the Interaction of CuI with HgClI in Solid State

SABA BEG*, AFAQ AHMAD, POOJA VARSHNEY and SARITA
Department of Chemistry, Aligarh Muslim University, Aligarh-202 002, India
E-mail: sababeg2003@yahoo.co.in

The reaction between CuI and HgClI in solid state has been studied by resistivity measurements, X-ray diffraction, reflectance and chemical analysis. The kinetics of the reaction has been studied by visual techniques. The reaction follows the rate law, $X^n = kt$, k's having the Arrhenius dependence. The reaction is diffusion controlled and is a multistep solid state ionic reaction initiated by the diffusion of HgClI molecules as such and not through counter diffusion of cations. The activation energy was found to be 56.423 ± 0.085 kJ/mol.

Key Words: Solid State, CuI, HgClI.

INTRODUCTION

Detailed studies of solid state reactions where more than one product is formed have generally not been studied due to their complexity. Evidence for the formation of $AgHgClI_2$ was first reported[1] during the study of solid state reaction between $HgCl_2$ and AgI. The reaction rate data[2] at 728–850°C for CuO-η-Al_2O_3 and CuO-γ-Al_2O_3 follow the Jander equation but have different activation energies, whereas α-alumina does not react up to 975°C. Ferric oxide does not dissolve in silica, but silica at its transition temperature dissolves ferric oxide to give a stable solid solution[3].

The present paper describes the kinetics and mechanism of the solid state reaction between CuI and HgClI. The X-ray studies show that the reaction takes place differently in different molar ratios. The reaction is multistep. A transitory scarlet red colour was obtained instantly on mixing the well powdered reactants due to the formation of HgI_2. When maintained at 80°C this reaction mixture turned chocolate brown due to the formation of Cu_2HgI_4. But later this turned brownish red due to the formation of HgI_2, CuCl and regeneration of Cu_2HgI_4 as end products.

EXPERIMENTAL

CuI was prepared following the methods[4, 5]. HgClI was obtained by heating for four days an equimolar mixture of $HgCl_2$ (BDH, AR) and HgI_2 (E. Merck) in the solid state in an air thermostat maintained at 100 ± 1°C.

Electrical resistivity measurements were made as reported elsewhere[6]. Powdered CuI and HgClI (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 400 lb pressure with a hydraulic press. Resistance measurements were made at 80°C by keeping the compressed disc between polished platinum electrodes mounted on a Teflon conductivity cell using an RLC Digi bridge (Gen Rad model 1659 USA) at a fixed frequency (10 kHz). The results are plotted against time for various molar mixtures in Fig. 1.

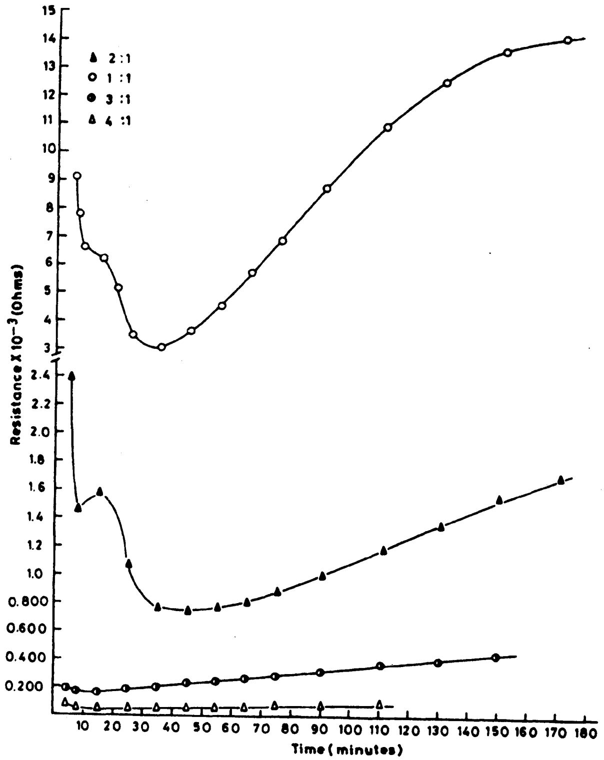

Fig. 1. Resistivity change as a function of time for the reaction between CuI and HgClI in different molar ratios

The kinetics of the reaction between CuI and HgClI was studied using the visual technique[6]. A weighed amount of HgClI was placed and pressed over a weighed and pressed CuI in a vertically held pyrex glass tube about 0.5 cm in diameter and the tube was placed in an air thermostat maintained at ±0.5°C. The thickness of the product layer formed at the interface was measured by a calibrated travelling microscope. Each experiment was run in triplicate and the average values were used to calculate the rate constants. The results are given in Table-1.

