

## Studies on Silver Tungstate-Mercuric Iodide Reaction in Solid State

M. A. BEG, AMITA JAIN, AND K. M. GHOUSE\*

*Department of Chemistry, Aligarh Muslim University, Aligarh 202001, India*

Received June 5, 1987; in revised form August 15, 1987

The kinetics and mechanism of reaction of silver tungstate with rhombic and tetragonal mercuric iodide in solid state have been studied using X-ray diffraction, chemical analysis, and electrical conductivity measurements. The reaction is diffusion controlled and the data for lateral diffusion best fit the equation  $X^n = kt$ . Activation energies suggest that rhombic  $HgI_2$  is more reactive toward  $Ag_2WO_4$  than its tetragonal form. The reaction rate that rises abruptly near the transition temperature records a smooth rise with increase in temperature both below and above this temperature. © 1988 Academic Press, Inc.

### Introduction

As lattice imperfections play a vital role in solid-state processes, the kinetics of diffusion-controlled solid-state reactions are expected to be greatly influenced by the polymorphic forms of reactants. There appears to be few references in the literature regarding this. Hedvall (1) as early as 1934 suggested that a considerable increase in reaction velocity could be observed at the temperature at which a crystallographic transformation occurs in one of the reactants. Ordinarily ferric oxide does not dissolve in silica, but silica at its transition temperature dissolves ferric oxide to give a stable solid solution (2). Oxides of Ba, Sr, and Ca react with rhombohedral  $AgNO_3$  but not with the rhombic form. Their reaction temperatures are, respectively, 170, 172, and 164°C, which are well above the transition temperature of  $AgNO_3$ . The reaction rate data (3) at 725–850°C for  $CuO$ - $\eta$ - $Al_2O_3$

and  $CuO$ - $\gamma$ - $Al_2O_3$  follow the Jander equation but have different activation energies whereas  $\alpha$ -alumina does not react up to 975°C.

Despite the increased attention that has been paid to the study of solid-state reactions in recent years, no clear cut understanding of the role of physical transformation in solid-state reaction has yet been developed. In this paper we shall endeavor to study the mechanism of solid-state interaction of  $Ag_2WO_4$  with the rhombic and tetragonal  $HgI_2$  with an aim toward understanding the role of crystallographic transformation in chemical reaction.

### Experimental

*Materials and methods.* Silver nitrate (E. Merck), sodium tungstate (E. Merck), and mercuric iodide (BDH) were used without further purification. Silver monotungstate was precipitated (4), in the dark, in the pH range 8–10, from approximately 0.5 M aqueous  $Na_2WO_4$  solution at 85–90°C by Ag

\* X-ray division, R.R.L., Hyderabad.

$\text{NO}_3$  solution of similar concentration. The precipitate was washed, dried in the dark at  $60^\circ\text{C}$  for 2 days, and kept in a dark bottle. An X-ray diffractogram of the product was recorded. All  $d$  values were the same as reported in ASTM Card 28-1023.

**Kinetic studies.** The kinetics were followed as cited earlier (5) in a vertical Pyrex glass tube of 0.5 cm internal diameter whose one end was sealed. A weighed amount of  $\text{Ag}_2\text{WO}_4$  was placed in the tube and pressed gently; then, the weighed amount of  $\text{HgI}_2$  was placed over  $\text{Ag}_2\text{WO}_4$  and pressed again and the reaction tube was kept in an air thermostat controlled to  $\pm 0.5^\circ\text{C}$ . A dark yellow boundary appeared at the interphase and grew with time on the silver tungstate side. Simultaneously, a red colored layer formed next to the yellow boundary. On cooling to room temperature the red colored product turned light yellow. The progress of the reaction was followed by measuring the total thickness of the product layers formed at the interphase by a traveling microscope, having a calibrated scale in its eyepiece. Each experiment was run in triplicate and the average values are reported (Table I).

