

Kinetics and Mechanism of Reaction between Silver Molybdate and Mercuric Iodide in Solid State

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The kinetics and the mechanism of the reaction between silver molybdate and mercuric iodide were studied in the solid state by X-ray, chemical analysis, and electrical conductivity measurements. This is a multistep reaction where Ag_2HgI_4 is formed as an intermediate. In an equimolar mixture of Ag_2MoO_4 and HgI_2 , AgI and HgMoO_4 are formed, whereas in a 1:2 molar mixture Ag_2HgI_4 and HgMoO_4 are formed. The data for lateral diffusion best fit the equation $X^n = kt$, where X is the product thickness, t is time, and k and n are constants. This is a multistep solid state ionic reaction initiated by the diffusion of HgI_2 molecules as such and not through counterdiffusion of cations. © 1987 Academic Press, Inc.

Introduction

In previous communications (1, 2) we described the interaction of Hg(II) halides with silver(I) and copper(I) halides in the solid state and reported the formation of AgHgCl_2I , AgHgClI_2 , and CuHgBr_3 , which were not known earlier. These mixed halides are stable only in the solid state and decompose when combined with water or alcohol. Highly conducting iodomercurates of silver and copper in the solid state are formed easily and are considered to be due to the propensity of silver ions to occupy interstitial positions rather than to form vacancy pairs. The electrical conductance of solid Ag_2MoO_4 is of the same order- (3) as that of solid AgI ; these materials are called superionic conductors. Silver salts are gaining importance for their microwave conductivity (4) and their promise in applications in high-energy-density batteries. The present investigation was undertaken to

elucidate fundamental aspects of complex solid state reactions and to provide information on the mode of variation of electrical conductance of solid electrolytes during chemical interaction.

Experimental

Materials. Analytical grade HgI_2 (Merck) was used without further purification. Ag_2MoO_4 was prepared (5) in the dark by precipitation from aqueous solutions of 1.0 M Na_2MoO_4 (Baker) and 1.0 M silver nitrate (Merck, analytical grade). The solutions were poured into a beaker containing 500 ml water maintained at 80–90°C. To avoid polymerization of molybdate ions, the pH of the medium was maintained at 9–10 throughout the course of precipitation. The precipitate was washed with distilled water and dried in a vacuum desiccator for several days. The dried precipitate was powdered in a mortar and dissolved in ammo-

TABLE I
TEMPERATURE DEPENDENCE OF THE
PARAMETERS OF EQUATION $X^n = kt$ FOR
THE $\text{Ag}_2\text{MoO}_4\text{-HgI}_2$ REACTION

Temperature ($\pm 1^\circ\text{C}$)	k (cm/hr)	n
80	1.285×10^{-6}	2.3
92	4.123×10^{-6}	2.4
105	7.975×10^{-6}	2.5
120	20.785×10^{-6}	2.7
135	45.124×10^{-6}	2.8

nium hydroxide. Slow evaporation yielded small bright yellow octahedral crystals of Ag_2MoO_4 . The product was stored in a dark bottle and an X-ray diffractogram showed (6) it to be single-phase Ag_2MoO_4 .

Rate measurements. The kinetics of the reaction were studied by placing HgI_2 over Ag_2MoO_4 in a Pyrex glass tube of 0.5 cm internal diameter as reported by Rastogi and Dubey (7). Each experiment was run in triplicate and the agreement between the corresponding values of different sets was quite satisfactory (average values are reported in Table I).

Soon after placing the HgI_2 over the Ag_2MoO_4 in the reaction tube, a yellow-colored boundary appeared at the interface and this grew with time on the Ag_2MoO_4 side. After some time a red-colored product started to develop between the yellow boundary and the HgI_2 , and a gap developed between the HgI_2 and the red product (Fig. 1). On cooling to room temperature, the red product turned yellow (Ag_2HgI_4 is red above and yellow below 50.7°C) (8). When lateral diffusion experiments were run, maintaining an air gap of 0.25 cm between the two reactants, the reaction proceeded at a slower rate, giving the same products.

