

KINETICS OF PRECIPITATION OF HYDRATED TiO_2 FROM TITANYL SULPHATE SOLUTIONS

O.SÖHNEL

Research Institute of Inorganic Chemistry, 400 60 Ústí n. Labem

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Kinetics of precipitation of hydrated TiO_2 from titanyl sulphate solutions within the thermal hydrolysis of nucleation has been examined. The growth of nuclei is controlled by polynuclear layer mechanism of the kinetic order of $p = 1$. At the beginning of hydrolysis, new particles are being formed by a mechanism of homogeneous nucleation. Interfacial tension crystal-solution was for the given case estimated to $\sigma \sim 270 \text{ erg/cm}^2$. The established mechanism of the growth of particles is in accordance with the model of the chemism of hydrolysis, suggested in the literature.

In the production of titanium white, quality of the resulting pigment is to a great extent defined by properties (structure and composition) of hydrated TiO_2 gel produced during hydrolysis of a titanyl sulphate solution. For that reason, a great attention has been given in the literature to hydrolysis of the solutions of titanium compounds, both from the viewpoint of the kinetics of the solid phase separation¹⁻⁵ and from the point of view of the solution^{6,7} and hydrolysate structures^{1,2,8-11}. But the results obtained are not quite unambiguous and do not allow to characterize the hydrolysate as being dependent on conditions of the hydrolysis. The present paper deals, therefore, with the kinetics and mechanism of hydrolysis of titanium solutions.

THEORETICAL

The separation of a solid phase on the nuclei from a supersaturated solution is controlled by a mechanism of the growth of particles, which may be of diffusion, mononuclear, or polynuclear character. The combinations of the three types may also be involved. If there are N spherical particles of equal size present in a supersaturated solution, the kinetic curve of the increase of a solid phase for individual control mechanisms may be derived. According to Nielsen¹² it holds for

a) the diffusion controlled growth that

$$t = D^{-1} [48\pi^2 v N^2 (c_0 - s)]^{1/3} \int_0^\alpha x^{-1/3} (1-x)^{-1} dx = K_D I_D, \quad (I)$$

b) mononuclear growth that

$$t = 0.54\omega^{-1} d^2 N^{1/3} D^{-1} c_0^{-1/3} \exp(\Delta G^*/kT) \int_{\alpha_0}^{\alpha} x^{-4/3} (1-x)^{-m} dx = K_m^+ I_m^+(\alpha_0, \alpha) \quad (2)$$

and for

c) polynuclear growth that

$$t = 0.33D^{-1} [c_0/(c_0 - s)^2 N]^{1/3} \exp(\Delta G^*/3kT) \int_0^{\alpha} x^{-2/3} (1-x)^{-p} dx = K_p I_p(\alpha), \quad (3)$$

where

$$p = (m + 2)/3. \quad (4)$$

It follows from the theory that m equals the number of molecules which form the critical nucleus n^* .

The growth mechanism of the nuclei can be on the basis of equation (1)–(3) established by plotting I_D , $I_m^+(\alpha_0, \alpha)$ and $I_p(\alpha)$, calculated from experimentally found data $\alpha(t)$, against the corresponding t . The alternative which provides linear dependence t – I in the studied part of the reaction is then the determining mechanism of the growth.

Provided that polynuclear growth is the determining mechanism, equation (3) attains for $\alpha \rightarrow 0$ a form

$$\begin{aligned} t &\approx K_p \int_0^{\alpha} x^{-2/3} dx = K_p 3\alpha^{1/3} \\ &\approx 27^{-1} K_p^{-3} t^3 = 1.03 D^3 (c_0 - s)^2 N c_0^{-1} \exp(-\Delta G^*/kT) t^3. \end{aligned} \quad (5)$$

Up to now, increase of the solid phase only due to the growth of nuclei in the solution, has been considered. However, we cannot exclude formation of new particles in the solution, as a result of homogeneous, heterogeneous, or secondary nucleations and their further growth, which becomes evident in a higher α value at a given time than it would correspond to a mere growth of the nuclei. Because of the theory of heterogeneous and secondary nucleations being not at present sufficiently elaborated, we shall for simplification use an idea of a homogeneous nucleation formation of new particles in the solution.

