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# Solid-State Reaction between Silver Molybdate and Mercuric Chlorobromide

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The reaction between silver molybdate and mercuric chlorobromide in solid state was followed by X-ray powder diffraction, chemical analysis, and thermal and electrical conductivity measurements. Kinetics of reaction were studied in detail using a visual technique. Diffusion coefficients of HgClBr were determined. The process is reaction controlled at low temperatures while at high temperatures it is diffusion controlled. $Ag_2MoO_4$ and HgClBr react in solid state in an equimolar ratio and the reaction proceeds via vapor phase diffusion controlled mechanism. © 1989 Academic Press, Inc.

## Introduction

Solids exhibiting ionic conductivities comparable to those of metals or liquids are called superionic conductors or solid electrolytes. The formation of technologically important highly electrically conducting species, silver tetraiodomercurate, $Ag_2HgI_4$ (*1*) from the solid-state reaction of $Ag_2MoO_4$ with HgBrI (*2*), prompted us to study the reaction of $Ag_2MoO_4$ with other complex halides of mercury in the hope that some new compounds exhibiting solid electrolyte behavior will be obtained. This paper reports the results of a study on the $Ag_2MoO_4$–HgClBr reaction and kinetics of solid-state reaction between $Ag_2MoO_4$ and HgClBr leading to the formation of AgCl, AgBr, and $HgMoO_4$ using chemical analysis, X-ray powder diffractometry, and thermal and electrical conductivity techniques.

## Experimental

Octahedral crystals of $Ag_2MoO_4$ were prepared in the dark as described earlier (*2*). HgClBr was prepared by Rastogi and Dubey's (*3*) method by passing bromine vapor over $Hg_2Cl_2$ (Merck) kept in a glass bulb. White crystals were obtained. Its X-ray diffractogram showed it to be orthorhombic HgClBr.

*Rate measurements.* The kinetics of solid-state reaction were studied by placing HgClBr over $Ag_2MoO_4$ (both powdered above 300 mesh) in a glass capillary of uniform bore. The capillary was kept in an air thermostat maintained to ±0.5°C.

Soon after placing HgClBr powder over $Ag_2MoO_4$ in the tube a yellow boundary formed at the interface and this grew with time on $Ag_2MoO_4$ side. Simultaneously a gap developed between the yellow boundary and HgClBr. The progress of the reaction was followed by measuring the total thickness of the product layer formed at the interface by a calibrated traveling microscope. Each experiment was run in triplicate and the average values used for calculating the rate constants are given in Table I. The kinetics were likewise studied at different temperatures.

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TABLE I

TEMPERATURE DEPENDENCE OF PARAMETERS OF THE EQUATION $X^n = kt$ FOR $Ag_2MoO_4$–HgClBr REACTION

| Temperature (°C ± 0.5) | $k$ (cm/hr) | Mean deviation | $n$ |
|---|---|---|---|
| 65 | $1.04 \times 10^{-5}$ | $2.56 \times 10^{-4}$ | 2.60 |
| 76 | $1.67 \times 10^{-5}$ | $2.50 \times 10^{-4}$ | 2.40 |
| 88 | $5.00 \times 10^{-5}$ | $2.33 \times 10^{-4}$ | 2.24 |
| 108 | $1.50 \times 10^{-4}$ | $1.168 \times 10^{-4}$ | 2.10 |
| 118 | $2.69 \times 10^{-4}$ | $2.2 \times 10^{-5}$ | 2.00 |
| 129 | $5.01 \times 10^{-4}$ | $2.3 \times 10^{-4}$ | 2.00 |
| 140 | $8.709 \times 10^{-4}$ | $6.04 \times 10^{-4}$ | 2.00 |

TABLE II

DEPENDENCE OF RATE CONSTANT ON THE LENGTH OF AIR GAP BETWEEN $Ag_2MoO_4$ AND HgClBr SURFACE IN GLASS CAPILLARY AT CONSTANT TEMPERATURE

| Length of air gap $d$ (cm) | $k'$ (cm/hr) | Mean deviation |
|---|---|---|
| 0.3 | $6.75 \times 10^{-4}$ | $3.69 \times 10^{-4}$ |
| 0.8 | $3.22 \times 10^{-4}$ | $1.70 \times 10^{-5}$ |
| 1.2 | $1.41 \times 10^{-4}$ | $1.64 \times 10^{-4}$ |
| 1.6 | $8.24 \times 10^{-5}$ | $2.226 \times 10^{-4}$ |

*Note.* Temperature 160 ± 0.5°C; particle size above 300 mesh.