Analysis of the product layers. A reaction tube containing the two distinct product layers was broken and the two layers

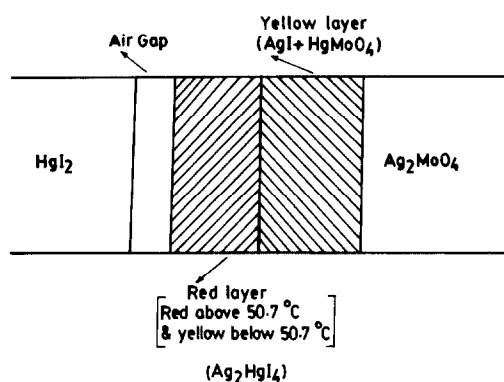


FIG. 1. Diagrammatic representation of the sequence of products formed in lateral diffusion between Ag_2MoO_4 and HgI_2 in the solid state.

were collected separately. The X-ray and chemical analyses revealed the yellow layer to be a mixture of AgI and HgMoO_4 and the red layer (red above 50.7°C and yellow below) to be Ag_2HgI_4 .

X-ray studies. The powdered reactants Ag_2MoO_4 and HgI_2 were mixed thoroughly in a mortar, in different molar ratios. These samples were heated for 24 hr in an air thermostat maintained at $100 \pm 0.5^\circ\text{C}$. The X-ray diffractograms were recorded with a Norelco Geiger counter X-ray diffractometer (PP 1010 Philips) using $\text{CuK}\alpha$ radiation with a Ni filter. The compounds identified are given in Table II.

Conductivity measurements. Powdered Ag_2MoO_4 and HgI_2 were thoroughly mixed

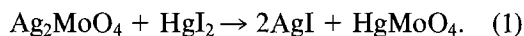
TABLE II
COMPOUNDS PRESENT IN DIFFERENT MOLAR RATIO
MIXTURES OF Ag_2MoO_4 AND HgI_2 HEATED AT 100°C

Molar ratio of Ag_2MoO_4 and HgI_2	Compounds present in the mixture
2:1	Ag_2MoO_4 , AgI , HgMoO_4
1:1	AgI , HgMoO_4
1:2	Ag_2HgI_4 , HgMoO_4
1:3	Ag_2HgI_4 , HgMoO_4 , HgI_2

with each other in different molar ratios. Each mixture was immediately poured into a die and pressed into a disk about 0.2 cm thick and 0.31 cm² in surface area. The disk was then fixed between two platinum electrodes of a conductivity cell placed in a thermostat maintained at $100 \pm 0.5^\circ\text{C}$, and electrical conductance was recorded on an Elico conductivity bridge.

Discussion

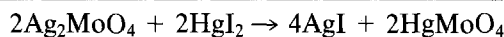
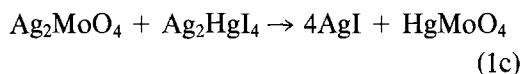
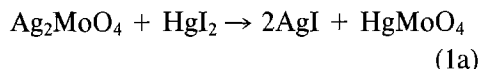
X-ray analysis of an equimolar mixture of Ag_2MoO_4 and HgI_2 , heated at 100°C for 24 hr, showed the presence of only AgI and HgMoO_4 . This points to simple double decomposition represented by Eq. (1) and is in conformity with the principle (9) of larger cations interacting with larger anions and smaller cations with smaller anions:



AgI is known to react rapidly with HgI_2 to give (10) Ag_2HgI_4 , but the analysis of the end product does not show its presence. However, the following observation does indicate its transitory formation in the reaction. The dark brown reaction mixture, on heating at 100°C , turned yellow (AgI and HgMoO_4 are yellow) and then slowly turned dirty white. Another portion of this reaction mixture kept at room temperature slowly turned orange. This orange material turned red when heated above 50.7°C and became orange if immediately cooled below this temperature (without allowing sufficient time for the reaction to reach completion). An equimolar mixture of Ag_2MoO_4 and HgI_2 , heated at 100°C for 24 hr, completely changed into AgI and HgMoO_4 .

The plot of conductivity versus time for a Ag_2MoO_4 - HgI_2 mixture, 1:1 molar ratio (Fig. 2, 1), clearly shows that the reaction represented by Eq. (1) is not simple and that it is comprised of at least three steps. As AgI and Ag_2MoO_4 have comparable

conductances (Table III), the very small change in conductance at the start of the reaction is probably due to the predominance of reaction (1a) over the others. The rapid increase thereafter is due to the formation of highly conducting (10) Ag_2HgI_4 through reaction (1b). The final fall in conductance is due to the predominance in the rate of disappearance of Ag_2HgI_4 through reaction (1c) over its formation rate through reaction (1b).



