

HgCl₂-AgI Reaction in Solid State

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Ag HgClI₂ and Ag HgCl₂I were obtained by the interaction of HgCl₂ and AgI in the solid state at 100°C. A diffusion-controlled HgCl₂-AgI reaction proceeds via counterdiffusion of Ag⁺ and Hg²⁺ and its activation energy is 23.90 kcal/mole. At the start, the process is surface or grain boundary diffusion-controlled having an activation energy of 8.32 kcal/mole. Different molar ratios of the reactants gave rise to different end products. The reaction was followed by X-ray, chemical analysis, thermal, conductivity measurements. Evidence for the formation of solid solution between Ag₂HgI₄ and AgCl is reported.

Introduction

Raman spectra (1) for aqueous solutions of HgX₂ + KX (X = Cl, Br, or I) indicated the existence of tetrahedral HgX₄²⁻ anions and mixed bromoiodide complexes of the type HgI₃Br²⁻, HgI₂Br₂²⁻, and HgIBr₃²⁻. Evidence for the existence of HgCl₄²⁻ and HgCl₃⁻ in melts (2) was also provided by Raman's spectroscopy. The existence in the solid state (3) of mixed halide complexes of mercury of coordination numbers 3 and 4, based on thermodynamic considerations, was also proposed about the same time. Otherwise our knowledge is scant except for Ag₂HgI₄, which has a very high electrical conductivity (4) and is easily formed in both solution and the solid state. On the basis of this and our findings (5, 6) of solid solutions in HgBrI-AgI and HgBr₂-AgI systems, we have studied HgCl₂-AgI solid-state reactions in the hope that chloroiodide complexes of mercury could be proposed.

It has been observed that the rate of HgCl₂-AgI reaction is diffusion-controlled. Gaseous HgCl₂ diffuses through product layers and, at the reaction interface, the counterdiffusion of Ag⁺ and Hg²⁺ takes place with simultaneous

separation of AgCl and Ag₂HgI₄ layers. This reaction is multistep and gives rise to two new complexes, AgHgCl₂I and AgHgClI₂. The miscibility of Ag₂HgI₄ in AgCl has also been investigated.

Experimental

HgCl₂ (BDH, A.R.) and HgI₂ (E. Merck) were used without further purification. γ-AgI and Ag₂HgI₄ were prepared as before (5).

AgHgClI₂ was prepared in solid state by heating a powdered mixture of HgCl₂, HgI₂, and AgI (above 300 mesh), in 1:1:2 molar ratio, in a sealed tube for 5 days at 100°C. The product was yellow and had a sharp melting point¹ (145°C). The X-ray pattern (Table I) showed it to be a single-phase orthorhombic system having unit cell dimensions: *a* = 8.658 Å, *b* = 9.599 Å, *c* = 14.26 Å.

AgHgCl₂I was prepared by heating a 1:1 molar mixture of HgCl₂ and AgI in a sealed tube for 5 days at 100°C. The bright yellow material melted sharply at 134°C. The X-ray

¹ Melting point was determined by KOFLAR micro-hot stage, Austria.

TABLE I
X-RAY DATA FOR AgHgCl_2^a

d (Å)	I/I_0	hkl	d (Å)	I/I_0	hkl
7.132	12	002	2.185	24	314
4.792	12	020	2.099	78	240
4.329	19	200	2.093	46	411
4.277	7	013	2.012	6	242
3.973	100	022	1.962	44	403
3.559	9	004	1.955	23	421
3.477	14	212	1.920	22	243
3.290	8	104	1.915	14	226
3.211	10	220	1.886	12	027
3.097	76	114	1.763	9	250,431
3.025	32	213	1.738	27	432
2.990	22	130	1.734	14	500
2.846	29	005	1.612	15	521,440
2.786	18	132	1.550	6	345
2.569	12	230	1.545	7	523
2.388	9	312,224	1.461	11	247,064
2.376	15	006	1.458	6	354
2.371	9	041	1.422	8	229
2.189	38	323	1.385	10	516

^a $\lambda = 1.5405$ Å.