**Analysis of the product layers.** By X-ray analysis the dark yellow boundary was identified to be  $\text{Ag}_2\text{HgI}_4$  and the light yellow

TABLE I  
DEPENDENCE OF PARAMETERS OF EQUATION,  
 $X^n = kt$ , ON TEMPERATURE

Temperature ( $^\circ\text{C} \pm 0.5$ )	$k$ (cm/hr)	Mean deviation	$n$
90	$5.62 \times 10^{-5}$	$0.010 \times 10^{-5}$	1.75
100	$9.44 \times 10^{-5}$	$0.009 \times 10^{-5}$	1.75
112	$2.69 \times 10^{-4}$	$0.008 \times 10^{-4}$	1.75
120	$3.86 \times 10^{-4}$	$0.008 \times 10^{-4}$	1.75
130	$8.13 \times 10^{-3}$	$0.009 \times 10^{-3}$	1.55
138	$1.01 \times 10^{-2}$	$0.008 \times 10^{-2}$	1.56
150	$1.62 \times 10^{-2}$	$0.010 \times 10^{-2}$	1.56
160	$2.75 \times 10^{-2}$	$0.008 \times 10^{-2}$	1.56
170	$3.63 \times 10^{-2}$	$0.009 \times 10^{-2}$	1.56

TABLE II  
COMPOUNDS PRESENT IN DIFFERENT MOLAR RATIO  
MIXTURES OF  $\text{Ag}_2\text{WO}_4$  AND  $\text{HgI}_2$

Molar ratio of $\text{Ag}_2\text{WO}_4$ and $\text{HgI}_2$	Compounds identified in mixtures heated at $150^\circ\text{C}$ and then cooled to room temperature
2:1	$\text{AgI}$ , $\text{HgWO}_4$ , and $\text{Ag}_2\text{WO}_4$
1:1	$\text{AgI}$ and $\text{HgWO}_4$
1:2	$\text{Ag}_2\text{HgI}_4$ and $\text{HgWO}_4$
1:3	$\text{Ag}_2\text{HgI}_4$ , $\text{HgWO}_4$ , and $\text{HgI}_2$

one to be a mixture of  $\text{AgI}$  and  $\text{HgWO}_4$ . Identification of product layers was also done by chemical analysis.

**X-ray studies.** The reactants  $\text{Ag}_2\text{WO}_4$  and  $\text{HgI}_2$  (both above 300 mesh) were mixed thoroughly in an agate mortar in different molar ratio and heated for 3 days in an air oven maintained at  $150 \pm 0.5^\circ\text{C}$ . The X-ray diffractograms of the reaction mixtures were recorded at room temperature by Norelco Geiger Counter X-ray diffractometer (PW 1010 Philips) using  $\text{CuK}\alpha$  radiation and Ni-filter, applying 32 kV at 12 mA. The compounds identified in different mixtures are given in Table II.

**Conductivity measurements.**  $\text{Ag}_2\text{WO}_4$

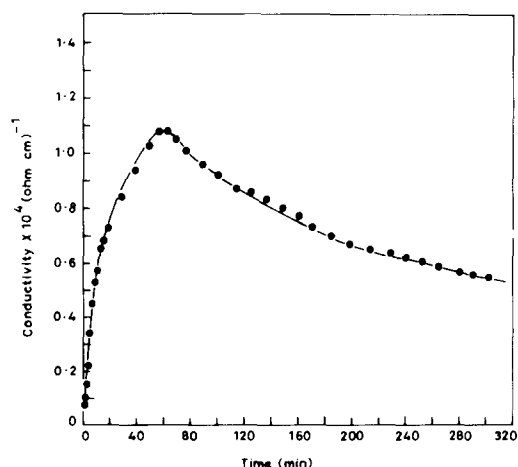


FIG. 1. Variation of electrical conductivity with time for the reaction between  $\text{Ag}_2\text{WO}_4$  and  $\text{HgI}_2$  (1:1 molar) at  $120^\circ\text{C}$ .

and  $\text{HgI}_2$  (molar ratio 1 : 1) were mixed and pressed into a disk. The disk was fixed between platinum electrodes and the change in conductivity with time was measured by Conductivity Bridge (Cambridge Instrument Co.) at 50 c/sec. Similar conductivity experiments were made with disks prepared out of other molar ratio mixtures. Results are plotted in Figs. 1 and 2.