Strangely enough the stoichiometry of the initial step represented by Eq. (1a) also turns out to be the overall stoichiometry of the reaction represented by Eq. (1). As the conductance curve (Fig. 2, 1) essentially monitors the concentration of Ag_2HgI_4 , it resembles the curve that represents the concentration of the transient species in a consecutive reaction (11). To confirm reac-

TABLE III
ELECTRICAL
CONDUCTANCE AT 100°C

Material	Conductance (ohm ⁻¹ cm ⁻¹)
Ag_2HgI_4	4.3×10^{-4}
AgI	9.5×10^{-6}
Ag_2MoO_4	8.7×10^{-6}
HgMoO_4	4.5×10^{-6}
HgI_2	0.6×10^{-6}

Note. Materials were in disk form and of about the same thickness and surface area.

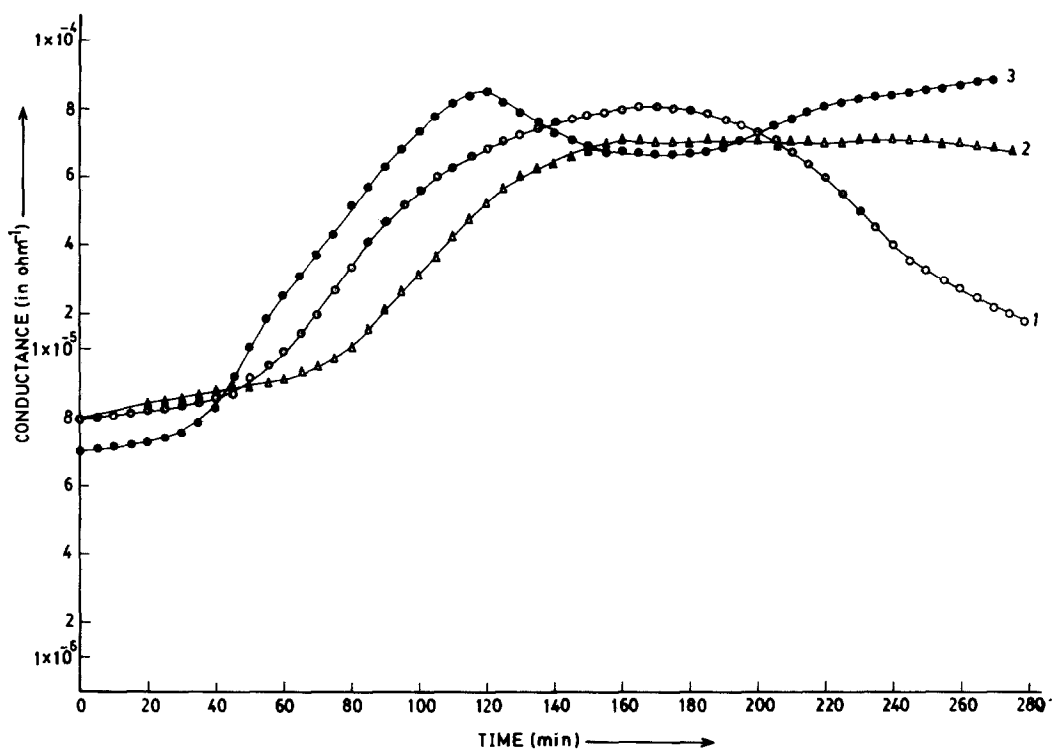


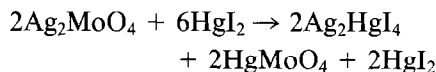
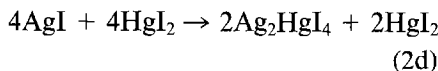
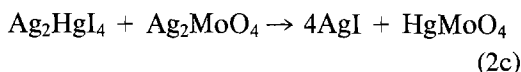
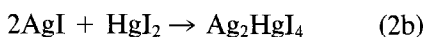
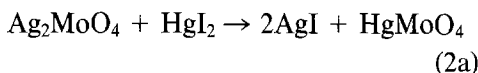
FIG. 2. The change in conductance as a function of time for the reaction between Ag_2MoO_4 and HgI_2 at 100°C . Molar ratios of Ag_2MoO_4 : HgI_2 are (1) 1:1, (2) 1:2, and (3) 1:3.

tion (1c), an equimolar mixture of Ag_2MoO_4 and Ag_2HgI_4 was heated at 100°C for 24 hr and analyzed by X-ray. The analysis indicated complete conversion into AgI and HgMoO_4 .

In a 1:2 molar mixture of Ag_2MoO_4 and HgI_2 , heated at 100°C for 24 hr, the only compounds identified were Ag_2HgI_4 and HgMoO_4 . The conductance of the aforementioned mixture, maintained at 100°C , rises first slowly and then rapidly to a constant value (Fig. 2, 2). The constancy in conductance after the sharp rise seems to suggest that reaction (1c) either does not proceed in this case, or, if it does, not to any significant extent. But what actually may be happening is that the slow reaction (1c) must be consuming some Ag_2HgI_4 which would be quantitatively regenerated

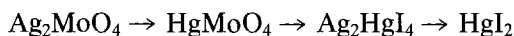
through the fast reaction (1b). In the light of the conductance values reported in Table III, reactions (1c) and (1b) are expected to have a compensatory effect on the variation in conductance; hence, the observed conductance does not change after registering the sharp rise.

