Solid-Gas Reaction between Tricalcium Phosphate & Anhydrous Hydrogen Chloride

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The solid-gas reaction between anhydrous hydrogen chloride and β-$Ca_3(PO_4)_2$ has been studied. The reaction occurs as a single stage protonation giving rise to $CaHPO_4$ and $CaCl_2$. The kinetic studies indicate that the heterogeneous reaction proceeds in two steps: (i) the initial deceleratory process which essentially involves the adsorption and dissociation of HCl molecule on the surface of calcium phosphate as the rate determining step and obeying first order rate law, (ii) the latter one obeying the parabolic rate law, which corresponds to the diffusion of constituent ions through the product layer. The present results lend support to the mechanism proposed earlier, for the solid-solid reaction between urea nitrate and tricalcium phosphate.

THE solid-solid reaction between calcium phosphate and urea nitrate has been reported earlier[1]. A mechanistic study showed that the first step in the reaction is the formation of HPO_4^{2-}, involving the transfer of mobile proton from urea nitrate to calcium phosphate[2]. It has also been observed that the kinetics of the reaction alter with particle size of tricalcium phosphate and that nucleation as well as diffusion processes play important roles in bringing about the reaction in the solid state. To verify the above mechanism, special situation can be assumed where one of the reactants in the solid-solid reaction is taken in excess, the minor component will be surrounded by a large number of particles of the other. The reaction starts at the points of contact between these particles. The situation is analogous to the heterogeneous reaction between the solid and a gas taken in excess. Each solid particle will be surrounded by a large number of gas molecules. It tends to be more realistic when the gas phase contains the active species of one of the solid reactants. In the present case, nitric acid associated with urea nitrate is the active species which brings about the protonation of calcium phosphate. It would, therefore, be appropriate to study the reaction between calcium phosphate and nitric acid vapour. Anhydrous nitric acid is not stable even at room temperature. Therefore, anhydrous hydrogen chloride is taken as the alternative to study the protonation of tricalcium phosphate.

Materials and Methods

All the chemicals used were either BDH analar or Merck pro analysi grade. Anhydrous hydrogen chloride was prepared by the reaction of ammonium chloride and concentrated sulphuric acid. The gas was condensed in liquid nitrogen trap and then sublimed into evacuated gas bulbs through P_2O_5 drying tower. The gas was transferred to gas burette and metered out into the absorption unit containing calcium phosphate.

β-$Ca_3(PO_4)_2$ was prepared by the reaction of $CaHPO_4$ and $CaCO_3$ at 1000°, following the method of Fowler et al.[3]. The resulting product was powdered and sieved to batches consisting of —180 (+200) mesh and —300(+320) mesh. Surface area of the sample, as determined by nitrogen adsorption, using BET method, at —194° were as follows:

	Monolayer vol. (ml/g)	Surface area (m²/g)
—100+320 mesh	1·50	6·54
—380+200 mesh	1·10	4·81

Procedure — The extent of reaction between anhydrous HCl and $Ca_3(PO_4)_2$ was evaluated by two independent methods. In the first method, a known amount of $Ca_3(PO_4)_2$ was allowed to remain in contact with excess HCl for a definite time interval. The solid was then freed from HCl gas by pumping out and was analysed for $CaCl_2$ by leaching with absolute ethyl alcohol (99·9%) in a soxhlet extractor. A different aliquot of the sample was reacted with standard acid and titrated back with alkali to the first neutralization of phosphoric acid (pH $\simeq 4·0$), using methyl orange-methylene blue mixed indicator. This gave the amount of acid phosphate present in the solid.

In the second method, known amount of $Ca_3(PO_4)_2$ was allowed to absorb anhydrous HCl at constant pressure and temperature. The extent of HCl taken up was measured at different intervals in an all-glass vacuum manifold, whose internal volume was calibrated. By maintaining the sample tube at appropriate temperature (accuracy $\pm 0·03°$) kinetics of the reaction could be followed by measuring the volume of HCl admitted into the system to keep constant pressure. This operation was carried out at definite time intervals. A differential glass spiral manometer, accurate to 0·2 mm of Hg was used to measure the pressure. Even though anhydrous HCl is inert to mercury, this procedure avoids any

possible corrosion of manometric liquid. From the volume of gas taken up by the solid at any time, the fraction of the reaction, was calculated as $\alpha = Vt/V_\infty$ where Vt is the volume of the gas taken up at any time t; V_∞ being the volume of HCl required for the formation of CaHPO₄. The α-value so obtained was cross-checked by the chemical analysis and was found to be in good agreement.