The number of particles produced in a unit volume at time τ , $\tau + d\tau$ is

$$dN = J d\tau. \quad (6)$$

The growth rate of spherical particles by polynuclear mechanism is¹³

$$dr/dt = Dv^{1/3} (c_t - s)^{2/3} \exp(-\Delta G^*/3kT). \quad (7)$$

At time ϑ , $\vartheta + d\vartheta$, radius of a particle increases by

$$dr = Dv^{1/3} (c_t - s)^{2/3} \exp(-\Delta G^*/3kT) d\vartheta \quad (8)$$

and radius of the particle growing in a time interval $\tau - t$ is then

$$r = Dv^{1/3} \exp(-\Delta G^*/3kT) \int_{\tau}^t (c_t - s)^{2/3} d\vartheta. \quad (9)$$

Total volume of spherical particles produced at time τ , $\tau + d\tau$ is

$$4/3\pi r^3 dN = D^3 v \exp(-\Delta G^*/kT) \left[\int_{\tau}^t (c_t - s)^{2/3} d\vartheta \right]^3 \cdot J d\tau \quad (10)$$

and volume of crystals produced by nucleation at time t is

$$V(t) = D^3 v \exp(-\Delta G^*/kT) \int_0^t \left[\int_{\tau}^t (c_t - s)^{2/3} d\vartheta \right]^3 \cdot J d\tau. \quad (11)$$

Because of c_t for a small t being $c_t \approx c_0$ and $c_0 \gg s$, relationship (11) can be partially integrated

$$V(t) = D^3 v \exp(-\Delta G^*/kT) c_0^2 \int_0^t (t - \tau)^3 J d\tau. \quad (12)$$

In the first approximation $J \sim J_0$ is for $c \sim c_0$, and consequently

$$V(t) = D^3 v \exp(-\Delta G^*/kT) c_0^2 J_0 1/4 t^4. \quad (13)$$

Since $V(t) = v(c_0 - c_t) = v\alpha c_0$, equation (13) can be modified to

$$\alpha = 0.25 D^3 \exp(-\Delta G^*/kT) c_0 J_0 t^4. \quad (14)$$

Relation (14) denotes increase of the solid phase on account of nucleation of new particles and their subsequent growth. Provided that formation of the new particles with their subsequent growth takes place simultaneously with the growth of the nuclei, the resulting α is given by relation

$$\alpha = D^3 c_0 \exp(-\Delta G^*/kT) t^3 [1.03N + 0.25J_0 t]. \quad (15)$$

Equation (15) holds for the case that c_0 does not differ too much from c_t .

EXPERIMENTAL

Precipitation of hydrated TiO_2 from nucleated titanium solutions of approx. composition 220 g TiO_2 /l, 4 g Ti^{3+} /l, 65 g Fe^{2+} /l and 550 g H_2SO_4 /l, was examined. Equal amount of the TiO_2 hydrosol prepared by neutralizing dilute titanium solution with NaOH solution up to pH 3.5 [ref.¹⁴] was always used for the nucleation. The Ti concentration is in the nucleated hydrosol approximately 25 g TiO_2 /l.

The nucleation suspension was added to the titanium solution which was brought to boiling ($\sim 110^\circ\text{C}$). After the boiling point has been reached, ($t' = 0$) samples of the hydrolysing solutions, in which the Ti content in the liquid phase was determined analytically, were taken at appropriate time intervals. Procedure: 50 ml of the sample was diluted with 200 ml H_2SO_4 (1 : 10) and the solid phase centrifuged, or filtered off. The filtrate was under an inert atmosphere

reduced to Ti³⁺ which was determined titrimetrically. The values thus obtained were converted to the degree of hydrolysis, according to relationship

$$\alpha = (c_0 - c_t)/c_0, \quad (16)$$

where c_0 is total TiO₂ content at the moment of reaching the boiling point. This way of following the hydrolysis does not allow to determine with a sufficient precision a state, when $\alpha < 0.1$.

RESULTS

A typical kinetic curve of hydrolysis is shown in Fig. 1. For the origin, the time is chosen, when the solution reached the boiling point. Shapes of the kinetic curves of the hydrolysis examined are essentially consistent. For $\alpha < 0.1$, the experimentally determined dependence $\alpha-t$, is for the reasons given formerly, not enough reliable. In the hydrolyses studied, for individual times t' the corresponding I_D, I_{1-4} values were calculated according to (1)–(3) from appropriate experimentally found values α . Dependences $t'-I$ for the hydrolysis described in Fig. 1 are graphically presented in Fig. 2. It follows from Fig. 2 that for the given case, function I_1 satisfies best the part of thermal hydrolysis (*i.e.* $0.1 < \alpha \lesssim 0.7$), which means that the determining mechanism of the particles growth, is polynuclear layer growth of the order of $p = 1$ within the given limits. For $\alpha \gtrsim 0.7$, the increase of precipitated TiO₂ is greater