*Reflectance studies.* The reflectance measurements for various molar ratio mixtures of reactants, heated at  $150^\circ\text{C}$  for 2 days, were made with a VSU-2P spectrophotometer, using magnesium carbonate as the reference material. The results are plotted in Fig. 3.

## Results and Discussion

*Mechanism of chemical interaction.* The results of X-ray analysis, summarized in

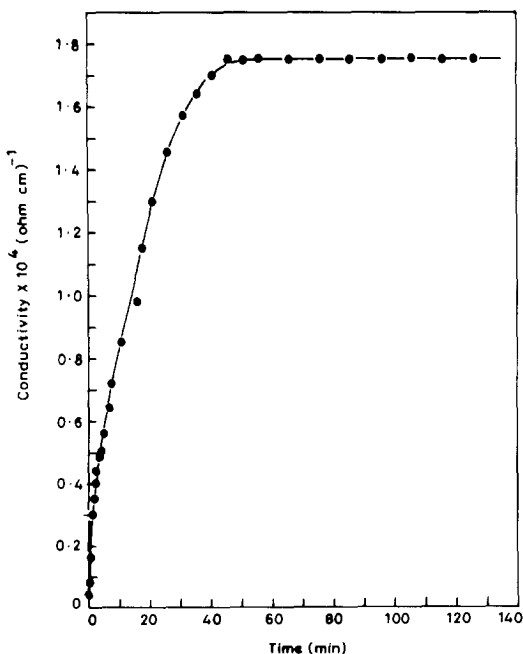
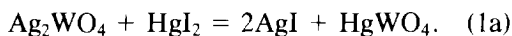
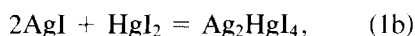


FIG. 2. Variation of electrical conductivity with time for the reaction between  $\text{Ag}_2\text{WO}_4$  and  $\text{HgI}_2$  (1 : 2 molar) at  $120^\circ\text{C}$ .

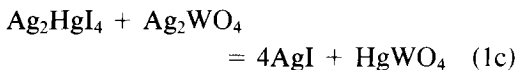
Table II, and reflectance studies reveal that in a 1 : 1 molar mixture of  $\text{Ag}_2\text{WO}_4$  and  $\text{HgI}_2$  maintained at  $150^\circ\text{C}$  for 3 days, the reactants had completely changed into  $\text{AgI}$  and  $\text{HgWO}_4$ . This analysis, in light of the principle (6) of larger cations going well with larger anions and smaller cations with smaller anions, suggests it to be a simple double decomposition reaction:



Because  $\text{AgI}$  reacts fast (7) with  $\text{HgI}_2$  giving  $\text{Ag}_2\text{HgI}_4$  through



one would ordinarily expect  $\text{Ag}_2\text{HgI}_4$  as one of the end products. But the analysis of the end product did not show the presence of  $\text{Ag}_2\text{HgI}_4$ . Its formation during the progress of this reaction was, however, revealed by the following observation. The reaction mixture that was red in color became yellow when heated at  $150^\circ\text{C}$  ( $\text{AgI}$  and  $\text{HgWO}_4$  are yellow) and remained yellow on cooling. However, the red reaction mixture, maintained at room temperature, slowly turned yellowish orange and this when heated above  $50.7^\circ\text{C}$  turned red, which again became yellowish orange on cooling ( $\text{Ag}_2\text{HgI}_4$  is yellow below  $50.7^\circ\text{C}$  and red above it). X-ray analysis of an equimolar mixture of  $\text{Ag}_2\text{WO}_4$  and  $\text{HgI}_2$  maintained at room temperature for 24 hr showed the presence of  $\text{Ag}_2\text{HgI}_4$ ,  $\text{AgI}$ ,  $\text{Ag}_2\text{WO}_4$ , and  $\text{HgWO}_4$ . It thus confirms that  $\text{Ag}_2\text{HgI}_4$  is formed and subsequently consumed.  $\text{Ag}_2\text{HgI}_4$ , formed during the reaction, reacts with  $\text{Ag}_2\text{WO}_4$  giving  $\text{AgI}$  and  $\text{HgWO}_4$ .