X-ray powder diffraction patterns were taken with a Rich-Seifert Debyeflex unit using CuK$_\alpha$ radiation and Philips Debye-Scherrer camera (57·3 mm diam.). Infrared spectra were recorded on a Carl-Zeiss UR 10 spectrophotometer, using KBr pellet technique.

Results

At appropriate temperatures and time intervals, the maximum amount of anhydrous HCl absorbed by Ca₃(PO₄)₂ is around 150 ml (NTP)/g solid. This corresponds to two moles of HCl per mole of Ca₃(PO₄)₂. Also, only one g mole of CaCl₂ is formed per mole of Ca₃(PO₄)₂. Infrared spectrum and X-ray powder diffraction pattern of the residue show the presence of CaHPO₄ as the only product. Therefore, the reaction can be represented by Eq. (1)

$$Ca_3(PO_4)_2 + 2HCl = 2CaHPO_4 + CaCl_2 \qquad ...(1)$$

Further reaction of CaHPO₄ with hydrogen chloride to form Ca(H₂PO₄)₂ does not take place. This is indicated by the absence of alcohol-soluble phosphate [Ca(H₂PO₄)₂ has some solubility in absolute alcohol]. The titration experiments show that one equivalent of acid is taken up by the solid product, while the presence of Ca(H₂PO₄)₂ will reduce this value considerably.

Hydrogen chloride is taken up by the solid as as soon as it is admitted into the system. Sufficient gas is absorbed within 1 min to cover the solid with more than a monolayer. The solid continues to take up the gas very slowly, and the reaction becomes
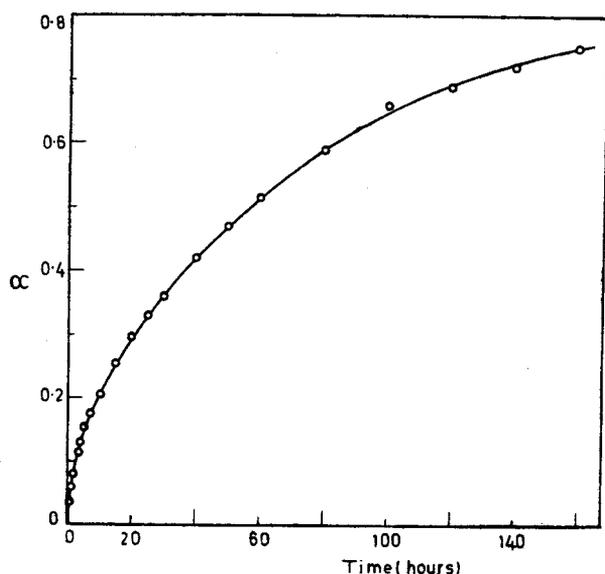
slower with progress of time. The initial part of (α) vs (t) curve shows a steep gradient while the later part of the curve is inclined more towards the time axis (Fig. 1). The two distinct regions of the curve indicate that protonation is rapid in the beginning, which decelerates with time. The latter region of the curve shows parabolic relation. These two stages are separately characterized.

The initial stage of the reaction obeys the first order kinetics law, log $(1-\alpha) = k_1 t$ and the plot of $-$log $(1-\alpha)$ against time t is linear (Fig. 2). Kinetic data obtained in the temperature range of 35-50° for the Ca₃(PO₄)₂-HCl reaction cut the y-axis slightly above the origin, indicating that the gas absorption is instantaneous. The region of (α, t) curve, which obeys the first order equation varies from $\alpha = 0$ to $\alpha = 0·25$, depending upon the temperature. Beyond these α-values, the reaction deviates from the first order plot.

The latter part of the reaction follows a parabolic rate equation, $\alpha = k_2 t^{\frac{1}{2}}$; linear plots are obtained when α is plotted against $\sqrt{t}$ (Fig. 3). The kinetic data, however, do not fit into other parabolic rate law like Jander's equation[4] $[1-(1-\alpha)^{\frac{1}{3}}]^2 = kt$.

It is of interest to point out that the extent of reaction reaches a limiting value depending upon the temperature. Hardly, 55% of the reaction takes place at 35°. On the other hand, complete conversion occurs at 50°.

The rate constants are calculated from the slopes of the linear plots for the two stages of the reaction. Energy of activation corresponding to each of these processes is calculated from the Arrhenius plot. A value of 25·64 kcal/mol is obtained for the deceleratory stage and 22·6 kcal/mol for the parabolic step.

Effect of pressure, particle size and the presence of the products of reaction on the rate of the reaction — Pressure of the gas, particle size of the reactant and the presence of one of the products of reaction can influence any gas-solid reaction. The effect of these three factors has been investigated for Ca₃(PO₄)₂-HCl reaction at 45°.

