Kinetic Studies of Crystal Growth of the Sparingly Soluble Salt by the Pressure-Jump Technique

I. Thallium Sulfate

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The pressure-jump technique with conductivity detection has been adopted for the kinetic study of crystal growth of sparingly soluble salt. The single relaxation was observed in aqueous suspension of thallium sulfate. The reciprocal relaxation time observed increases linearly with the concentration of crystal. According to the chemical relaxation treatment, the rate constants of crystal growth and dissolution in the suspension of crystal were determined to be 4.6×10^{-1} mol^{-1} dm^3 s^{-1} and 2.1×10^{-2} s^{-1}, respectively, at 25°C. © 1993 Academic Press, Inc.

INTRODUCTION

The crystal growth of sparingly soluble salts is a fascinating process and is essential to gaining an understanding of *in vivo* biological mineralization processes. In most experimental studies aimed at elucidating the mechanism of crystal growth, the reactions are induced by the addition of aged seed crystals and the rates are monitored by following the decrease in lattice ion concentrations. However, the conventional seeded crystallization techniques present shortcomings which cannot make the mixture uniform within a short time. On the other hand, the pressure-jump technique with conductivity detection may be down to 100 μs and is suitable to study over extended periods the crystal growth of salt whose solubility changes with pressure.

In this paper, we present the results of pressure-jump experiments in the aqueous thallium sulfate suspension which is sensitive to pressure, and discuss kinetically the mechanism of relaxation from the point of view of crystal growth as the starting paper of the main subject.

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EXPERIMENTAL

The pressure-jump apparatus with conductivity detection generally applicable to the solution was used with minor modification. The sectional view of the unmodified pressure-jump apparatus has been described previously (1) and is drown in Fig. 1. It has the time constant of 100 μs at the bursting pressure of 100 atm. The special attachment shown in Fig. 2 was fixed to the central pressure-jump chamber in exchange for the sample cell in Fig. 1 to make uniform the aqueous suspension of the crystal particle.

The sample cell is 6 mm inner depth and 6 mm inner diameter and contains the teflon-coated magnetic stirring bar of 5 mm length and 2 mm diameter to stir the suspension. The uniformity of the sample suspension in cell was checked by the change in the balance of the bridge with stirring speed, that is, the balance signal of the carrier wave spread on the oscilloscope becomes constant above some stirring speed.

The thallium sulfate was selected as the sample because the dependence of solubility in water on pressure is fairly large compared with general salts (2). The thallium sulfate (reagent-grade chemicals, Wako Chemical Co.) was ground into pieces by the vibrating mill (MRK-Retsch) and was washed several times with distilled water to remove impurities. The particle size was 4–10 μm diameter and the specific surface area determined by the BET method was 0.14 m^2 g^{-1}. The sample suspension immersed in the thermostat was stirred with the magnetic stirrer until the conductivity of the supernatant of the suspension reaches a constant value.

RESULTS

Figure 3a shows the typical relaxation curve observed in the suspension of Tl$_2$SO$_4$ crystal. This relaxation curve in-
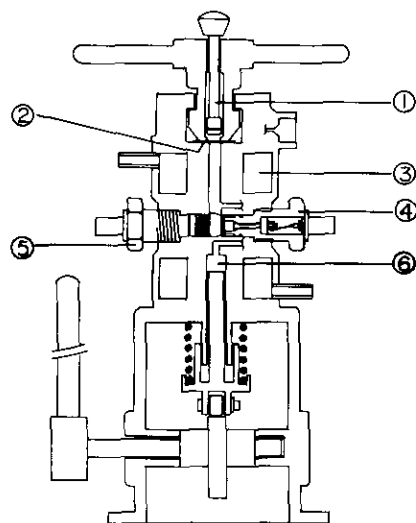
FIG. 1. Sectional view of the autoclave of the pressure-jump apparatus: ① vacuum pump, ② rupture diaphragm, ③ heat exchanger, ④ sample cell, ⑤ reference cell, and ⑥ pressure pump

FIG. 3. (a) Typical relaxation curve for the Tl_2SO_4 system observed by using the pressure-jump method with electric conductivity detection at concentration $= 0.36$ mol dm^{-3} and 25°C. (b) Semilogarithmic plot of relaxation curve.

