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Studies on the Interaction between Mercury(II) Chloride and Copper(I) Halides in Solid State

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Kinetics and mechanism of $HgCl_2$–CuI and $HgCl_2$–CuBr reactions were studied in solid state. It has been demonstrated that $HgCl_2$ reaches CuI by surface migration and the reaction proceeds through counter diffusion of Cu^+ and Hg^{2+}. Both the reactions follow the parabolic rate law and the activation energies are 77.11 ± 3.84 and 51.08 ± 1.29 kJ/mol. While the former is a complex multi-stage reaction, the latter is a simple exchange process.

Like Ag_2HgI_4, Cu_2HgI_4 is also known to be formed from the reaction of CuI and HgI_2 in solid state[1] but neither the kinetics and mechanisms of this reaction nor the interaction of CuI with other mercury(II) halides seem to be reported. In an attempt to obtain some new solid state materials and mixed halide complexes like $AgHgClI_2$ and $AgHgCl_2I$ formed in solid state[2], we studied the reaction of $HgCl_2$ with CuI and CuBr in solid state. Though the expected mixed halides could not be detected, the information obtained on the mechanistic aspect is worth reporting. The reaction of $HgCl_2$ with CuI is multi-step, and different molar ratios of reactants give rise to different products, HgI_2 being formed as an intermediate in all cases. Contrary to the above, $HgCl_2$–CuBr reaction is a simple exchange process. Formation of several solid solutions among the reactants and products were also noted.

Experimental

Materials. $HgCl_2$ (BDH, AR Grade) was used without further purification. Copper(I) iodide and copper(I) bromide, being photosenstive, were prepared afresh for each set of experiments following the methods of Berthemot,[3] Guichard[4] and Lean and Whatmough.[5] X-Ray patterns of the products showed them to be single phase γ-CuI[6] and γ-CuBr.[7]

Cu_2HgI_4 was prepared as reported elsewhere.[8] Its X-ray pattern showed it to be single phase β-Cu_2HgI_4.[9]

Rate Measurements. The kinetics of the reactions were studied by placing mercury(II) chloride over copper(I) halides (each above 300 mesh size) in a vertically held glass tube described elsewhere[10,11] (The readability of the microscope was 0.001 cm and the average deviation of the measured values was ± 0.00043 cm). Each experiment was performed in triplicate and the average of the three respective values was taken as the thickness of the product.

X-Ray Studies. Different molar mixtures of the reacants (above 300 mesh size) were mixed thoroughly in an agate mortar. One part of each mixture was heated in an air thermostat at 120 ± 0.05 °C, while the other was kept at 25 °C. Each set of mixtures was analysed, after about 60 h by Norelco Geiger Counter Diffractometer using Cu $K\alpha$ radiations with a Ni-Filter, applying 32 kV at 12 mA. The compounds present were identified by calculating the d values and comparing them with the standard values of the expected compounds.

Thermal Studies. Weighed amounts of $HgCl_2$ and CuI in molar ratios 1:4, 1:3, 1:2, and 1:1 were mixed in a Dewar flask, and the rise in temperature was noted against time. Similarly, thermal studies were carried out with different molar mixtures of $HgCl_2$ and CuBr. Same proportions of $HgCl_2$ and CuX (X is Br^- or I^-) as weighed for thermal studies were weighed separately, mixed thoroughly and pressed into tablets. Conductance of each tablet was measured by current ratio I–C bridge, applying 0.2 V and frequency 5×10^3 Hz.

TABLE 1. DEPENDENCE OF PARABOLIC RATE CONSTANT ON TEMPERATURE FOR CuI–$HgCl_2$ REACTION

Temperature / °C	K/cm h^{-1}
80	4.01×10^{-9}
95	11.11×10^{-9}
110	23.33×10^{-9}
115	43.25×10^{-9}
121	80.00×10^{-9}

TABLE 2. DEPENDENCE OF PARABOLIC RATE CONSTANT ON TEMPERATURE FOR CuBr–$HgCl_2$ REACTION

Temperature / °C	K/cm h^{-1}
75	0.4×10^{-7}
85	0.72×10^{-7}
96	1.11×10^{-7}
101	1.50×10^{-7}
107	1.75×10^{-7}

Results and Discussion

It is clear from Tables 3 and 4 that $HgCl_2$ reacts differently with CuBr and CuI.