From the X-ray analysis of the product of a 1:3 molar mixture of Ag_2MoO_4 and HgI_2 , one may wrongly infer that the overall reaction taking place is in no way different from that occurring in the 1:2 molar mixture. But the conductance curve in this case (Fig. 2, 3) is different from others. The second rise in conductance in this case points to the predominance of the rate of formation of Ag_2HgI_4 through reaction (2d), and the complete reaction sequence in this case is presumed to be as follows:



Mechanism of lateral diffusion. In lateral diffusion experiments it was observed that immediately after placing HgI_2 over Ag_2MoO_4 in the reaction capillary, a yellow boundary formed at the interface; the yellow boundary grew with time on the Ag_2MoO_4 side; soon afterward, a red layer formed between HgI_2 and the yellow product. A gap developed between HgI_2 and the red product layer. Later, when the experiments were repeated, maintaining an air gap of 0.25 cm between the reactants, the reaction proceeded as before but at a much slower rate. This demonstrates that HgI_2 , which has a vapor pressure of 3.39×10^{-2} mm Hg at 100°C , must be reacting at least partly via vapor phase. The vapor pressure values of the other reactants could not be found in the literature.

If this reaction proceeds through the usually accepted mechanism of counterdiffusion of cations (10), the product layers in the reaction tube are expected to be in the following sequence:



Further, if the reaction proceeds through counterdiffusion of cations, AgI should not be detected in the product, or if it is found, it should be found with Ag_2HgI_4 and not with HgMoO_4 . Since it is found to exist with HgMoO_4 (Fig. 1), it is suggested that this reaction proceeds through HgI_2 diffusion into Ag_2MoO_4 and not through counterdiffusion of cations. From this, the ob-

served sequence of products in the reaction capillary follows. Once HgI_2 enters the reaction zone (into Ag_2MoO_4 grain), AgI and HgMoO_4 are formed. AgI then reacts with the incoming HgI_2 to give Ag_2HgI_4 , yielding the observed product sequence. AgI formed in the initial stages is completely converted into Ag_2HgI_4 . As the Ag_2HgI_4 layer is formed between HgI_2 and HgMoO_4 , some of the AgI formed in the later stages escapes conversion to Ag_2HgI_4 and is detected with HgMoO_4 in the analysis of the yellow layer. Silver molybdate has a MoO_4^{2-} framework, i.e., sublattice MoO_4^{2-} units, where highly mobile Ag^+ prefers an interstitial site over a Schottky disorder. HgI_2 penetrates into the open anionic framework, yielding HgMoO_4 and AgI. Further interaction of AgI with incoming HgI_2 produces Ag_2HgI_4 germ nuclei the growth of which results in a kind of collapse of the earlier Ag_2MoO_4 lattice yielding HgMoO_4 and Ag_2HgI_4 crystallites.

The rate of reaction decreases (Fig. 3) with an increase in the thickness of the product layer. Initially the chemical reaction is fast, but the rate decreases with an increase in the thickness of product layers.

Lateral diffusion data from each isothermal reaction set fit Eq. (3) (Fig. 4):

$$X^n = kt, \quad (3)$$

where X is the product thickness at time t , and k and n are constants. The rate constant, k related to diffusion, follows the Arrhenius equation (Fig. 5). The activation energy, measured from a plot of $\log k$ versus the inverse temperature, is 95.93 kJ/mol. The magnitude of the activation energy suggests that the reaction proceeds through bulk diffusion (12). In diffusion-controlled solid state processes where the reaction rate is inversely proportional to the product thickness and the diffusion coefficient remains constant over the period of measurement, the constant n in Eq. (3) assumes a value of 2 and expression (3) be-