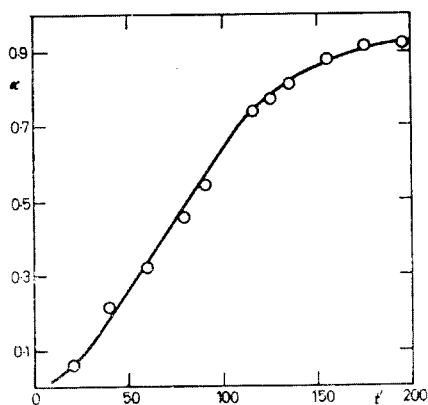


FIG. 1
Kinetic Curve of Hydrolysis for Sample No 10

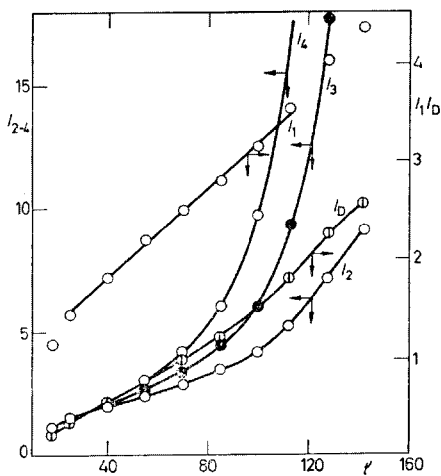


FIG. 2
Plot of I_D, I_{1-4} against t for Hydrolysis of Sample No 10

than it would correspond only to the growth on the particles already present. An analogous result was obtained for all hydrolyses examined, taking into account that in some cases it was not possible to determine definitely, whether I_D or I_1 satisfy better. In no case, however, I_{2-4} and I_{1-4}^+ satisfy the kinetics of hydrolysis. A straight line

$$I_1 = at' + I_1^0, \quad (17)$$

was led with use of the least squares method through the linear section of the $t'-I_1$ dependence. Values of the constants are presented in Table I. For $t' = 0$, $I_1 = I_1^0$ and the straight line does not pass through the origin as is required by relation (3). This means that at the beginning of boiling the hydrolysis already proceeds and $\alpha = \alpha_0$. The proper separation of the solid phase from the solution starts then in the time, when the boiling point had not been reached, *i.e.* in the "warm-up-period".

The shift of the beginning of hydrolysis with respect to the boiling point, can be determined using condition $I_1 = 0$ for $t = 0$, provided that hydrolysis proceeds from its beginning by the same mechanism. Time t_0 indicating this shift, calculated from (17) is presented in Table I.

Time coordinates $t = t' + t_0$ fulfil condition $I_1 = 0$ for $t = 0$. It is not difficult to prove that

$$dt/dI_1 = dt'/dI_1 = K_1 = 1/a, \quad (18)$$

TABLE I

Constants of Equations (17) and (18) for Hydrolyses Examined

Linearity α expresses interval α in which equation (3) is for $p = 1$ fulfilled.

Sample Linearity	α	$a \cdot 10^2$	K_1 min	I_1^0	$\alpha_0 \cdot 10^4$	t_0 min
1	0.1—0.7	2.83	35.3	0.372	20	13.1
2	0.1—0.7	2.71	36.9	0.180	1.8	6.6
3	0.1—0.6	2.42	41.3	0.700	125	28.9
4	0.1—0.6	2.34	42.7	0.555	64	23.7
5	0.1—0.6	2.18	45.9	0.527	54	24.2
6	0.1—0.6	2.30	43.5	0.688	120	29.9
7	0.1—0.6	2.19	45.7	0.772	160	35.2
8	0.1—0.6	2.04	49.0	0.814	190	39.9
9	0.1—0.6	2.04	49.0	0.921	280	45.2
10	0.1—0.7	2.29	43.7	0.894	260	39.1