Later, lateral diffusion experiments were run keeping air gas of different lengths between the reactants at the start itself; the reaction proceeded smoothly and the yellow layer formed on the $Ag_2MoO_4$ surface grew with time. The average values and rate constants so obtained are given in Table II. The effect of size distribution and pressure on solid-state kinetics is well established. In the present work efforts have been made to fill in the material of same size (300 mesh) in the reaction tube under identical pressure as reported earlier (*4*). The photodecomposition of silver compounds was not detectable during the entire course of the lateral diffusion experiments.

*Analysis of the product layer.* The colored products were separated manually by breaking the reaction tube and were analyzed by "spot tests" (*5*) to identify the various components of the solid phases.

*X-ray studies.* X-ray diffraction patterns of different reaction mixtures were obtained using a Norelco geiger counter X-ray diffractometer by Cu$K\alpha$ radiation with a Ni filter applying 32 kV at 12 mA. Diffraction patterns at elevated temperatures were recorded with a high-temperature accessory attached to the Norelco unit. Compounds identified in different mixtures are given in Table III. The products present in different molar mixtures of $Ag_2MoO_4$ and HgClBr were identified by calculating $d$ values and intensities from their X-ray diffractograms and comparing them with the standard $d$ values and intensities of expected compounds given in their ASTM files as is the usual method of identification of compounds by X-ray analysis in mixtures.

*Thermal studies.* Thermal changes during the course of the reaction were studied by mixing powdered $Ag_2MoO_4$ and HgClBr in a double-walled flask kept in a calorimeter. The basic accuracy of the calorimeter was 0.1%. The rise and fall in temperature were noted using a Beckman thermometer reading up to 0.01°C.

TABLE III

COMPOUNDS PRESENT IN $Ag_2MoO_4$–HgClBr REACTION MIXTURE

| Molar ratios of $Ag_2MoO_4$ and HgClBr in different mixtures | Compounds identified in mixtures | |
|---|---|---|
| | Kept at room temperature for 15 days | Heated at 100°C for 24 hr and then cooled to room temperature |
| 2:1 | AgCl, AgBr, $HgMoO_4$, and $Ag_2MoO_4$ | AgCl, AgBr, $HgMoO_4$, and $Ag_2MoO_4$ |
| 1:1 | AgCl, AgBr, and $HgMoO_4$ | AgCl, AgBr, and $HgMoO_4$ |
| 1:2 | AgCl, AgBr, $HgMoO_4$, and HgClBr | AgCl, AgBr, $HgMoO_4$, and HgClBr |
| 1:3 | AgCl, AgBr, $HgMoO_4$, and HgClBr | AgCl, AgBr, $HgMoO_4$, and HgClBr |

*Electrical conductivity measurements.* Electrical conductivity measurements were made on compressed polycrystalline samples using a stainless-steel conductivity cell following the procedure described earlier (*2*). The sample was in the form of a disk of about 2 mm thick and 31 $mm^2$ in surface area and was held between platinum electrodes. The electrical conductivity was measured using a GenRad Model 1657 RLC Dibridge (120 Hz). The basic accuracy of conductivity measurement was 0.2%.

*Diffusion coefficient measurements.* The vapor phase and the surface diffusion coefficient of HgClBr were determined as described earlier (*2*). Glass tubes of known diameter were filled with known amounts of HgClBr such that the distance of the HgClBr surface from the open end of the tube was the same in each case. Tubes were kept in an air thermostat maintained at 150 ± 0.5°C and the amount of HgClBr diffusing away was measured by weighing each tube at fixed time intervals. The vapor pressure of HgClBr was measured using a manometer.