CuI–$HgCl_2$ Reaction. CuI reacts with $HgCl_2$ in 4:1 molar ratio, giving Cu_2HgI_4 and CuCl.

$$4CuI + HgCl_2 \longrightarrow 2CuCl + Cu_2HgI_4 \quad (1)$$

Thermal (Fig. 1) as well as conductance (Fig. 2) measurements carried out at 25 °C provided no evidence for any sub-step in this reaction. However, the presence of HgI_2 (Table 3) in addtion to CuCl and Cu_2HgI_4 in the mixture kept at 25 °C, is indicative of the fact that HgI_2 is first formed:

$$2CuI + HgCl_2 \longrightarrow 2CuCl + HgI_2, \quad (1a)$$

which subsequently disappears giving Cu_2HgI_4 through (1b)

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

Table 3. X-Ray diffraction analyses of $CuI-HgCl_2$ reaction mixtures

Molar ratio $CuI : HgCl_2$	Compounds identified in mixtures	
	Kept at 25 °C	Heated at 120 °C and then cooled to 25 °C
4 : 1	CuCl, Cu_2HgI_4, and HgI_2	CuCl and Cu_2HgI_4
3 : 1	CuCl, Cu_2HgI_4, and HgI_2	CuCl, Cu_2HgI_4, and HgI_2
2 : 1	CuCl, Cu_2HgI_4, and HgI_2	CuCl and HgI
1 : 1	CuCl, Cu_2HgI_4, HgI_2, and $HgCl_2$	CuCl, HgI_2, and $HgCl_2$
1 : 2	CuCl, HgI_2, and $HgCl_2$	CuCl, HgI_2, and $HgCl_2$

Table 4. X-Ray diffraction analyses of $CuBr-HgCl_2$ reaction mixtures

Molar ratio $CuBr : HgCl_2$	Compounds identified in mixtures	
	Kept at 25°C	Heated at 120 °C and then cooled to 25 °C
4 : 1	CuBr, CuCl, and $HgBr_2$	CuBr, CuCl, and $HgBr_2$
3 : 1	CuBr, CuCl, and $HgBr_2$	CuBr, CuCl, and $HgBr_2$
2 : 1	$HgBr_2$ and CuCl	CuCl and $HgBr_2$
1 : 1	CuCl, $HgCl_2$, CuBr, $HgBr_2$, and $HgCl_2$	CuCl and HgClBr
1 : 2	CuCl, HgClBr, $HgBr_2$, and $HgCl_2$	CuCl, HgClBr, and $HgCl_2$

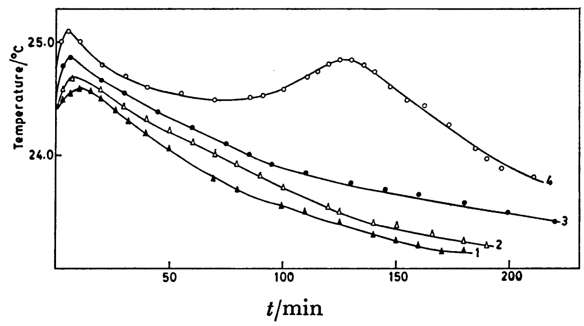

Fig. 1. Temperature rise as a function of time for CuI and $HgCl_2$ reaction.
Molar ratios (1) 4:1, (2) 3:1, (3) 2:1, (4) 1:1.