DISCUSSION

Function I_1 in most cases satisfies best the kinetics of separating hydrated TiO₂ from titanium solutions in the thermal hydrolysis of nucleation and in some cases only it is difficult to decide between I_D and I_1 . Becker¹ found for the same type of hydrolysis dependence

$$\alpha = \text{const} \cdot Nt^3 \quad (19)$$

valid for $\alpha \sim 0.25$, which is consistent with equation (5) describing kinetics determined by a polynuclear mechanism for $\alpha \rightarrow 0$. Bobyrenko⁵ as well, found the same type of dependence as is that expressed by (19). The hydrolysis is then controlled by polynuclear mechanism of the particles growth, since in the diffusion controlled growth, relation (1) is for $\alpha \rightarrow 0$ modified to

$$t \approx K_D \int_0^\alpha x^{-1/3} dx = 1.5\alpha^{2/3}, \quad (20)$$

$$\alpha \approx (0.66/K_D)^{3/2} t^{3/2},$$

which does not correspond to the exponent found experimentally.

It has been established^{1,16} that the activation energy of hydrolysis amounts approximately to 25–30 kcal/mol. The activation energy of diffusion in aqueous solutions varies within 2–4 kcal/mol, and for the case examined, it will not differ too much from this value. This fact proves again that the determining step in the hydrolysis is reaction in the surface of a solid and not diffusion in the solution.

On the basis of these facts it may be concluded that the kinetics of separating hydrated TiO₂ from titanium solutions is in the thermal hydrolysis of nucleation controlled by a polynuclear layer mechanism of the nuclei growth of the kinetic order of $p = 1$. The established order of the polynuclear growth of hydrated TiO₂ particles is $p = 1$, which means according to (4) that $m = n^* = 1$. The critical nucleus of a new layer on the TiO₂ crystal surface is then formed by one molecule only. From the molecular point of view this means that the molecule, which adopts in the crystal surface a favourable orientation of the substrate (or an active place in the surface), is attached by chemical bond to the crystal. Such a conclusion is, from the viewpoint of thermodynamic conceptions associated with the formation of a new lattice plane during crystallization without a chemical reaction proceeding simultaneously, quite absurd.

On the basis of the chemism of hydrolysis⁷ of titanium solutions, a model has been suggested, according to which the polynuclear complex of titanium with hydroxyl bridges, which occurs in the solution, condensates in contact with the nucleus surface, the chemical bonds with the

substrate being simultaneously produced. To achieve this, molecule of the complex must be brought to a suitable orientation with the substrate in order that the chemical bond should be possible. This means that not every molecule brought to the surface of the nucleated crystal can be attached to the surface, but only that which has a favourable orientation. For that reason, no diffusion of molecules to the crystal surface, but the surface reaction can be the determining mechanism, this fact being in accordance with experimentally found data. The attachment of a further molecule to the nucleus of a new layer is then considerably easier and the growth will therefore proceed in layers. It follows from the fact that the growth is of polynuclear nature that more of molecules are brought to a suitable orientation, and the new layer is therefore produced in several places of the surface at the same time. Obviously, the growth mechanism of TiO_2 particles, found by us, is in agreement with the model of hydrolysis, suggested in paper⁷.

For the polynuclear growth of the first order, ΔG^* is the energetic barrier connected with orientation and attachment of the molecule to the crystal surface. In spite of this, we shall use relations derived in the theory of nucleation¹² to calculate interfacial tensions crystal-solution. Constant K_1 in relation (3), provided that $c_0 \gg s$, attains the form

$$K_1 = 0.33D^{-1}(c_0N)^{-1/3} \exp(\Delta G^*/3kT). \quad (21)$$

According to ref. 12 it holds that

$$\Delta G^* = \beta\sigma^2v^{4/3}/k^2T^2 \ln S. \quad (22)$$

By combining (21) and (22) and modifying the result we obtain

$$\sigma = kTv^{-2/3}[(2.303 \ln S)/\beta \log(K_1D/0.33)^3 c_0N]^{0/5}. \quad (23)$$

By inserting individual quantities, estimated from experimental conditions, into (23) — $\ln S = 1.61$, $D = 10^{-6} \text{ cm}^2/\text{s}$, $K_1 = 2.6 \cdot 10^3 \text{ s}$, $kT = 1.38 \cdot 10^{-16} \cdot 383 = 5.3 \cdot 10^{-14} \text{ erg}$, $v^{2/3} = 10^{-15} \text{ cm}^2$, $\beta = 4$, $c_0 = (220/6.99)(6.10^{23} \cdot 10^{-3}) = 2.2 \cdot 10^{20}$ of $[\text{Ti}(\text{OH})_3]_6^+$ /cm³ particles¹⁷, $N = 2.4 \cdot 10^{14}$ particles/cm³ — we obtain