TABLE II
X-RAY DATA FOR AgHgCl_2I PRODUCT OF HgCl_2 - AgI REACTION (1:1) AT 100°C^a

d (Å)	I/I_0	hkl	d (Å)	I/I_0	hkl
5.980	14	110	2.384	22	104
4.396 ^b	34		2.279	14	114
2.247	52	200	2.215 ^c	12	223
4.111 ^{b,c}	22		2.125	11	322
3.897	47	201	2.079	17	313
3.500 ^c	14		2.000	50	330
3.398 ^b	17		1.960 ^d	72	331
3.276	47	003	1.920	11	105
3.206 ^d	53	202	1.883	10	420
3.035 ^c	21	103	1.868	11	115
2.778 ^{c,d}	100		1.708	12	333
2.727	17	301	1.679 ^d	19	431,501
2.680	8	310	1.607 ^d	19	404
2.597	14	203	1.538	12	206
2.459	17	004			

^a $\lambda = 1.5405$ Å.

^b Corresponds to HgCl_2 (7).

^c Corresponds to HgI_2 (8).

^d Corresponds to AgCl (9).

TABLE III
COMPOUNDS PRESENT IN HgCl₂-AgI REACTION MIXTURE AFTER COMPLETION OF THE REACTION

Mixture	Molar ratio of HgCl ₂ and AgI	Compounds identified in mixture	
		Maintained at 30°C	Maintained at 100°C
a	1:4	Ag ₂ HgI ₄ , AgCl	Ag ₂ HgI ₄ , AgCl
b	1:3	Ag ₂ HgI ₄ , HgI ₂ , AgCl	Ag ₂ HgI ₄ , AgHgClI ₂ , AgCl
c	1:2	HgI ₂ , AgCl	AgHgClI ₂ , AgCl
d	1:1	HgCl ₂ , HgI ₂ , AgCl	AgHgCl ₂ I, HgCl ₂ , HgI ₂ , AgCl

pattern (Table II) contains lines for AgHgCl₂I and HgCl₂, HgI₂, and AgCl. The data suggest that AgHgCl₂I is tetragonal having unit cell dimensions: $a = 8.494 \text{ \AA}$, $c = 9.828 \text{ \AA}$.

Reaction rate, X-ray studies² of different molar mixtures of HgCl₂ and AgI at 30 and 100°C (Table III), thermal and electrical conductivity³ measurements, and chemical analyses of the product layers formed in lateral diffusion experiments were made as described earlier (5). Rate constants calculated at various temperatures are listed in Table IV.

Results and Discussion

In a 1:4 molar HgCl₂-AgI reaction, Ag₂HgI₄ and AgCl were the end products, both at 30 and 100°C:



Although thermal (Fig. 1(1)) and electrical conductivity (Fig. 2(1)) measurements with a 1:4 molar mixture do not offer any evidence for the existence of a substep of the process, at 30°C, the yellow reaction mixture changed to yellowish orange, then to reddish, and finally back to yellowish orange. The transitory appearance of the reddish color during the progress of the reaction is presumed to be due

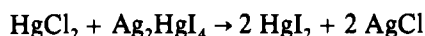
² By "Norelco Geiger" counter X-ray diffractometer using CuK α radiation applying 32 kV at 12 mA with a Ni filter.

³ By current ratio I.C. Bridge applying 0.2 V (rms) at frequency $2 \times 10^3 \text{ Hz}$.

TABLE IV
TEMPERATURE DEPENDENCE OF PARAMETERS OF THE EQUATION $X_t^n = kt$, FOR THE HgCl₂-AgI REACTION

Temperature (°C \pm 0.5)	k (cm/hr)	n
65.0	8.89×10^{-9}	3.3
72.5	18.97×10^{-9}	
81.5	37.58×10^{-9}	
89.5	100.90×10^{-9}	
99.0	159.20×10^{-9}	
106.5	367.30×10^{-9}	

to the formation of red HgI₂ through the side reaction



and its subsequent consumption through its reaction with unreacted AgI:



The X-ray analyses showed that the d values for Ag₂HgI₄ had decreased while those for AgCl had increased (Table V). The miscibility of Ag₂HgI₄ and AgCl may arise because the AgCl can develop vacant cationic sites and Ag₂HgI₄ can take in cations into cationic site vacancies, associated with the exchange equilibrium between Ag⁺ and Hg²⁺.