As reaction (1b) is extremely fast, disappearance of HgI_2 through (1c) looks improbable:

$$HgCl_2 + HgI_2 \longrightarrow 2HgClI. \quad (1c)$$

However, at higher temperature, reaction (1c) is known to occur appreciably, but on cooling the product HgClI decomposes immediately into its components.[12)]

An equimolar mixture of HgI_2 and $HgCl_2$ kept at 25 °C did not show any evidence for the formation of HgClI even after about 6 d. Hence, the possibility that HgI_2 is consumed by $HgCl_2$ through step (1c) is completely ruled out. The overall reaction in 4:1 molar mixture of CuI and $HgCl_2$ will therefore, be as follows:

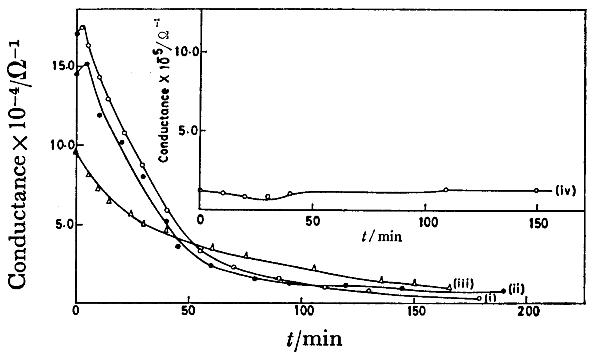

Fig. 2. Change in conductance as function of time for CuI and $HgCl_2$ reaction.
Molar ratios (i) 4:1, (ii) 3:1, (iii) 2:1, (iv) 1:1.

$$2CuI + HgCl_2 \longrightarrow 2CuCl + HgI_2 \quad \text{(Slow)}$$
$$2CuI + HgI_2 \longrightarrow Cu_2HgI_4 \quad \text{(Fast)}$$
$$4CuI + HgCl_2 \longrightarrow Cu_2HgI_4 + 2CuCl$$

The results of thermal (Fig. 1) and conductance (Fig. 2) measurements made with 3:1 molar mixture are similar to those obtained with 4:1 molar mixture. The presence of HgI_2 in 3:1 molar mixture even at higher temperature confirms the above view point and it is detected here in the end products because CuI in these mixture is not sufficient to convert whole of HgI_2 into Cu_2HgI_4. Hence, the overall reaction in 3:1 molar mixture is as follows:

$$4CuI + 2HgCl_2 \longrightarrow 2HgI_2 + 4CuCl \quad (2a)$$
$$2CuI + HgI_2 \longrightarrow Cu_2HgI_4 \quad (2b)$$
$$6CuI + 2HgCl_2 \longrightarrow Cu_2HgI_4 + HgI_2 + 4CuCl$$

The X-ray analysis of the products of 2:1 molar mixture of CuI and $HgCl_2$ heated at 120 °C and cooled to 25 °C indicated the presence of only CuCl and HgI_2.

$$2CuI + HgCl_2 \longrightarrow 2CuCl + HgI_2 \quad (3)$$

The thermal (Fig. 1) curve for 2:1 molar mixture of CuI and $HgCl_2$ has only one inflection. It thus appears that this is a simple exchange reaction. The X-ray analysis of this mixture kept at 25 °C did show the presence of Cu_2HgI_4 but the one that was heated to 120 °C and then cooled to 25 °C did not indicate the presence of Cu_2HgI_4. It is presumed that Cu_2HgI_4 is consumed at higher temperature by the excess $HgCl_2$ present in this mixture:

$$Cu_2HgI_4 + HgCl_2 \longrightarrow 2HgI_2 + 2CuCl. \quad (3a)$$

This was confirmed by heating an equimolarmixture of Cu_2HgI_4 and $HgCl_2$ at 120 °C. The X-ray analysis showed only the presence of HgI_2 and CuCl. Hence, the overall reaction sequence for 2:1 molar ratio at high temperatures is as follows:

$$2CuI + HgCl_2 \longrightarrow HgI_2 + 2CuCl \quad (3a)$$
$$2CuI + HgI_2 \longrightarrow Cu_2HgI_4 \quad (3b)$$
$$Cu_2HgI_4 + HgCl_2 \longrightarrow 2HgI_2 + 2CuCl \quad (3c)$$
$$4CuI + 2HgCl_2 \longrightarrow 2HgI_2 + 4CuCl$$