The X-ray diffratograms of CuI and HgClI mixed in different molar ratios were recorded by Norelco Geiger X-ray diffractometer (PW 1010 Philips) using CuK_α radiation with 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 three 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-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-2.

TABLE-1

TEMPERATURE DEPENDENCE OF PARAMETERS OF THE EQUATION $X^n = kt$

Temperature (°C ± 0.5)	k (cm/h)	Standard deviation	Relative standard deviation	n
60	1.055×10^{-3}	8.250×10^{-5}	5.95×10^{-2}	1.94
70	2.078×10^{-3}	3.207×10^{-4}	9.41×10^{-2}	1.97
80	3.583×10^{-3}	$1.784 x 10^{-4}$	2.97×10^{-2}	1.96
90	5.924×10^{-3}	3.490×10^{-4}	4.61×10^{-2}	1.98
100	1.196×10^{-2}	5.705×10^{-4}	3.78×10^{-2}	1.90
110	2.152×10^{-2}	2.380×10^{-3}	5.85×10^{-2}	1.90

TABLE-2

COMPOUNDS PRESENT IN DIFFERENT MOLAR MIXTURES OF CuI AND HgClI AFTER BEING HEATED AT 80°C FOR 3 DAYS AND THEREAFTER COOLING TO ROOM TEMPERATURE

Reactants molar ratios CuI : HgClI	Compounds identified
1 : 1	CuCl and HgI_2
2 : 1	CuCl, HgI_2 and Cu_2HgI_4
3 : 1	CuCl and Cu_2HgI_4
4 : 1	CuCl, CuI and Cu_2HgI_4

The reflectance measurements for the different molar mixtures of the reactants, heated previously at 80°C for three days were made at room temperature with Pye-Unicam PU 8800 UV/Vis spectrophotometer (Philips) using white standard as a reference material. The results are depicted in Fig. 2.

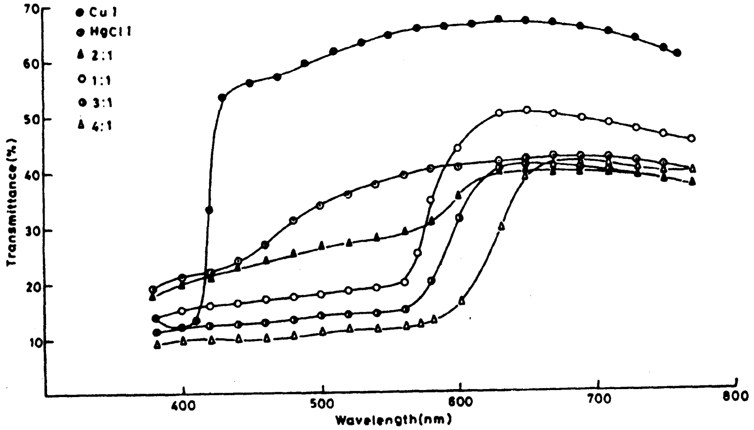

Fig. 2. Reflectance spectra for the reaction between CuI and HgClI in different molar ratios

RESULTS AND DISCUSSION

In order to understand the reaction between CuI and HgClI, two aspects must be considered: (i) mechanism of chemical interaction when the reactants are intimately mixed and (ii) the mechanism of lateral diffusion when the experiments are carried out in a capillary under isothermal conditions.