A 1:2 molar mixture of HgCl₂ and AgI at 30°C first changed to yellowish orange and then gradually to red. The X-ray pattern of the red material showed the presence of HgI₂ and

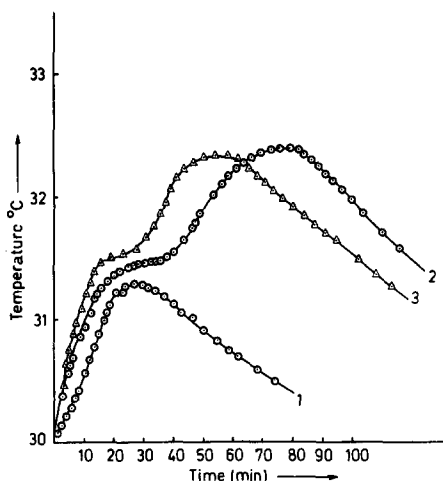


FIG. 1. Temperature rise as a function of time for the reaction between HgCl_2 and AgI . Molar ratios are: (1) 1:4, (2) 1:2, and (3) 1:1.

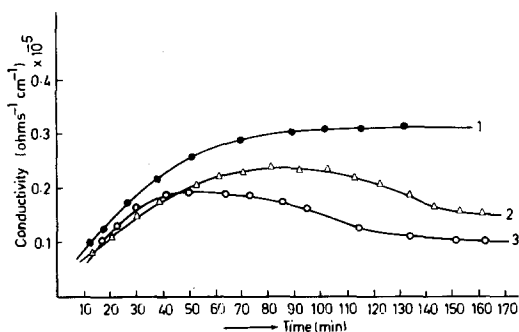
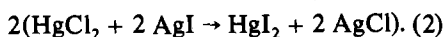
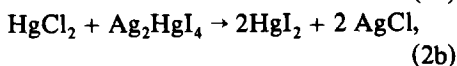
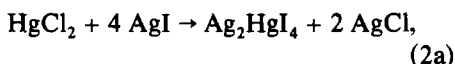


FIG. 2. Variation of conductivity with time for the reaction between HgCl_2 and AgI at 30°C . Molar ratios are: (1) 1:4, (2) 1:2, and (3) 1:1. Applied voltage, 0.2 V (rms); frequency 2×10^3 Hz.

AgCl . The sequence of color changes and X-ray analyses suggest the following reactions:



Thermal (Fig. 1(2)) and electrical conductivity (Fig. 2(2)) measurements also show it to be a two-step process. The first increase in

TABLE V

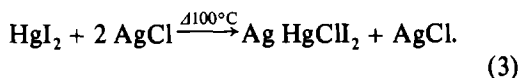
DEVIATIONS IN THE d VALUES OF Ag_2HgI_4 AND AgCl IN THE PRODUCT OF 1:4 MOLAR REACTION MIXTURE OF HgCl_2 AND AgI^a

Ag_2HgI_4		AgCl	
Standard d (\AA) (10)	Observed d (\AA)	Standard d (\AA) (9)	Observed d (\AA)
3.66	3.64	3.20	3.24
2.24	2.23	2.77	2.81
1.91	1.90	1.96	1.98
1.59	1.58	1.67	1.69
1.46	1.45	1.60	1.63

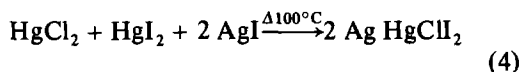
^a Scanning speed $\frac{1}{2}^\circ/\text{min}$.

conductivity is due to the formation of highly conducting Ag_2HgI_4 and the subsequent decrease is due to its disappearance through step (2b).

The red product, on heating at 100°C for about 24 h, turned orange, which on cooling to 30°C changed to yellow. The yellow product is analyzed to be a mixture of Ag HgClI_2 and AgCl .