dicates the decrease of the conductivity with time. Considering that the heat of solution of Tl_2SO_4 crystal in water is endothermic, the relaxation in Fig. 3a can be attributed to the reaction between ions. No relaxation could be observed in the supernatant solution of the suspension of Tl_2SO_4. These facts suggest that the Tl_2SO_4 particle relates to the observed relaxation. The semilogarithmic plot of the typical curve in Fig. 3a is expressed by a straight line as shown in Fig. 3b, showing that the relaxation curve consists of a single relaxation process. Figure 4 shows the dependence of reciprocal relaxation time, τ^{-1}, on the concentration of Tl_2SO_4

crystal. As can be seen from Fig. 4, the reciprocal relaxation time increases linearly with the concentration of crystal. This fact emphasizes that the relaxation observed is closely related to the growth of Tl_2SO_4 crystal.

DISCUSSION

First, let us examine the following simple mechanism for the relaxation:

$$SO_4^{-2} \underset{Tl^+}{\overset{l}{\rightleftharpoons}} TlSO_4^- \underset{Tl^+}{\overset{l}{\rightleftharpoons}} Tl_2SO_4. \qquad [I]$$
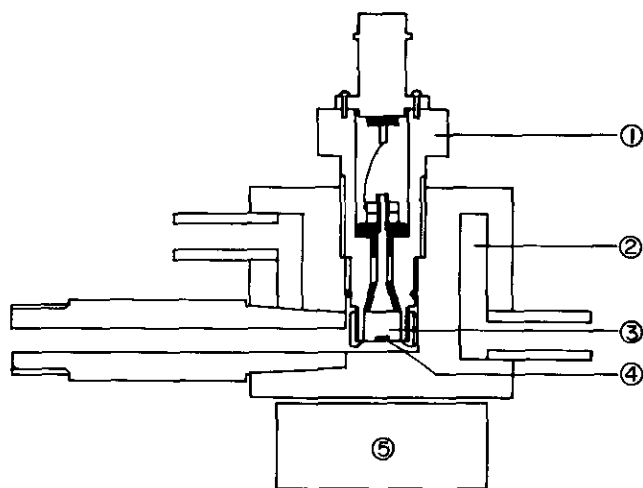

FIG. 2. Sectional view of the attachment: ① sample cell, ② heat exchanger, ③ sample, ④ teflon-coated magnetic stirring bar, and ⑤ magnetic stirrer.
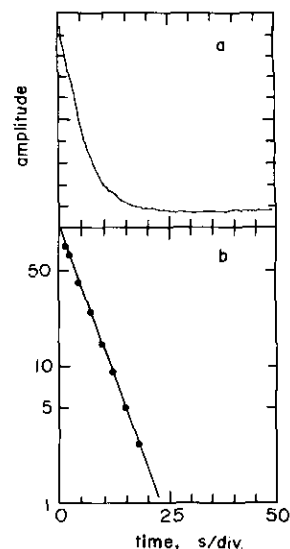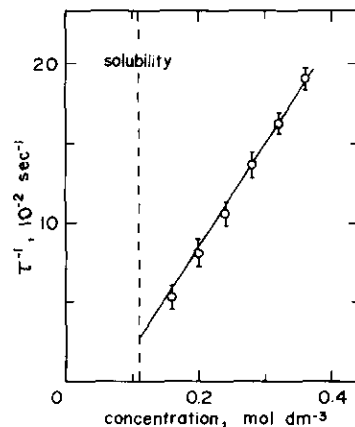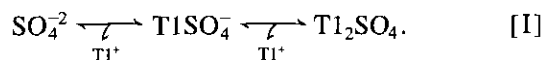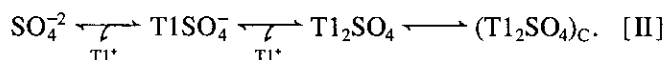

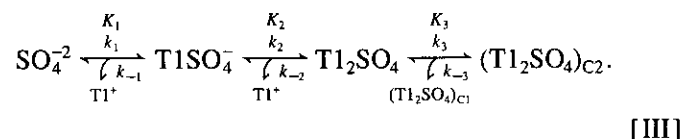FIG. 4. Dependence of τ^{-1} on the concentration of Tl_2SO_4 at 25°C; the dotted line indicates the solubility of Tl_2SO_4.

