Kinetics and Mechanism of Solid State Reactions in the AgI-TlI System

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The kinetics of the solid state reactions

$$AgI + TlI \rightarrow AgTlI_2 \qquad (I)$$
$$AgI + AgTl_2I_3 \rightarrow 2\ AgTlI_2 \qquad (II)$$
$$AgTlI_2 + TlI \rightarrow AgTl_2I_3 \qquad (III)$$

are investigated with reactant pellets by the contact method.

With the aid of inert marker experiments and transport number determinations it was possible to state that the governing mechanism is the cation counter-diffusion in all cases and that the rate determining step is the diffusion of Tl^+.

The experimental reaction rate constants agree reasonably with those calculated on the basis of the Wagner's thermodynamic theory.

Introduction

The solid state reactions between AgI and univalent cation iodides yield compounds with relatively high (in some cases very high) values of the electrical conductivity[1]. From electrical conductivity and transport number measurements it is rather easy to determine the mobility of the component species for these compounds and thus to evaluate the rate-determining step.

Up to date the kinetics of these reactions have been studied for the AgI-(K, Rb)I system only[2]. In the present work the results obtained in a kinetic study of the AgI-TlI system are reported.

The relevant phase diagram shows two different compounds: $AgTlI_2$ which melts incongruently at $240\ ^{\circ}C$ and $AgTl_2I_3$ which melts congruently at $327\ ^{\circ}C$[3]. Therefore, the kinetics was investigated for the formation reactions of $AgTlI_2$ and $AgTl_2I_3$ from α-AgI + α- or β-TlI (α-AgI, stable form between $147\ ^{\circ}C$ and mp; $T_{\alpha,\beta}$ of TlI $= 170\ ^{\circ}C$[4, 5]) in the temperature range $150.5 - 197\ ^{\circ}C$, $AgTlI_2$ from α-AgI + $AgTl_2I_3$ at $180\ ^{\circ}C$ and $AgTl_2I_3$ from $AgTlI_2$ + α-TlI at $180\ ^{\circ}C$. Couples of reagent pellets were used and the thickness of the product formed was measured by optical microscopy.

Moreover, in order to obtain information on the reaction mechanism, the inert marker method was used.

Finally, the measured rate constants were compared with those calculated on the basis of the Schmalzried equation[6] employing the transport number of Tl^+ and the electrical conductivity values as determined on $AgTlI_2$ and $AgTl_2I_3$.

Experimental

Fluka "puriss." AgI and TlI were used. $AgTlI_2$ and $AgTl_2I_3$ were prepared by melting under nitrogen AgI + TlI mixtures of proper composition, by quenching in liquid nitrogen and then annealing for 150 h at 215 and 300 $^{\circ}C$ respectively. The products so obtained were powdered, pelletized and again annealed at the same temperatures. The completion of compound formation was confirmed by X-ray, DSC and especially electrical conductivity measurements[7].

All the products were used in form of pellets (8 mm wide and ~ 1.5 mm thick) obtained by pressing the powders at $1.5 \cdot 10^3\ kg/cm^2$.

The apparatus employed for the rate measurements has been previously described[8]. Transport number determinations on $AgTlI_2$ and $AgTl_2I_3$ were carried out by the Tubandt method using as source of constant d. c. an Amel mod. 551 galvanostat. Conductometric data were obtained by a Wayne Kerr autobalance bridge B 331.

Results and Discussion

a) Kinetics Measurements

(I) Reaction AgI + TlI. From marker (Pt wires) experiments on the diffusion couples AgI|TlI kept at 180 °C for 120 h it was observed that the marker is located in the middle of a homogeneous deep yellow product layer, 350 μm thick. X-ray analysis on the finely powdered product exhibited only the reflections of $AgTlI_2$ [9], whereas some of the most intense reflections of $AgTl_2I_3$ could only be brought into evidence by X-ray analysis of the product surface in contact with TlI. It can be deduced that the thickness of this product layer is very small, anyhow lower than the minimum observable under the microscope.
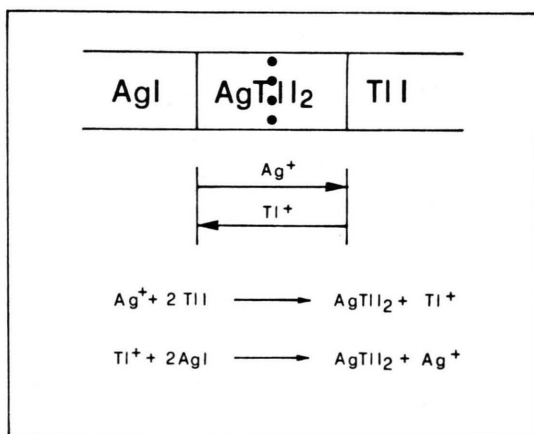

Fig. 1. Scheme for reaction (I) mechanism.

Figure 1 (where the marker position is indicated by dots) shows that the process mechanism is a cation counter-diffusion.

Strictly similar results were obtained at 160 °C, TlI being in the β form.