Product analysis of 1:1 molar mixture of CuI and $HgCl_2$ heated to 120 °C (Table 3) indicated that CuCl and HgI_2 are the final products. The presence of Cu_2HgI_4 in addition to CuCl, HgI_2, and $HgCl_2$, in the 1:1 mixture kept at room temperature (25 °C) indicated that the reaction is multi-step. Thermal (Fig. 1) and conductance (Fig. 2) measurements at room temperature did show two maxima in the curves.

The first inflection in the curve may be due to the formation of HgI_2 and its subsequent elimination by excess of CuI giving Cu_2HgI_4, both the steps being fast.

$$2CuI + HgCl_2 \longrightarrow 2CuCl + HgI_2 \quad (4a)$$

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

The second inflection in the curve may be due to the fact that presence of $HgCl_2$ pushes the reaction (3c) to an appreciable extent. This reaction, however, does not occur to an appreciable extent in 2:1 and other molar mixtures at the room temperature, hence the second inflection does not show up. This viewpoint is confirmed by the fact that Cu_2HgI_4 is completely consumed and is not detected even at room temperature in 1:2 mixture (Table 3).

1:1 Molar mixture of CuI and $HgCl_2$, kept at 120 °C, turns yellow after some time which on cooling to room temperature changes into red. HgClI is light yellow and stable at high temperature, and decomposes into HgI_2 and $HgCl_2$ when brought to room temperature.[12)]

$$HgI_2 + HgCl_2 \xrightarrow{120°C} 2HgClI \xrightarrow{\text{cooled}} HgI_2 + HgCl_2 \quad (4d)$$

Hence, the overall reaction sequence in 1:1 molar mixture will be as follows:

$$2CuI + HgCl_2 \longrightarrow HgI_2 + 2CuCl \quad (4a)$$

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

$$Cu_2HgI_4 + HgCl_2 \longrightarrow 2CuCl + 2HgI_2 \quad (3c)$$

$$2HgCl_2 + 2HgI_2 \longrightarrow 4HgClI \quad (4d)$$

$$4CuI + 4HgCl_2 \longrightarrow 2HgI_2 + 2HgCl_2 + 4CuCl \quad (4d')$$

The X-ray analysis of 1:2 molar mixtures of CuI and $HgCl_2$ (Table 3) showed the presence of CuCl, HgI_2, and $HgCl_2$. By all account, the reaction sequence occurring in this mixture is the same as that in 1:1 molar mixture.

CuBr–$HgCl_2$ Reaction. CuBr reacts with $HgCl_2$ in 2:1 molar ratio giving CuCl and $HgBr_2$ (Table 4).

$$2CuBr + HgCl_2 \longrightarrow 2CuCl + HgBe_2 \quad (5)$$

Product analysis (Table 4) suggests that the reaction sequence in 4:1 and 3:1 molar mixtures is the same as in 2:1 molar mixture. CuBr in excess over 2:1 stoichiometry is left as such. Thermal (Fig. 3) and conductance (Fig. 4) measurements also support this view.

The products obtained in 1:1 molar mixture heated at 120 °C are CuCl and HgClBr (Table 4). In addition to these, the room temperature mixture shows $HgCl_2$ and $HgBr_2$.