The reaction

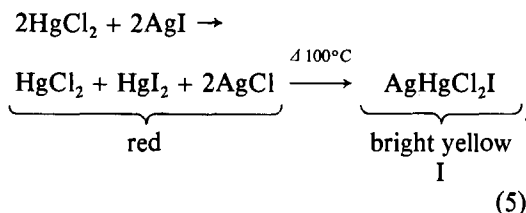


for the formation of AgHgClI_2 may be explained in three ways:

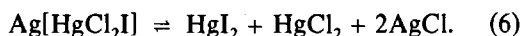
- (i) $\text{HgI}_2 + 2 \text{AgI} \rightarrow \text{Ag}_2\text{HgI}_4$,
 $\text{HgCl}_2 + \text{Ag}_2\text{HgI}_4 \rightarrow 2 \text{Ag HgClI}_2$;
- (ii) $\text{HgCl}_2 + 2 \text{AgI} \rightarrow \text{HgI}_2 + 2 \text{AgCl}$,
 $2 \text{HgI}_2 + 2 \text{AgCl} \rightarrow 2 \text{AgHgClI}_2$;
- (iii) $\text{HgCl}_2 + \text{HgI}_2 \rightarrow 2 \text{HgClI}$,
 $2 \text{HgClI} + 2 \text{AgI} \rightarrow 2 \text{AgHgClI}_2$.

Evidently the compound (10) $\text{HgI}_2 \cdot 2 \text{AgCl}$ does not form since the 1:2 molar mixture of HgCl_2 and AgI , heated at 100°C , showed the X-ray pattern of AgCl .

At room temperature (30°C) reactions in 1:1 molar mixture are in no way different to those in the case of 1:2 molar mixture. In this case as well the reaction proceeds according to Eq. (2) leaving excess of HgCl_2 . But, on heating to 100°C , the yellow reaction mixture first changed to red and finally to bright yellow color.



Although the sharp melting point of the bright yellow product (134°C) indicated it to be a single phase, the X-ray analysis at room temperature (30°C) showed the presence of HgCl_2 , HgI_2 , and AgCl along with new compound AgHgCl_2I (Table II). This suggests that at lower temperatures, AgHgCl_2I dissociates although there may be an equilibrium:



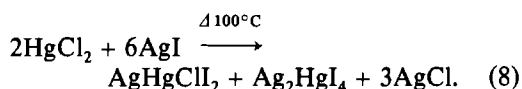
The deviation in d values (Table II) of HgCl_2 and HgI_2 may be due to their miscibility (12).

That the 1:1 molar mixture of HgCl_2 and AgI gives AgHgCl_2I whereas with a higher proportion of AgI , AgHgCl_2I is favored and is consistent with the stronger coordination of I^- with Hg^{2+} than Cl^- . This is consonant with higher formation energy (3) of $\text{K}[\text{HgCl}_2\text{I}]$ compared with $\text{K}[\text{HgCl}_2]$. Thus, as I^- (in the form of AgI) is added to $\text{Ag}[\text{HgCl}_2\text{I}]$, the following process occurs:



In the hope of getting $\text{Ag}[\text{HgI}_3]$ or $\text{Ag}_2[\text{HgCl}_3]$, a 1:3 molar mixture of HgCl_2 and AgI was heated and analyzed. The X-ray pattern revealed that the reactants had com-

pletely disappeared, giving rise to AgHgCl_2I along with Ag_2HgI_4 and AgCl :



The lateral diffusion of HgCl_2 in AgI (Fig. 3) follows the general equation

$$X_i^n = kt,$$

where X_i is the thickness of the product layer formed in time t and n and k are constants.

The activation energy of 23.90 kCal/mole (Fig. 4a) and the plot of thickness of the product layer versus time (Fig. 5) show that the reaction is diffusion-controlled. The low activation energy (8.32 kCal/mole) for the initial stage of the diffusion process obtained from the logarithm of zero time slope, k' , (of thickness versus time plot) against inverse temperature plot (Fig. 4b), suggests that the rate of the process is controlled by surface or grain boundary diffusion.