Fairly good linear plots of x^2 (x = average thickness of the product layer as measured by the microscope) vs. t are obtained as reported in Figure 2. The process follows the parabolic law [10]

$$x^2 = 2\,k\,v\,t \tag{1}$$

where k is the reaction rate constant and v, which is the volume increase of the reaction layer caused by transfer of one equivalent, takes different values according to the reaction mechanism (for $AgTlI_2$ formation, in this case, $v = 160$ cm^3/eq).

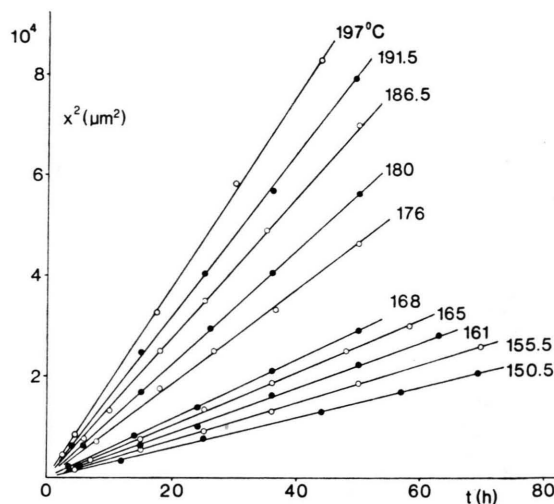The Arrhenius plot shown in Fig. 3 is characterized by two straight lines fitted by the equations
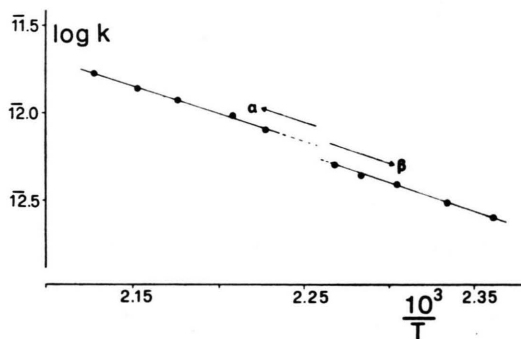

Fig. 2. Isotherms for reaction (I).

Fig. 3. Arrhenius plot for reaction (I).

$$(150.5 - 168\ ^{\circ}\text{C})\ \log k = -4.05 - 14{,}622/4.576\,T, \tag{2}$$

$$(176 - 197\ ^{\circ}\text{C})\ \ \log k = -4.06 - 14{,}439/4.576\,T \tag{3}$$

where k is expressed in eq cm^{-1} sec^{-1}.

(II) Reaction $AgI + AgTl_2I_3$. Marker experiments at 180 °C for 120 h on the diffusion couples AgI|$AgTl_2I_3$ showed that the marker position divided the formed $AgTlI_2$ layer (360 μm) in a 1:3 ratio. It follows that the reaction is governed by the cation counter-diffusion mechanism shown in Figure 4.

Measurements of the product thickness as a function of t were carried out at 180 °C: by Eq. (1), $k = 4.7 \cdot 10^{-12}$ (eq cm^{-1} sec^{-1}) was obtained (for $AgTlI_2$ formation, in this case, $v = 320$ cm^3/eq).

(III) Reaction $AgTlI_2 + TlI$. Marker experiments carried out on the couples $AgTlI_2$|TlI
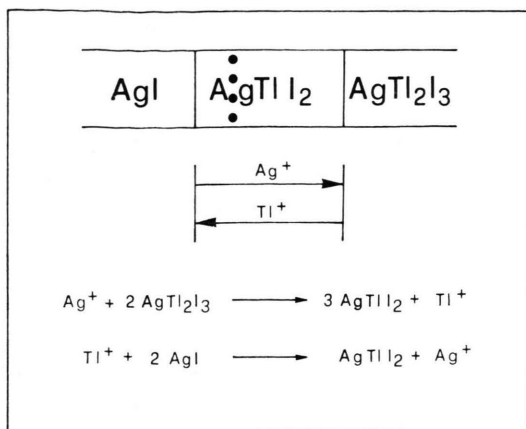
Fig. 4. Scheme for reaction (II) mechanism.

at 180 °C once again showed the marker inside the white product ($AgTl_2I_3$) layer. The thickness of the latter, however, even after very long reaction times (130 μm in 360 h) was not sufficient to allow an accurate estimate of the marker position. Anyhow, the following cation counter-diffusion mechanism can be reasonably proposed: at the $AgTl_2I_3 \mid TlI$ interface

$$Ag^+ + 3\,TlI \rightarrow AgTl_2I_3 + Tl^+$$
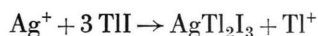
at the $AgTlI_2 \mid AgTl_2I_3$ interface

$$Tl^+ + 3\,AgTlI_2 \rightarrow 2\,AgTl_2I_3 + Ag^+ \,.$$
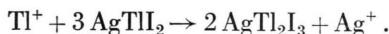
Also for this reaction, measurements of the product layer thickness as a function of t were carried out at 180 °C, yielding $k = 0.2 \cdot 10^{-12}$ eq cm^{-1} sec^{-1} (for $AgTl_2I_3$ formation, $v = 374$ cm^3/eq).

b) Transport Numbers and Conductivity Measurements

For the determination of the transport numbers of Ag^+ and Tl^+ in $AgTlI_2$, the pellet sequence

$$+Ag \mid AgI \mid AgTlI_2 \mid AgTlI_2 \mid AgTlI_2 \mid AgI \mid Ag-$$

was used *.