Both of equilibrium hold in the saturated aqueous solution of Tl_2SO_4. Since no relaxation could be observed in the supernatant solution of the Tl_2SO_4 suspension, mechanism [I] must be easily eliminated as a possibility.

Next, the following three-step mechanism of crystal growth from the saturated solution was considered:

$$SO_4^{-2} \underset{Tl^+}{\overset{}{\rightleftharpoons}} TlSO_4^- \underset{Tl^+}{\overset{}{\rightleftharpoons}} Tl_2SO_4 \longrightarrow (Tl_2SO_4)_c. \quad [II]$$

Here $(Tl_2SO_4)_c$ denotes the crystal of Tl_2SO_4. In this mechanism the expression of reciprocal relaxation time for the last step is invalid for the concentration of $(Tl_2SO_4)_c$. Thus, mechanism [II] could be also ruled out because the reciprocal relaxation time observed increases with the amount of crystal.

Finally, we considered another type of three-step mechanism for the crystal growth as follows:

$$SO_4^{-2} \underset{Tl^+}{\overset{K_1}{\underset{k_{-1}}{\rightleftharpoons}}} TlSO_4^- \underset{Tl^+}{\overset{K_2}{\underset{k_{-2}}{\rightleftharpoons}}} Tl_2SO_4 \underset{(Tl_2SO_4)_{c1}}{\overset{K_3}{\underset{k_{-3}}{\rightleftharpoons}}} (Tl_2SO_4)_{c2}.$$

$$[III]$$

Here $(Tl_2SO_4)_{c1}$ and $(Tl_2SO_4)_{c2}$ are two kinds of crystals of Tl_2SO_4, k and K denote the rate and equilibrium constants, respectively. Under the assumption that both crystals have the same characteristics and are numerically equal, and the first and second steps equilibrate much more rapidly than the third step, the reciprocal relaxation time, τ^{-1}, for the slow step is given by

$$\tau^{-1} = k_{-3} + k_3[\overline{Tl_2SO_4}] + k_3 a\alpha[\overline{(Tl_2SO_4)_{c1}}] \quad [1]$$

with

$$a = \frac{A}{1 + K_1([SO_4^{2-}] + [Tl^+]) + A}$$

$$A = K_2\{2[\overline{TlSO_4^-}] + K_1[\overline{Tl^+}](2[\overline{SO_4^{2-}}]$$
$$+ [\overline{Tl^+}] + [\overline{TlSO_4^-}])\},$$

where α is a parameter and the bar over the concentration symbols, [ ], denotes equilibrium concentration. Equation [1] indicates the linearity of the plots of τ^{-1} versus $[\overline{(Tl_2SO_4)_{c1}}]$, supporting the plausibility of mechanism [III].

TABLE 1

Rate Constants of Crystal Growth and Dissolution
of Tl_2SO_4 at 25°C

k_3 (mol^{-1} dm^3 s^{-1})	k_{-3} (s^{-1})
4.6×10^{-1}	2.1×10^{-2}

In order to determine kinetically the values of the rate constants, k_3 and k_{-3}, from Fig. 4 using Eq. [1], the concentrations of all of the species, and the values of the equilibrium constants and parameter in Eq. [1] should be decided. However, since the value of α is unknown, the estimation of the value of k_3 from the slope in Fig. 4 is impossible.

On the other hand, from the definition of the equilibrium constant, one is led to

$$K_{3D} = \frac{k_3}{k_{-3}} = K_{3S}, \quad [2]$$

where the subscripts D and S denote dynamic and static, respectively. Combing Eqs. [1] and [2] yields the simple relation for the intercept of Fig. 4:

$$\text{Intercept} = 2k_3[\overline{Tl_2SO_4}] = 2k_{-3}. \quad [3]$$

The values of the rate constants, k_3 and k_{-3}, were calculated from the intercept of the obtained straight line using the values of solubility (3) and ionization (4) for aqueous Tl_2SO_4 solution and are listed in Table 1. Unfortunately useful information on parameter α is not available and we cannot pursue the discussion further.

Similar kinetic studies of crystal growth of various sparingly soluble salts are now in progress. The results will be reported in due course.

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