## Results and Discussion

*Mechanism of chemical interaction.* Soon after mixing $Ag_2MoO_4$ and HgClBr (both powdered above 300 mesh) in an equimolar ratio at room temperature the white mixture gradually changed to yellow and remained as such even after a week. X-ray diffraction analysis (Table III) of the yellow mixture showed the presence of AgCl, AgBr, and $HgMoO_4$ only. This suggests that an equimolar mixture of $Ag_2MoO_4$ and HgClBr kept at room temperature for a week completely changed into AgCl, AgBr, and $HgMoO_4$ and the reaction seems to follow a simple exchange mechanism:

$$Ag_2MoO_4 + HgClBr \rightarrow AgCl + AgBr + HgMoO_4. \quad (1)$$

AgCl, AgBr, and $HgMoO_4$ were the products when a 1 : 1 molar mixture of $Ag_2MoO_4$ and HgClBr was heated at 100°C for 24 hr. Thermal measurement (Fig. 1) with a 1 : 1 molar mixture of $Ag_2MoO_4$ and HgClBr gives one inflection only, thereby offering no evidence of a two-step reaction. Ther-

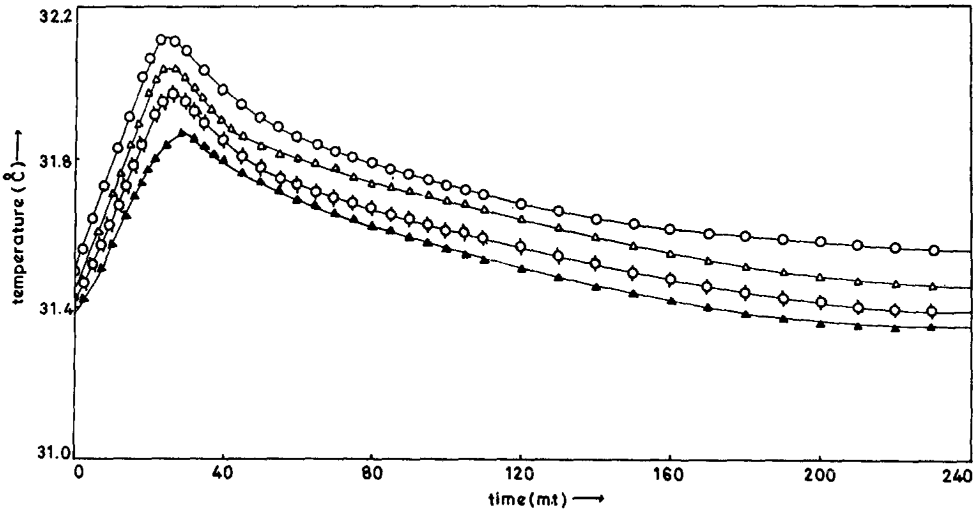

FIG. 1. Temperature rise as a function of time for the reaction between $Ag_2MoO_4$ and HgClBr. Molar ratios are (○) 2 : 1, (△) 1 : 1, (ϕ) 1 : 2, and (▲) 1 : 3.

mal maxima occur after 20 min of mixing powdered $Ag_2MoO_4$ and HgClBr and the continuous fall thereafter seems to be due to the dominance of dissipation of heat over the evolution rate. Electrical conductivity measurements made with disks prepared from a 1 : 1 molar mixture of $Ag_2MoO_4$ and HgClBr show a sharp rise and constancy thereafter. The initial rise in electrical conductivity is due to the formation of AgCl and AgBr which are more conducting than reactants and its constancy thereafter is due to completion of the reaction.

On heating this mixture of $Ag_2MoO_4$ and HgClBr above 100°C, the yellow mixture changed to reddish yellow at 200°C and this reddish-yellow color again changed to yellow when cooled below this temperature. X-ray powder diffraction measurements of this reddish-yellow mixture at 200°C give no evidence of the presence of any new compound. Electrical conductivity measurements of the mixture taken up to 220°C also do not show any sharp changes; rather, a gradual rise in electrical conductivity with a corresponding rise in temperature was observed.

The X-ray diffraction patterns with stoichiometric as well as nonstoichiometric mixtures of $Ag_2MoO_4$ and HgClBr have lines characteristic of AgCl, AgBr, and Hg $MoO_4$ only at both room temperature and 100°C. This suggests that $Ag_2MoO_4$ and HgClBr react in an equimolar ratio to give AgCl, AgBr, and $HgMoO_4$ as products at both room temperature and 100°C and excess of either of the reactants was left unreacted.