Table 1 reports the mass variations (mg) of each pellet for three different runs at 180 °C. The following transport number values were then obtained:

$$t_{Ag^+} = 0.97_5, \quad t_{Tl^+} = 0.02_5 \,.$$

As regards $AgTl_2I_3$ the measurements (carried out at the same temperature on a similar pellet sequence) yielded less accurate results owing to the disturbing reaction of AgI with $AgTl_2I_3$. It was possible, however, by means of a proper procedure to minimize this effect and to state that t_{Ag^+} and t_{Tl^+} in $AgTl_2I_3$ are of the same order of magnitude as in $AgTlI_2$.

The electrical conductivity (σ) measurements on $AgTlI_2$ were made in the temperature range 150 – 200 °C. In order to reduce the contact resistance, pellets of a $Ag + AgTlI_2$ mixture were used as electrodes.

The log σ values show a linear dependence on $1/T$ according to the equation

$$\log \sigma = 3.5 - 14{,}451/4.576\,T \,. \tag{4}$$

It should be noted that the slopes given by the Eqs. (2), (3), and (4) are practically the same.

For $AgTl_2I_3$ at 180 °C the value $\sigma = 5.0 \cdot 10^{-5}$ (ohm^{-1} cm^{-1}) was obtained.

c) Further Remarks

The marker experiments and the transport number determinations on Ag^+ and Tl^+ in $AgTlI_2$ and $AgTl_2I_3$ allow to conclude that the governing mechanism of the three reactions is the cation counter-diffusion and that the rate-determining step is the diffusion of Tl^+ in the product layer.

The rate constants for the reactions (I), (II) and (III) can be calculated by means of the thermodynamic theory proposed by Wagner [12] and developed by Schmalzried [6]. In the present case, the equation proposed by the latter author for cation

Charge flowed (coul.)	+Ag	AgI	AgTlI$_2$	AgTlI$_2$	AgTlI$_2$	AgI $\mid$ Ag−
36	−40.10	0	−0.70	−0.30	0	+41.10
60.8	−67.80	0	−1.15	−1.15	+0.05	+69.05
36	−40.00	0	−0.75	−0.05	−0.05	+40.70

Table 1. Transport number determinations of Ag^+ and Tl^+ on $AgTlI_2$ according to Tubandt. Mass variation (mg) at 180 °C.

* $AgTlI_2$ and $AgTl_2I_3$ show no electronic conductivity and have been classified as silver ion conductors [7]; the AgI pellets were inserted in order to avoid dendrite formation [11].

counter-diffusion is of the form

$$k = \gamma\, D_{Tl^+}\, c_{Tl^+}\, |\Delta G^0|/RT$$

were γ = numerical factor whose value depends on the reaction mechanism; D_{Tl^+} = self-diffusion coefficient of Tl^+ in the reaction layer **; c_{Tl^+} = equivalent concentration of Tl^+ in the reaction product; ΔG^0 = molar standard free energy of the reaction.

The ΔG^0 values of these reactions were estimated by the Wagner method [13] applied to the AgI-TlI phase diagram. These values, necessarily obtained only for particular temperatures, were used at 180 °C.

In spite of the approximations involved, the calculated values are in satisfactory agreement with those directly obtained at 180° by kinetics measurements (Table 2).

Finally, the fact that reaction (III) is much slower than reaction (II) might reasonably account for the observed absence of appreciable amounts of $AgTl_2I_3$ in reaction (I).

The authors are indebted to Dr. G. Chiodelli for having kindly carried out the conductivity measurements.

Table 2. Comparison of k_{calc} and k_{exp} (eq cm^{-1} sec^{-1}) at 180 °C for reactions (I), (II) and (III).

Reaction	γ	$D_{Tl^+} \cdot 10^{10}$ (cm^2 sec^{-1})	$c_{Tl^+} \cdot 10^2$ (eq cm^{-3})	ΔG^0 (kcal mole^{-1})	$k_{calc} \cdot 10^{12}$ (eq cm^{-1} sec^{-1})	$k_{exp} \cdot 10^{12}$ (eq cm^{-1} sec^{-1})
(I)	2	2.7	1.25	−1 (202 °C)	7.5	9.6
(II)	4	2.7	1.25	−0.3 (175 °C)	4.5	4.7
(III)	1.5	0.3	1.60	−0.2 (175 °C)	0.2	0.2

** The D_{Tl^+} values at 180° have been evaluated by the Nernst-Einstein equation assuming a unitarian correlation factor:

$$D_{Tl^+} = (RT/F^2)\, t_{Tl^+}\,(\sigma/c_{Tl^+}) .$$

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