Mechanism of chemical interaction

X-ray patterns of reactants mixed in different ratios suggest that HgClI and CuI react somewhat differently in different molar mixtures. The X-ray analysis of the 1 : 1 molar mixtures heated at 100°C for three days prior to analysis showed the presence of CuCl and HgI_2. The reflectance curve is simple but the resistivity curve suggests it to be a multistep reaction. The initial fall in resistance may be due to consumption of more resisting HgClI to give much less resisting CuCl and HgI_2, through the exchange reaction

$$\mathrm{CuI + HgClI \longrightarrow CuCl + HgI_2} \qquad (1a)$$

Immediately on mixing the reactants transitory change to scarlet red colour is indicative of HgI_2 formation. Reaction (1a) goes well with the principle[7] of larger cations going well with larger anions and smaller cations with smaller anions. The subsequent rise in resistance is due to the conversion of poorly resisting CuI to Cu_2HgI_4[8] imparting chocolate brown colour to the mixture. Cu_2HgI_4 is red below 70°C (β-form) and chocolate brown above 70°C (α-form)[9].

As Cu_2HgI_4 is consumed by HgClI, it is not present in the end product analysis. The end product is orange in colour due to HgI_2 and CuCl. X-ray results, sequence of colour change, reflectance and resistivity curves are suggestive of the following mechanism:

$$\begin{array}{rcll}
\mathrm{CuI + HgClI} & \longrightarrow & \mathrm{CuCl + HgI_2} & (1a)\\
\mathrm{2CuI + HgI_2} & \longrightarrow & \mathrm{Cu_2HgI_4} & (1b)\\
\mathrm{HgClI + Cu_2HgI_4} & \longrightarrow & \mathrm{CuCl + CuI + 2HgI_2} & (1c)\\
\hline
\mathrm{2CuI + 2HgClI} & \longrightarrow & \mathrm{2CuCl + 2HgI_2} &
\end{array}$$

The reflectance curve for 2 : 1 molar mixture is somewhat similar to that of 1 : 1 mixture. The X-ray analysis of the 2 : 1 molar mixture showed the presence of Cu_2HgI_4 in addition to CuCl and HgI_2. The resistance initially decreases due to consumption of highly resisting HgClI and then increases due to conversion of CuI to Cu_2HgI_4. After attaining a maximum the resistance falls to rise again gradually. On the basis of X-ray analysis, resistivity and sequence of colour changes, the following mechanism is suggested.

$$\begin{array}{rcll}
\mathrm{CuI + HgClI} & \longrightarrow & \mathrm{CuCl + HgI_2} & (1a)\\
\mathrm{2CuI + HgI_2} & \longrightarrow & \mathrm{Cu_2HgI_4} & (1b)\\
\mathrm{HgClI + Cu_2HgI_4} & \longrightarrow & \mathrm{CuCl + CuI + 2HgI_2} & (1c)\\
\mathrm{HgI_2 + 2CuI} & \longrightarrow & \mathrm{Cu_2HgI_4} & (1d)\\
\hline
\mathrm{4CuI + 2HgClI} & \longrightarrow & \mathrm{Cu_2HgI_4 + 2CuCl + HgI_2} &
\end{array}$$

X-ray analysis of the product of 3 : 1 molar mixture showed it to be Cu_2HgI_4 and CuCl suggesting the over all reaction to be

$$3CuI + HgClI \longrightarrow Cu_2HgI_4 + CuCl$$

However, as the reaction proceeds at higher temperature, the reaction mass turns from red to chocolate colour. Even at higher temperatures red coloured crystals were present in the chocolate brown material. To identify this material, experiments in capillary were carried out with very large excess of HgClI. Whole of CuI was consumed; a red layer was formed towards CuI side in the reaction tube. This red layer was identified to be HgI_2 by X-ray analysis. This further confirms that the HgI_2 formed during the course of the reaction reacts further with CuI. Hence, it is concluded that the reaction proceeds through the formation of HgI_2. This was also confirmed as the reaction mixture immediately turned scarlet red on mixing. The resistivity measurements (Fig. 1) show that initially there is small decrease in resistance and then a gradual increase. Therefore, it is suggested that the reaction takes place in two steps: first is the formation of red HgI_2 followed by its quick consumption to give chocolate brown Cu_2HgI_4. In view of these, the following mechanism is proposed for 3 : 1 molar mixture of the reactants.

$$CuI + HgClI \longrightarrow CuCl + HgI_2 \quad (1a)$$

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

$$\overline{3CuI + HgClI \longrightarrow CuCl + Cu_2HgI_4}$$

The step (1b) has already been reported[10] to be taking place very fast. Here the reaction does not proceed beyond (1b) because the HgClI for step (1c) is not available. Hence, the reaction apparently stops after (1b). Under the law of mass action, excess CuI makes fast reactions (1a) and (1b) much faster, with the result that the reaction probably reaches completion before the resistivity measurements could be started; hence the resistivity curve is almost parallel to the time axis.