The gas absorption measurements are carried out at three different pressures between 600 and 200 mm of Hg. The kinetics of the reaction are found to be unchanged considerably at various
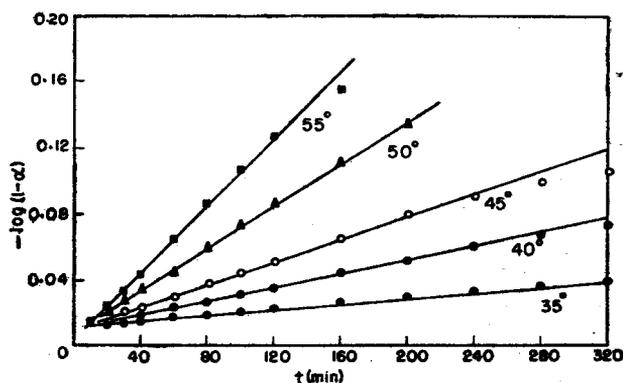

Fig. 1 — Typical (α, t) curve for β-Ca₃(PO₄)₂-HCl reaction [Temp. 40°; particle size of tricalcium phosphate −300 to +320 mesh]

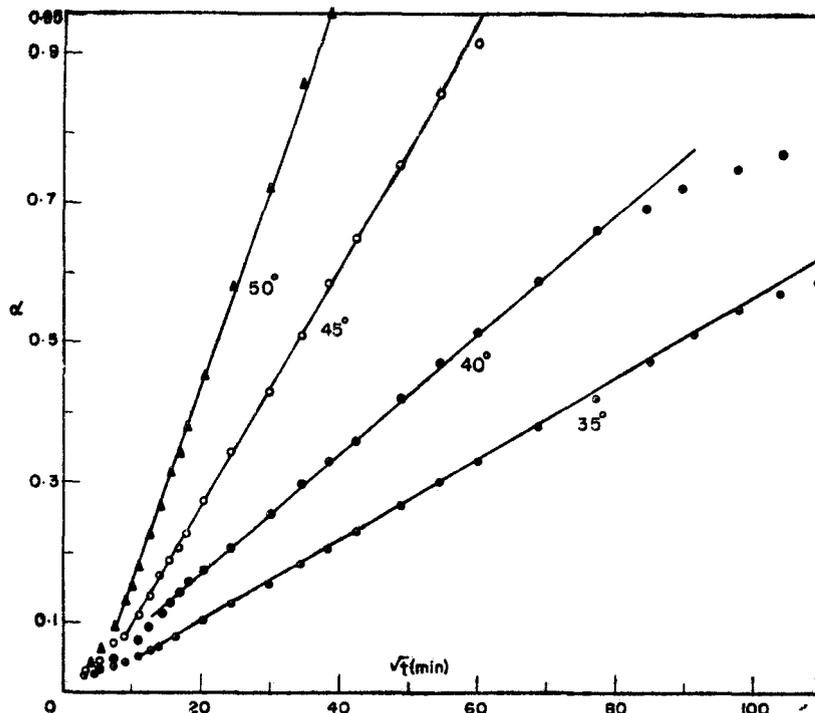Fig. 2 — First order plots for the early part of the reaction, at different temperatures [Particle size −300 to +320 mesh]

Fig. 3 — Parabolic rate law curves for β-Ca$_3$(PO$_4$)$_2$-HCl reaction [—300 to + 320 mesh]

pressures of the gas. Both the stages of the reaction persist even when the pressure of HCl is around 200 mm of Hg.

When the particle size of calcium phosphate is changed from —300(+320) mesh to —180(+200) mesh, no change in k_1 is observed. On the other hand, a decrease in k_2 values is noticed. The α-value up to which the reaction obey the first order kinetics is also reduced from 0·23 to 0·11.

The effect of the presence of different products of reaction is studied with the following Ca$_3$(PO$_4$)$_2$ samples: (i) mixed with finely powdered anhydrous CaCl$_2$ (8%) by wt; (ii) ground with 10% by weight of CaHPO$_4$; and (iii) treated with alcoholic solution of CaCl$_2$ and evaporated under vacuum at 200°. The solid thus obtained is in the form of fine powder.

There is no alteration in the rate constants k_1 and k_2 in the case of sample (ii). For sample (i), k_1 remains the same, but k_2 decreases. In the case of sample (iii), the initial deceleratory step is completely absent. The maximum extent of reaction is brought down to 70%, with sample (iii).