The occurrence of second inflection in thermal (Fig. 3) as well as in conductance (Fig. 4) curves clearly shows that this is a two step reaction. The first step in this case as well, may be the formation of $HgBr_2$ through the simple exchange reaction (5). The second inflection refers to the consecutive reaction of $HgBr_2$ with the remaining amount of $HgCl_2$ in the reaction mixture giving HgClBr[12)] through the much slower step:

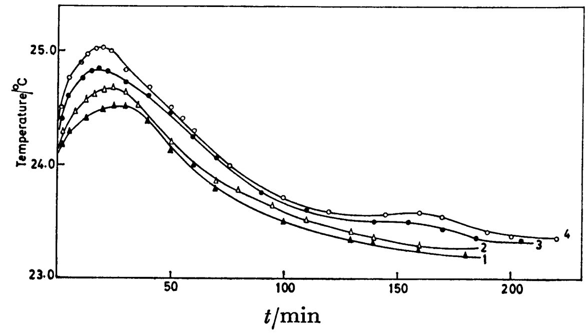

Fig. 3. Temperature rise as a function of time for CuBr–$HgCl_2$ reaction.
Molar ratios (1) 4:1, (2) 3:1, (3) 2:1, (4) 1:1.

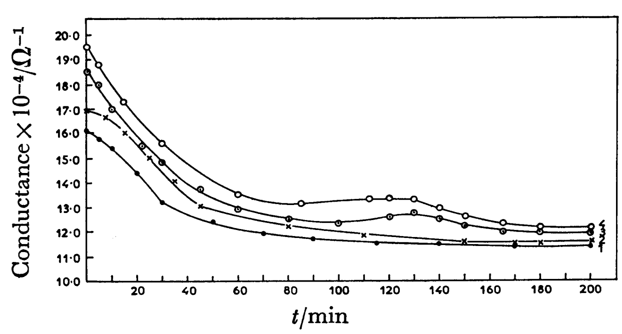

Fig. 4. Change in conductance as function of time for CuBr and $HgCl_2$ reaction. Molar ratios (1) 4:1, (2) 3:1, (3) 2:1, (4) 1:1.

$$HgCl_2 + HgBr_2 \longrightarrow 2HgClBr. \quad (6)$$

In case of 1:2 molar mixture, still larger proportion of $HgCl_2$ pushes reaction (6) to a still greater extent, making the second inflection slightly more pronounced. Hence, the complete reaction may be written as follows:

$$2CuBr + HgCl_2 \longrightarrow 2CuCl + HgBr_2$$

$$HgBr_2 + HgCl_2 \longrightarrow 2HgClBr$$

$$2CuBr + 2HgCl_2 \longrightarrow 2CuCl + 2HgClBr$$

Formation of HgClBr in earlier cases did not occur probably due to lesser proportion of $HgCl_2$ in the mixture.

Mechanism of Lateral Diffusion: In the kinetic experiment of the CuI–$HgCl_2$ system, soonafter the placement of $HgCl_2$ over CuI in the reaction tube, a dark brown layer appeared at the interface, which increased on CuI side with time, separating later into white and brown layers. On cooling to room temperature, the dark brown layer changed to scarlet red (Cu_2HgI_4 is dark brown above 70 °C and scarlet red below this temperature.[13)] The analyses of the white and scarlet product layer at room temperature revealed them to be CuCl and β-Cu_2HgI_4. In the CuBr–$HgCl_2$ system also, the layer appearing at the interface increased on CuBr side and later separated into white and very light yellowish layers. They were analysed for CuCl and HgClBr.

The growth rate of the thickness of the product layer in either case when reactants were in contact, follow the parabolic rate equation, $X^2=Kt$. The parabolic rate constant, K, in each case follows Arrehenius equation (Tables 1 and 2). The activation energies for the two reactions are respectively 77.11±3.84 and 51.08±1.29 kJ/mol.

The formation of the product on copper(I) halide side in another lateral diffusion experiment, where the reactants were placed with an air gap in between and the high vapour density of $HgCl_2$ suggest the possibility of vapour phase reaction. However, in a set of lateral diffusion experiments, the rate of product growth was found to decrease with increase in the length of the air gap. This fact and also the magnitude of activation energy[14] show that these reactions proceed through surface migration. The reaction continues *via* counter diffusion of Cu^+ and Hg^{2+} through the product layers.

Product analyses by X-ray diffraction, indicated the formation of solid solutions between CuI–CuCl, CuCl–Cu_2HgI_4, and CuBr–CuCl.

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