*Mechanism of lateral diffusion.* Soon after the placement of HgClBr over $Ag_2MoO_4$ in a glass capillary a yellow boundary formed at the interface and this grew only on $Ag_2MoO_4$ side and a gap developed simultaneously between the yellow layer and HgClBr. The lateral diffusion reaction proceeded well with the formation of yellow product on $Ag_2MoO_4$ surface even when the reactants were placed with an air gap at the start itself. This shows that solid HgClBr is the mobile species here and reacts with $Ag_2MoO_4$ grains at the interface between $Ag_2MoO_4$ and HgClBr to give AgCl, AgBr, and $HgMoO_4$ as products. For $Ag_2MoO_4$–HgClBr reaction lateral diffusion data for each isothermal reaction set fit (Fig. 2) best the equation

$$X^n = kt, \tag{2}$$

where $X$ is the thickness of product layer at time $t$ and $n$ and $k$ are constants. The value of $n$ varies from 2.60 to 2.10 in the temperature range 65–108°C and attains a constant value of 2 in the temperature range 118–140°C. The rate constant, $k$, is related to diffusion coefficient (*4*) and follows the Arrhenius equation. The activation energy was obtained from the Arrhenius plot of k (Fig. 3). The activation energies were 206 and 66 kJ/mole for low- and high-temperature ranges, respectively. The variation in the values of $n$ and activation energy suggest that the process occurring in the low-temperature range is different from the one that occurs in the high-temperature range. In lateral diffusion experiments the rate of growth of the product layer decreased with time. Initially the process is fast and reaction controlled. With the formation of product layers at the interface between two reactants, the reagents take more and more time to diffuse through the product layer; the process becomes diffusion controlled and the rate thus falls continuously with the growth of product layers. In diffusion-controlled solid-state processes where the reaction rate is inversely proportional to the product thickness, the constant $n$ in the above equation assumes a value of 2 and the expression becomes the parabolic rate law. In the present reaction the value of $n$ is 2 in the high-temperature range where the reaction is diffusion controlled while in the low-temperature range the rate of diffusion is comparatively fast and the overall pro-

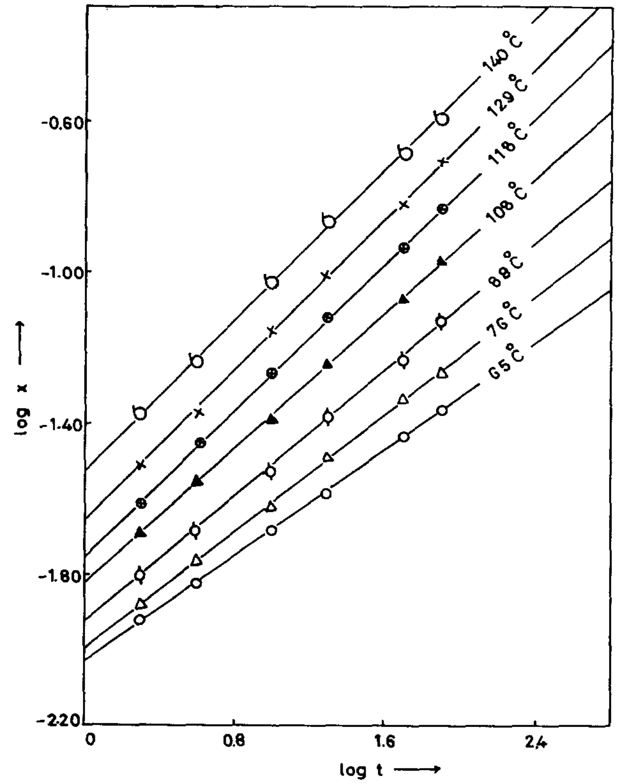

FIG. 2. Kinetic data for lateral diffusion and test of the equation $X^n = kt$ for the reaction between $Ag_2MoO_4$ and HgClBr.