Discussion

It can be seen from the results that the amount of gas taken up initially by the solid decreases with increase in temperature (Fig. 2). This is characteristic of any adsorption processes. The amount of HCl further taken up by the solid is larger as the temperature is raised. Therefore, it can be concluded that the initial adsorption process soon changes to a true chemical reaction. The first stage of this reaction is deceleratory in character and it follows a first order rate equation. In a collection of particles which are not of uniform size and shape,

the first order equation may be accounted for in the following manner: The reaction of each individual particle results in the formation of a single nucleus or a few independent nuclei on the surface of that particle. The reaction is thus controlled by the nucleation process and since each particle in the ensemble may be nucleated with equal probability, the rate of the reaction obeys the first order kinetics.

With the Avrami-Erofeyev[5] equation, (—log 1—α)$^{1/n}$ = $k't$, which is based on the concept of nucleation and growth, the first order equation can be considered as the limiting case with $n = 1$. Generally, n represents two parameters: (i) λ, the number of steps involved in the nucleus formation and (ii) β, the number of dimensions in which the nucleus is growing ($n = λ+β$). Two alternate approaches can be made to account for this step of the present reaction obeying the first order rate law. (1) Quick nucleation followed by a rate-determining growth-step which is slow in one of the dimensions. (2) One of the chemical steps in the formation of the product is slow while its growth is comparatively rapid.

Between the two alternatives, the latter seems to be more probable. The results indicate that the kinetics are least affected by the addition of any one of the products. On the other hand, when a more coherent layer of CaCl$_2$ is present on Ca$_3$(PO$_4$)$_2$ particles, the deceleratory part completely disappears. Therefore, the rate determining step in the deceleratory process is the chemical step, the rate of which is not affected by the total pressure of HCl and also by the change in particle size of the solid. The fraction of the reaction which obeys the first order equation is decreased with increase

in the particle size. The rate-determining step which satisfies all these conditions is the dissociation of hydrogen chloride getting adsorbed on the calcium phosphate phase. Anhydrous HCl is a chemically inert compound in the absence of moisture, at ordinary temperatures[6]. The HCl molecules physically adsorbed on calcium phosphate dissociate to the respective ions which in turn react with the phosphate itself. The reaction, therefore, obeys a first order kinetics. The observed energy of activation (25.6 kcal/mol) is a composite figure of both heat of adsorption and activation energy for the reaction. However, the two values cannot be resolved easily since the chemical reaction quickly sets in, following adsorption. The above processes occur until a coherent layer of the product of enough thickness is built up and subsequently the kinetics are altered. The coherency of the product layer varies with the change in temperature and hence the fraction of reaction obeying the first order kinetics also varies.

Once the product layer acquires a certain value, the kinetics are changed and the rate follows a parabolic relation, indicating that diffusion becomes the kinetically important step. In the case of oxidation of many metals, the rate of oxidation is retarded as the oxide film develops. The kinetics usually follow a parabolic, cubic or logarithmic growth law. In using a parabolic rate law, it is assumed that diffusion occurs across a constant area or that the interfacial area of the particles remains constant throughout the reaction. This assumption cannot be justified when the particles are small. However, it is found that a simple parabolic relation is more closely obeyed than that of any modified equation employed to characterize the diffusion-controlled process.

There are three possibilities for the diffusion process controlling the kinetics: (i) HCl may get dissolved in CaCl$_2$ and the dissolved HCl may diffuse through the solid, thus coming into contact with calcium phosphate phase. (ii) Ca^{2+} ions can migrate from inside to the surface of the product layer while the counter-diffusion of H$^+$ ions occurs. Ca^{2+} ions thus migrating may react with Cl$^-$ ions while the H$^+$ ions combine with PO$_4^{3-}$ groups. (iii) HCl molecules may diffuse from the surface to the interior through the nearly constant coherent product layer mainly through the grain boundaries and internal channels.

The solubility of HCl in CaCl$_2$ is negligible. Of the other two possibilities, the diffusion of gaseous HCl through the product layer cannot have the activation energy as high as 22.6 kcal/mol. Therefore, the second possibility involving the migration of ions may be more favoured. The activation energy of 22.6 kcal may be compared with 18.2 kcal for the parabolic step in the urea nitrate-tricalcium phosphate reaction, with an experimental error. Besides, the diffusion takes place in the present case through CaCl$_2$ while in the urea nitrate reaction through Ca(NO$_3$)$_2$ which may account for the difference in the two values.

In general, the mechanism proposed for the solid-solid reaction between urea nitrate and tricalcium phosphate is supported by the present data as well. However, there are differences in the early stages of the reaction. This is understandable since adsorption and the related processes are absent in the solid-solid reactions.

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