Reaction (1c) was confirmed by mixing  $\text{Ag}_2\text{WO}_4$  and  $\text{Ag}_2\text{HgI}_4$  in equimolar proportions and recording the X-ray pattern of the mixture, after heating it at  $150^\circ\text{C}$  for 72 hr. The pattern indicated complete conversion into  $\text{AgI}$  and  $\text{HgWO}_4$ .

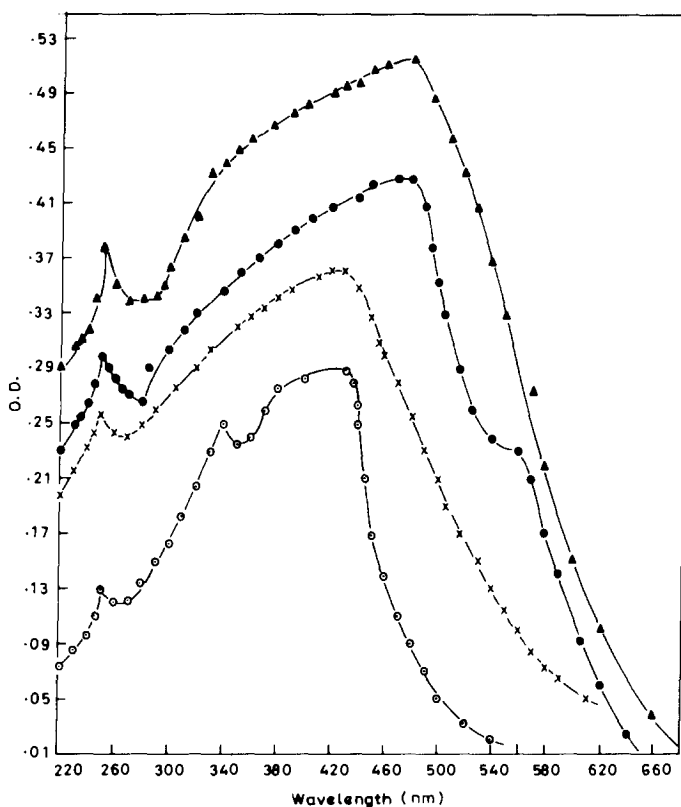
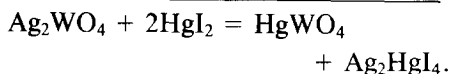
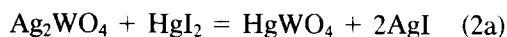


FIG. 3. Reflectance spectra for the  $\text{Ag}_2\text{WO}_4 + \text{HgI}_2$  reaction (○) 2:1, (×) 1:1, (▲) 1:2, (●) 1:3 cutoffs for pure  $\text{Ag}_2\text{WO}_4$ ,  $\text{HgI}_2$ ,  $\text{HgWO}_4$ ,  $\text{AgI}$ , and  $\text{Ag}_2\text{HgI}_4$  were at 340, 560, 250, 430, and 480 nm, respectively.

The plot of electrical conductivity versus time, for an equimolar mixture of  $\text{Ag}_2\text{WO}_4$  and  $\text{HgI}_2$  maintained at  $120^\circ\text{C}$ , shows that conductivity first rises and then falls off (Fig. 1). The rise in conductivity is probably due to the formation of the highly conducting  $\text{Ag}_2\text{HgI}_4$ , and the decrease thereafter is due to its disappearance through reaction (1c). Because the conductivity of the reactants and the end products is much lower than that of  $\text{Ag}_2\text{HgI}_4$ , this conductivity curve essentially monitors the concentration of  $\text{Ag}_2\text{HgI}_4$  in the reaction mixture during the course of this reaction and therefore it resembles (8) the curve which measures the concentration of an intermediate species in a consecutive reaction.