cess is reaction controlled and consequently $n$ assumes a higher value. This was also confirmed by determining the diffusion coefficient of HgClBr, which is related to $k$ in Eq. (2); since the diffusion coefficient depends on temperature, we have

$$D = D_0\, e^{-E_a/RT}, \tag{3}$$

where $D_0$ is a constant, $E_a$ is energy of activation involved in diffusion, and $D$ is the diffusion coefficient of HgClBr, and since the heat of sublimation of HgClBr is much less than the activation energy for the reaction. Therefore the sublimation of HgClBr into vapor is virtually at equilibrium in the gap between HgClBr and the product layer formed at the surface of $Ag_2MoO_4$. So the equilibrium is maintained though the reaction is going on because the rate of reaction being diffusion controlled is less than the rate at which HgClBr has sublimated. Therefore the diffusion coefficient is proportional to the equilibrium concentration $C$ of HgClBr which in turn is related to the vapor pressure of HgClBr by the equation

$$P = CRT, \tag{4}$$

where $P$ is vapor pressure, $R$ the gas constant, and $T$ the absolute temperature. Vapor pressure of HgClBr was determined experimentally and was found to be an average of vapor pressure of individual species $HgCl_2$ and $HgBr_2$. However, since the measured value of vapor pressures of $HgCl_2$ and $HgBr_2$ do not compare well with the valued reported (*6*) we have taken re-

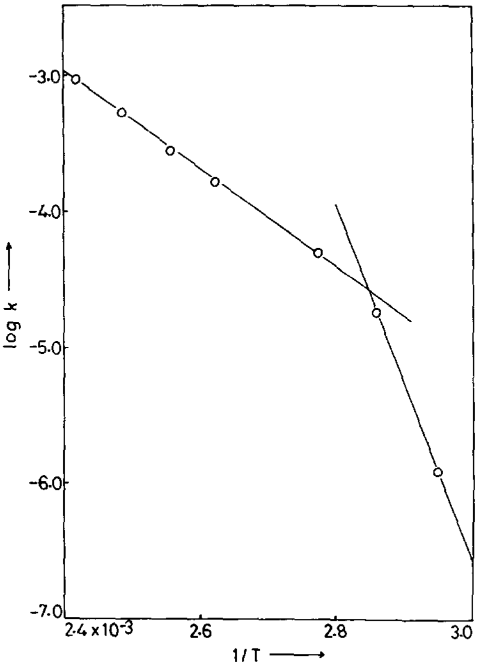

FIG. 3. Dependence of $k$ on temperature for the reaction between $Ag_2MoO_4$ and HgClBr.

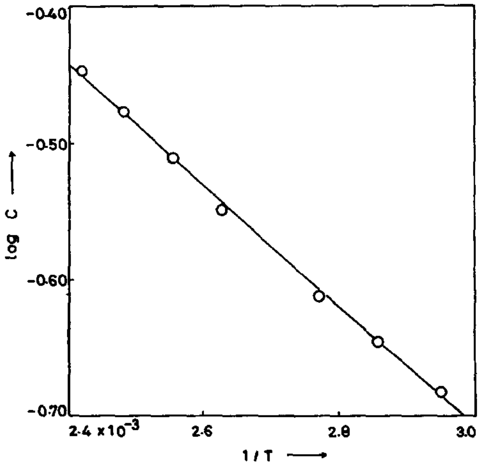

FIG. 4. Dependence of equilibrium concentration of HgClBr on temperature.

ported values of vapor pressure for all our calculations. Equilibrium concentration $C$ was calculated from Eq. (4) at different temperatures. When values of log $C$ are plotted against the reciprocal of absolute temperature, straight lines are obtained (Fig. 4). From Eq. (3) it follows that the slope gives the activation energy for diffusion. Activation energy $E_a$ in this case is 77.11 kJ/mole. This value is very close, taking all the approximations to the value of activation energy calculated from plots of log $k$ versus reciprocal of absolute temperature for the high-temperature range. This clearly suggests that the rate of reaction is diffusion controlled in the high-temperature range.

Rates of reaction were likewise studied with initial air gaps of different lengths between the reactants. The dimension of air gaps and respective rate constants are given in Table II. The rate constants $k'$ were found to depend on the length of air gap according to the equation

$$k' = Ae^{-bd}, \quad (5)$$

where $d$ is the length of air gap, and $A$ and $b$ are constants; when values of log $k'$ are plotted against $d$, straight lines are obtained. The linearity of plots in Fig. 5 indicates the decrease in reaction rate with an increase in the length of air gap and since

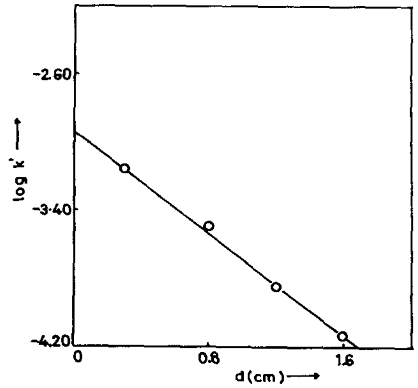

FIG. 5. Dependence of reaction rate on the length of air gap for the reaction between $Ag_2MoO_4$ and HgClBr.