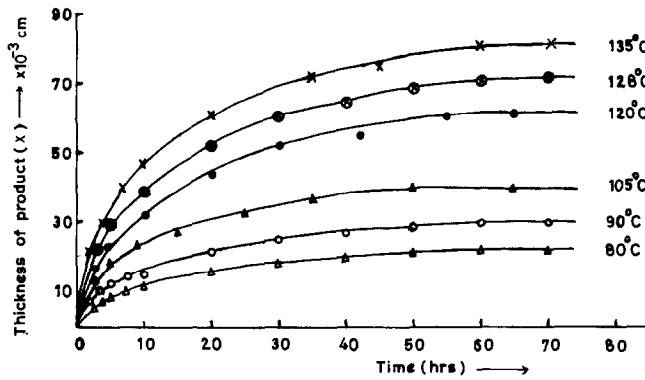


FIG. 3. Kinetic data for the reaction between Ag_2MoO_4 and HgI_2 in the solid state at various temperatures.

comes the well-known parabolic rate law. To identify the initial stage of the reaction, the slope of the product growth curve that measures the reaction rate was determined at zero time and its logarithm was plotted against the inverse of the temperature (Fig. 6). The curve shows that in lower and

higher temperature ranges the activation energies are, respectively, 20.90 and 90.49 kJ/mol. This suggests that the reaction at the start in lower temperature ranges is through surface migration whereas in higher temperature ranges, the process is bulk diffusion controlled (12) from the start.

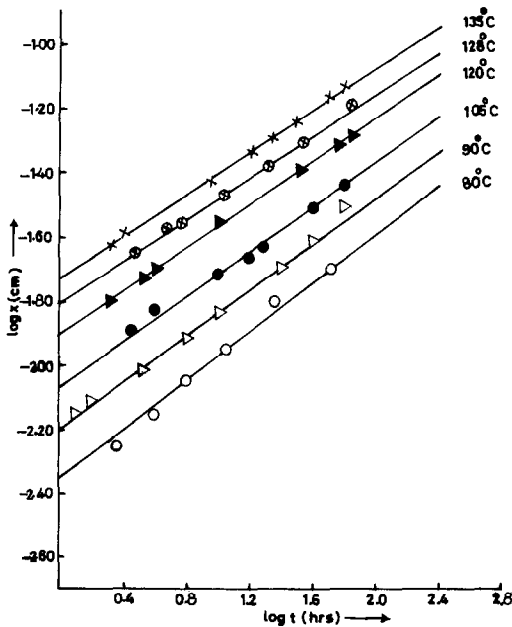


FIG. 4. Kinetic data for the lateral diffusion and the test of the equation $X^n = kt$ for the reaction between Ag_2MoO_4 and HgI_2 in the solid state.

Besides the solid-solid reaction, which may be following the parabolic rate law, $X^2 = kt$, the gas-solid reaction is expected to follow the same rate law with a different

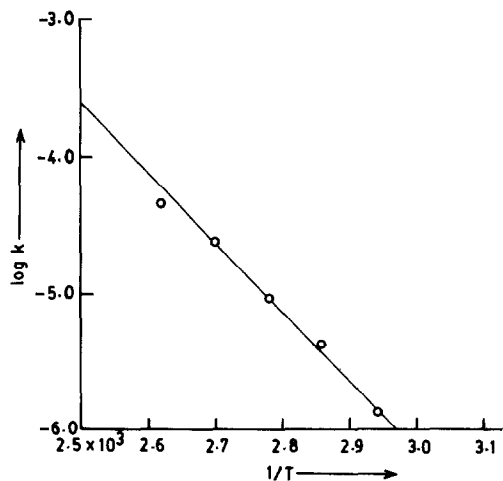


FIG. 5. Dependence of k on temperature for the reaction between Ag_2MoO_4 and HgI_2 in the solid state.

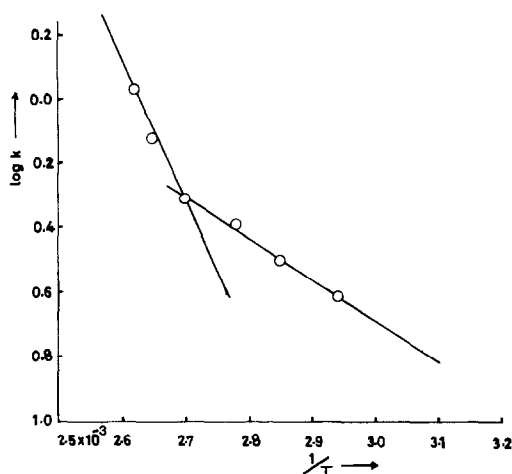


FIG. 6. Temperature dependence of the initial rate constant k for the $\text{Ag}_2\text{MoO}_4\text{-HgI}_2$ reaction.

rate constant. The net rate equation, $X^n = kt$, n being less than 2 in this case, should follow. The observed higher value of n , which rises further with rise in temperature, suggests additional resistance to rate, such as sintering, which rises further with an increase in temperature.

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