The reaction proceeded with simultaneous separation of AgCl and Ag_2HgI_4 layers. The

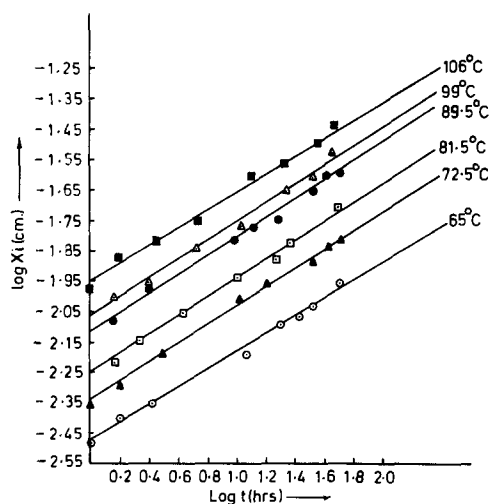


FIG. 3. Kinetic data for lateral diffusion and test of equation $X_i^n = kt$ for the reaction between HgCl_2 and AgI .

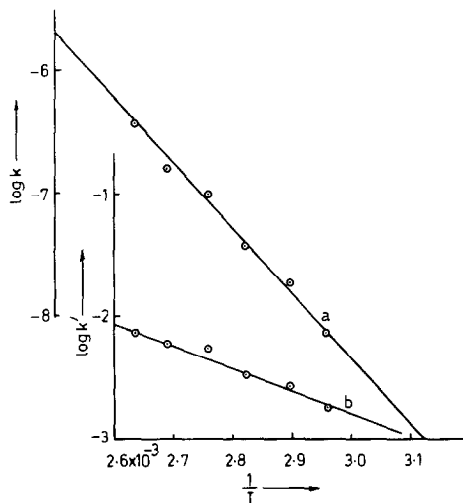


FIG. 4. Arrhenius plots for (a) overall process, (b) initial process for the reaction of HgCl_2 and AgI in solid state.

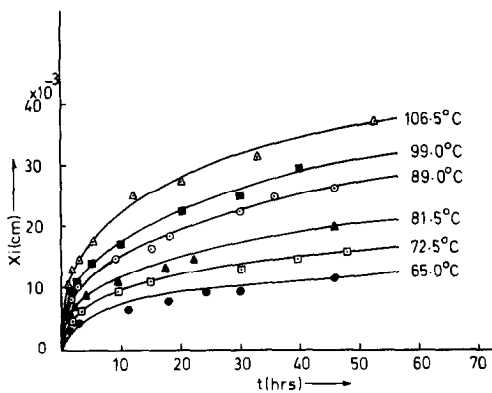


FIG. 5. Kinetic data for the reaction between HgCl_2 and AgI at various temperatures.

diffusion of HgCl_2 vapor and the separation of product layers follow the same mechanism as explained earlier (5, 6).

Acknowledgment

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References

1. J. A. ROLFE, D. E. SHEPPARD, AND L. A. WOODWARD, *Trans. Faraday Soc.* **50**, 1275 (1954).
2. G. J. JANZ AND D. W. JAMES, *J. Chem. Phys.* **38**, 905 (1963).
3. P. G. MASLOV, *Izv. Vyssh. Ucheb. Zaved., Khim. Khim. Tekhnol.* **2**, 335 (1959).
4. E. KOCH AND C. WAGNER, *Z. Physik. Chem. B* **34**, 317 (1936).
5. M. A. BEG AND S. M. ANSARI, *J. Solid State Chem.* **18**, 57 (1976).
6. M. A. BEG AND S. M. ANSARI, *J. Solid State Chem.* **20**, 103 (1977).
7. ASTM, Joint Committee for Powder Diffraction Systems, No. 4-0331.
8. ASTM, Joint Committee for Powder Diffraction Systems, No. 4-0454 and 4-0455.
9. ASTM, Joint Committee for Powder Diffraction Systems, No. 6-0480.
10. ASTM, Joint Committee for Powder Diffraction Systems, No. 3-0950.
11. M. C. LEA, "A Comprehensive Treatise on Inorganic and Theoretical Chemistry" (J. W. Mellor, Ed.), Vol. IV, p. 938, Longmans, London (1963).
12. J. W. MELLOR (Ed.), "A Comprehensive Treatise on Inorganic and Theoretical Chemistry," Vol. IV, p. 917, Longmans, London (1963).