HgClBr reacts predominantly in gaseous form, as it was confirmed by determining the diffusion coefficients of HgClBr, reaction continues to progress even after the formation of air gaps.

The vapor phase and the surface diffusion coefficients of HgClBr were determined as described previously (*2*) to ascertain their relative contributions in the diffusion-controlled $Ag_2MoO_4$–HgClBr solid-state reaction. The weight loss data best fit the relation

$$\Delta W = K_1 t, \qquad (6)$$

where $\Delta W$ is the amount of HgClBr diffused to the air in time $t$ and $K_1$ is a constant evaluated from $\Delta W$ versus $t$ plots (Fig. 6) for glass tubes of different radii. The values of $K_1$ depend on the diameter of tubes according to

$$K_1/r = \alpha r + \beta, \qquad (7)$$

where $r$ is the radius of tube. The test of Eq. (7) has been made by plotting $K_1/r$ against $r$ in Fig. 7, where $\alpha$ and $\beta$ are parameters (*7*) given by the equations

$$\alpha = \pi C D_v / l \qquad (8)$$

$$\beta = 2\pi C D_s, \qquad (9)$$

where $l$ is the distance of HgClBr surface from the open end of the tube, $C$ is the equilibrium concentration of HgClBr just above the surface and related to vapor pressure obeying the perfect gas law, $D_v$ is the vapor phase diffusion coefficient, and $D_s$ is the diffusion coefficient for surface migration. The values of $D_v$ and $D_s$ were calculated first by evaluating $\alpha$ and $\beta$ from the plots of $K_1/r$ against $r$ (Fig. 7) and then finding out the equilibrium concentration of HgClBr from vapor pressure. The vapor phase and surface diffusion coefficients of HgClBr are $2.25 \times 10^{-2}$ cm$^2$ sec$^{-1}$ and $2.15 \times 10^{-4}$ cm$^2$ sec$^{-1}$, respectively. These values of diffusion coefficients suggest that solid-state reaction of $Ag_2MoO_4$ with HgClBr is diffusion controlled and proceeds predominantly via gaseous phase, but the contribution of surface migration is also significant.

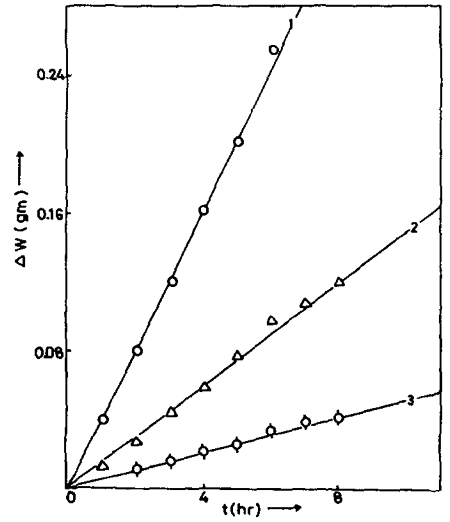

FIG. 6. Kinetic data for diffusion of HgClBr. Radius of glass tubes are (○) 0.4 cm, (△) 0.2 cm, and (ϕ) 0.1 cm.

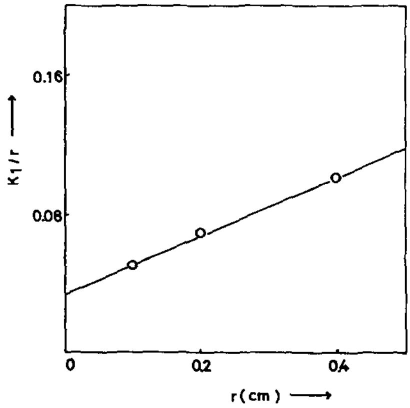

FIG. 7. Estimation of diffusion coefficient of HgClBr in air and surface migration.

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