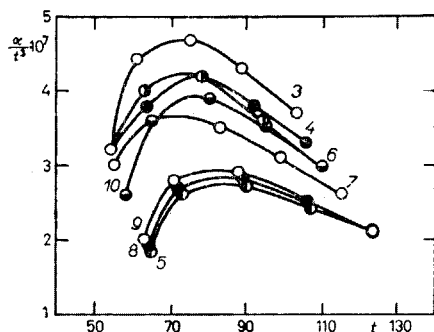


FIG. 3
Dependence (23) for Hydrolyses Examined

$\sigma \sim 270 \text{ erg/cm}^2$. Even though some of the quantities or even several quantities would be estimated with an error of one order of magnitude, the calculated σ will be still within limits determined¹⁵ for the interfacial tension crystal–solution at work. This fact may serve as verification of the correctness of the made analysis of precipitating TiO₂ from titanium solutions during thermal hydrolysis of nucleation.

A question remains, what happens in the first stage of hydrolysis, of which no sufficient information is up to now available. Into equation (15) in the form

$$\alpha/t^3 = A + Bt, \quad (24)$$

where

$$A = 1.03D^3c_0 \exp(-\Delta G^*/kT)N,$$

$$B = 0.25D^3c_0 \exp(-\Delta G^*/kT)J_0$$

experimental values of t for $\alpha = 0.05; 0.1; 0.2; 0.3; 0.4$ were inserted. Dependence (24) is for some examined hydrolyses, graphically presented in Fig. 3. Equation (15) or (24) is fulfilled up to $\alpha \sim 0.25$. Afterwards, a deviation takes place, since relation (5) can no longer be applied. For that reason α/t^3 decreases for $\alpha > 0.2-0.3$, even when it should possess a constant value. From the course of the dependence for $\alpha < 0.2$ it follows that $B > 0$, and consequently new particles are produced by primary nucleation at the beginning of hydrolysis. Value B , however, cannot be found as a tangent of straight line in Fig. 3, because of lack of reliable information for region $\alpha < 0.1$.

The conclusion on the formation of new particles in initial stages of the hydrolysis of nucleation is consistent with the finding of Bobyrenko⁴, made on somewhat different basis.

LIST OF SYMBOLS

- a tangent of straight line (17)
- A_i surface area of a nucleus
- c_0 concentration of solution at time $t = 0_*$
- c_t concentration of solution at time t
- D diffusion coefficient
- ΔG^* change in free enthalpy in the formation of the surface critical nucleus
- $I_D = \int_0^x x^{-1/3}(1-x)^{-1} dx$ diffusion integral
- $I_m^+ = \int_0^x x^{-4/3}(1-x)^{-m} dx$ mononuclear integral
- $I_p = \int_0^x x^{-2/3}(1-x)^{-p} dx$ polynuclear integral
- $I_{1-4} = I_p$ for $p = 1-4$
- I_1^0 value of integral I_1 at time $t' = 0$
- J rate of nucleation
- k Boltzmann's constant
- $K_D = D^{-1}[48\pi^2vN^2(c_0 - s)]^{-1/3}$ constant

- $K_m^+ = 0.53\omega^{-1}d^2N^{1/3}D^{-1}c_0^{-1/3} \exp(\Delta G^*/kT)$ constant
 $K_p = 0.33D^{-1}[c_0/(c_0 - s)^2 N]^{1/3} \exp(\Delta G^*/3kT)$ constant
 $K_1 = K_p$ for $p = 1$
 L_i circumference of nucleus
 $m = n^*$ kinetic order of the surface nucleation
 N number of particles
 n^* number of molecules in the critical surface nucleus
 p kinetic order of polynuclear growth
 r radius of a particle
 r_i radius of surface nucleus
 S supersaturation
 s equilibrium solubility
 T temperature
 t time
 t_0 shift of the beginning of hydrolysis before reaching the boiling point
 $t' = t - t_0$ time measured from the beginning of boiling
 V volume of the solid separated from the solution
 v volume of one molecule
 $\alpha_0 = \alpha$ corresponding to value of I_1^0
 α'_0 very small α arbitrarily chosen ($\alpha'_0 \rightarrow 0$)
 $\beta = L_i^2/4A_i$ geometric factor
 $\omega = A_i/r_i^2$ geometric factor
 σ interfacial tension crystal-solution

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