The X-ray analysis of the 1:2 molar mixture of  $\text{Ag}_2\text{WO}_4$  and  $\text{HgI}_2$  shows that  $\text{Ag}_2\text{HgI}_4$

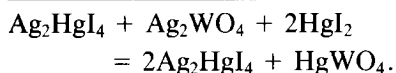
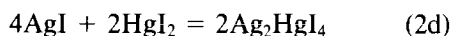
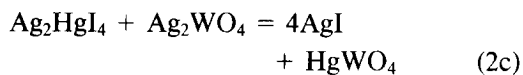
and  $\text{HgWO}_4$  are the end products. This, in light of foregoing discussions, suggests that this reaction is represented by the following:



Reaction (2b), being fast (7) in comparison to  $\text{AgI}$  formed in step (2a), is completely consumed by  $\text{HgI}_2$  giving  $\text{Ag}_2\text{HgI}_4$ .

As pointed out earlier,  $\text{Ag}_2\text{HgI}_4$  reacts with  $\text{Ag}_2\text{WO}_4$  giving  $\text{AgI}$  and  $\text{HgWO}_4$ , but as the X-ray analysis of 1:2 molar mixture of  $\text{Ag}_2\text{WO}_4$  and  $\text{HgI}_2$  shows  $\text{Ag}_2\text{HgI}_4$  and  $\text{HgWO}_4$  as the only end products, it is pre-

sumed that AgI formed in reaction (1c) is retransformed into  $\text{Ag}_2\text{HgI}_4$  by  $\text{HgI}_2$  (present in excess). The second sequence of reactions taking place in this mixture is therefore expected to be as follows:

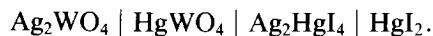


The two sets of reactions, viz. (2a) and (2b) and (2c) and (2d), occur simultaneously but because step (2c) is much slower, the present reaction may be taking place mostly through step (2a).

Although the conductivity curve (Fig. 2) for the 1:2 molar mixture of  $\text{Ag}_2\text{WO}_4$  and  $\text{HgI}_2$  looks different from that for 1:1 mixture, it actually confirms the proposition made earlier. The fall in conductivity (Fig. 1) marks the predominance of the reaction consuming  $\text{Ag}_2\text{HgI}_4$ . Because the slow disappearance of  $\text{Ag}_2\text{HgI}_4$  through reaction (2c) is followed by its fast regeneration through reaction (2d), the concentration of  $\text{Ag}_2\text{HgI}_4$  in the case of 1:2 molar mixture of  $\text{Ag}_2\text{WO}_4$  and  $\text{HgI}_2$  keeps on rising until the end of the reaction.

*Mechanism of lateral diffusion.* In the lateral diffusion experiments, a yellow colored boundary formed at the interphase, grew with time on the  $\text{Ag}_2\text{WO}_4$  side. After some time, a red product started to develop between  $\text{HgI}_2$  and the yellow product. On cooling to room temperature, the red product turned yellow ( $\text{Ag}_2\text{HgI}_4$  is red above and yellow below  $50.7^\circ\text{C}$ ). Later, when the experiment was repeated with an air-gap between the reactants, the product was formed on the  $\text{Ag}_2\text{WO}_4$  side but at a much slower rate. This shows that  $\text{HgI}_2$  is mostly reacting in solid form and not through vapor phase. Counter diffusion of cations would give the following product sequence

in the reaction tube:



Because this is different from the observed one (Fig. 4), it is suggested that  $\text{HgI}_2$  in molecular form diffuses and reacts.  $\text{HgI}_2$  first reacts with the host material,  $\text{Ag}_2\text{WO}_4$ , to give  $\text{HgWO}_4$  and AgI. The incoming  $\text{HgI}_2$  subsequently converts most of AgI into  $\text{Ag}_2\text{HgI}_4$ . However, some AgI escaped conversion into  $\text{Ag}_2\text{HgI}_4$  and was detected in the X-ray analysis of the yellow layer.