The X-ray analysis of the end product of the 4 : 1 molar mixture of CuI and HgClI showed the presence of CuCl, Cu_2HgI_4 and unreacted CuI. This and other evidences indicate that the reaction in this case proceeds as in 3 : 1 molar mixture.

Mechanism of lateral diffusion

Soon after placing HgClI over CuI in the reaction capillary at 50°C, scarlet red coloured layer developed at the interface. The product grew with time towards the CuI side. A gap developed between the white layer and HgClI. When the experiment was repeated with an air-gap of varying dimensions between the two reactants, the reaction proceeded in a similar way giving the same kinds of layers on CuI side as was the case when the reactants were in contact. The dimensions of the air-gap did not affect the sequence of the layers. This shows that the mobile component is HgClI. HgClI molecules react with CuI to form three coloured products. X-ray and chemical analysis of the different layers thus formed showed the following sequence of products in the reaction capillary.

CuI	HgI_2	Cu_2HgI_4	CuCl	HgClI
Cream colour	Red	Chocolate	White	Yellow
		(Red below 70°C)	(Orange below 25°C)	

The rate of growth of product layers decreases with time. Initially, the process is fast and the reaction controlled. As the thickness of the product layers becomes significant, HgClI takes greater time to diffuse through the product layers. The process now becomes diffusion controlled and the rate of the reaction thus falls regularly with the growth of the product layers. The lateral diffusion data best fit the rate equation (Fig. 3)

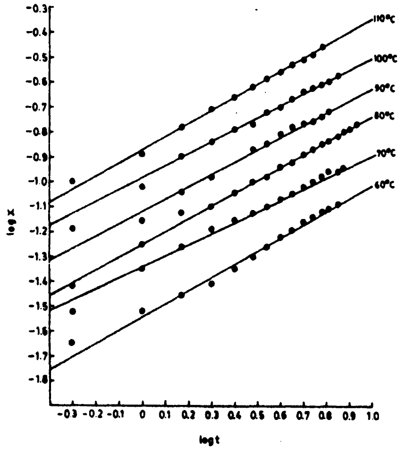

Fig. 3. Kinetic data for lateral diffusion and test for equation $X^n = kt$ for the reaction between HgClI and CuI

$$X^n = kt,$$

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

$$k = A \exp(-E_a/RT).$$

The activation energy evaluated from the log k *vs.* 1/T plot (Fig. 4) made by least square fit method was found to be 56.423 ± 0.085 kJ/mol.

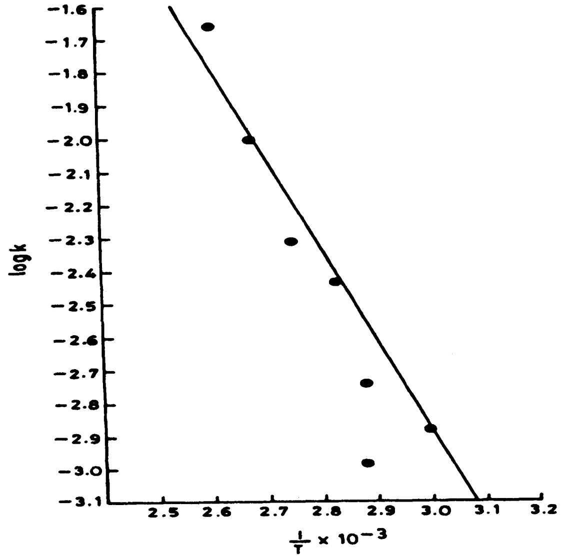

Fig. 4. Dependence of k on temperature for the reaction between HgClI and CuI

The reaction rate constant measured with an initial air gap between the reactants decreased with an increase in the length of the air gap. The energy of activation suggests that the reaction is diffusion controlled.

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