The following equation gives the best fit of our lateral diffusion data,

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

where  $X$  is the product thickness,  $t$  the time, and  $k$  and  $n$  constants. The activation energies, calculated from the Arrhenius plot (Fig. 5), for the two forms (9) of  $\text{HgI}_2$ , are respectively 78.62 and 56.35 kJ/mol. The two values of activation energies suggest that rhombic  $\text{HgI}_2$  is more reactive toward  $\text{Ag}_2\text{WO}_4$  than the tetragonal form. This being a diffusion controlled process, the rate constant  $k$  that is associated with diffusion is expected to rise smoothly with a rise in temperature. The variation in rate is indeed smooth except at the transition point where it rises abruptly. The sudden rise in reaction rate at the transition temperature of  $\text{HgI}_2$  is quite in line with Hedvall's remark (1) that materials become more reactive at transition temperature. Like the present one, the  $\text{BaCO}_3\text{-Fe}_2\text{O}_3$  re-

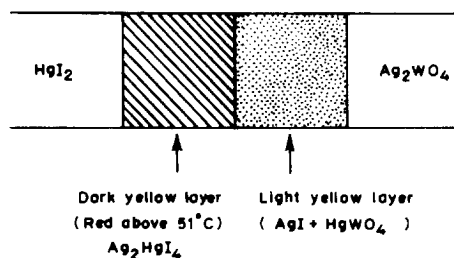


FIG. 4. Diagrammatic representation of product sequence in lateral diffusion experiment.

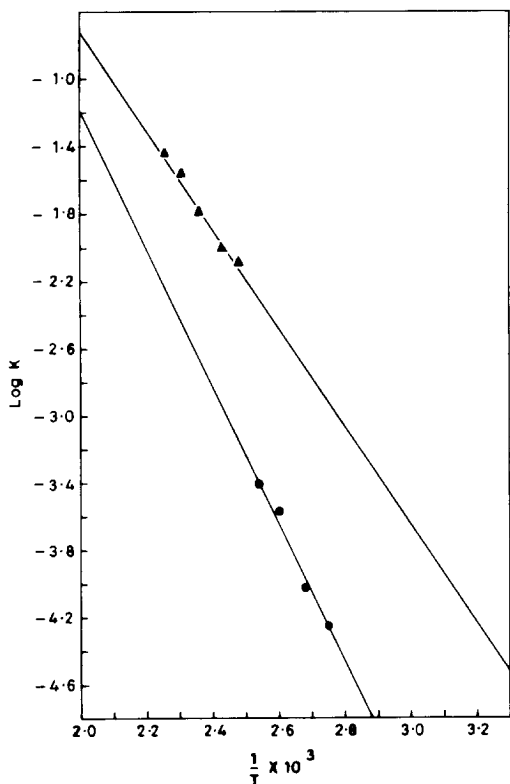


FIG. 5. Dependence of  $\log K$  on  $T^{-1}$  for the reaction of  $\text{Ag}_2\text{WO}_4$  with tetragonal (●) and rhombic (▲) forms of  $\text{HgI}_2$ .

action (10) is controlled by the diffusion of  $\text{BaCO}_3$ , both above and below its transition temperature.

### Acknowledgment

One of the authors (A.J.) acknowledges the financial assistance of DAE, Bombay.

### References

1. J. A. HEDVALL, *Chem. Rev.* **15**, 139 (1934).
2. J. A. HEDVALL AND E. NORSTROM, *Z. Anorg. Allg. Chem.* **154**, 12 (1926).
3. T. TSUCHIDA, T. SUKAGAWA, R. FURUICHI, AND T. ISHII, *Z. Phys. Chem. (Munich)*, **141**(1), 101 (1984).
4. J. S. MCKECHNIE AND L. D. S. TURNER, *J. Inorg. Nucl. Chem.* **41**, 177 (1979).
5. R. P. RASTOGI, P. S. BASSI, AND S. L. CHADDHA, *J. Phys. Chem. Ithaca* **67**, 2569 (1963).
6. H. LINK AND J. WOOD, *J. Amer. Chem. Soc.* **60**, 2320 (1938).
7. E. KOCH AND C. WAGNER, *Z. Physik. Chem. B* **34**, 317 (1936).
8. H. MARON SAMUEL, "Fundamentals of Physical Chemistry," p. 693, Macmillan, New York (1974).
9. G. A. JEFFERY AND M. VLASSE, *Inorg. Chem.* **6**, 396 (1967).
10. R. WARD AND J. D. STRUTHERS, *J. Amer. Chem. Soc.* **59**, 1849 (1937).