## Frequency Factor of Natta's Propylene Polymerization

ACCORDING to Natta and Pasquon[1], the stationary rate, $r_\infty$, of propylene polymerization with titanium trichloride-triethyl aluminium catalyst is expressed by:

$$r_\infty = A \exp(-10 \text{ kcal}/RT)\ PG \qquad (1)$$

where $P$ is the propylene pressure, $G$ the weight of the solid catalyst and $A$ the frequency factor. The observed values of $r_\infty$ at room temperature and atmospheric pressure are usually 5–35 $g$-propylene/h atm. $g$-titanium trichloride[1,2]. The surface areas of the commercial titanium trichloride catalysts (prepared from titanium tetrachloride by reduction with hydrogen, aluminium or titanium and activated by grinding) have been measured as 10–30 m²/g by the Brunauer–Emmett–Teller method with nitrogen adsorption[3]. From these values and (1) we have $10^{22}$–$10^{23}$ molecules/sec cm² for the order of magnitude of $A$. This value is almost the same as that of the surface collision number, $Z$, of gas molecule per unit area at the same temperature and pressure. Then the rate per $g$-titanium trichloride may be represented, denoting the surface area by $S$:

$$r_\infty = ZS \exp(-10 \text{ kcal}/RT) \qquad (2)$$

To note this may be valuable for discussing the reaction mechanism of this polymerization.

Since the polymerization is carried out with the use of solvent, the propylene participated in the reaction is, of course, that dissolved. Accordingly, the value of $A$ mentioned above is an apparent one which is referring to the gaseous state of propylene. The significance of this apparent value of $A$ can easily be obtained on the basis of the absolute rate theory[4] as follows. Denoting the concentration and the partition function of propylene in gas phase by $N_g$ and $f_g$, that in the solution by $N_L$ and $f_L$, that of the polymerization centre by $C$ and $f_c$, that of the activated complex by $C^{\neq}$ and $f_{\neq}$, the rate may be expressed by

$$r_\infty = \frac{kT}{h} K^{\neq} C N_L \qquad (3)$$

with

$$K^* = C^{\neq}/C N_L \qquad (4)$$

There exists Henry's law for the dissolution of propylene by $n$-heptane, which assures the equality of the absolute activities of propylene in both phases with the following form

$$\text{the abs. activity} = N_g/f_g = N_L/f_L \qquad (5)$$

Hence, the rate may be expressed by:

$$r_\infty = \frac{kT}{h} (f_{\neq}/f_c f_g)\ C N_g$$
$$= (kT/h)\ (f^0_{\neq}/f^0_c f^0_g)\ C N_g\ e^{-(\varepsilon_{\neq} - \varepsilon_g - \varepsilon_c)/kT} \qquad (6)$$

where $\varepsilon$ is the energy of the ground-state. The partition function of gaseous propylene is given by

$$f^0_g = \frac{(2\pi m\, kT)^{3/2}}{h^3} f_{\text{rot}} f_{\text{vib}} \qquad (7)$$

where $m$ is the mass of a propylene molecule, $f_{\text{rot}}$ and $f_{\text{vib}}$ its rotational and vibrational partition functions. Comparing (6) with (1), we have:

$$A = \frac{kT}{h} \frac{f^0_{\neq}}{f^0_c f^0_g}\ C N_g$$
$$= \text{the surface collision number} = ZS \qquad (8)$$

The surface collision number is given by Herz-Knudsen equation as

$$ZS = \frac{PS}{(2\pi mkT)^{1/2}} = \left(\frac{kT}{2\pi m}\right)^{1/2} N_g S \qquad (9)$$

Using equations (8), (7) and (9), the following relation can be obtained

$$f^0_{\neq} = f^0_c f_{\text{rot}} f_{\text{vib}} \left(\frac{2\pi\, mkT}{h^2\, C}\right) \qquad (10)$$

This expression for the partition function of the activated complex shows that the attacking propylene monomer, that is, a component of the activated complex, has the same internal motions as that of gaseous propylene and the two-dimensional motion within the small extent, $1/C$ cm², that belongs to a polymerization centre. This corresponds to the simple collision of propylene monomer to the whole surface of the solid catalyst. One of another possibility to explain the equality $A = Z\ S$ is the simple collision of a propylene monomer to one of the polymerization centre, of which concentration is its maximum value, that is, $10^{15}$ cm$^{-2}$. In the latter case the partition function of the activated complex is

$$f^0_{\neq} = f^0_c f_{\text{rot}} f_{\text{vib}} \qquad (11)$$

which also corresponds to the simple collision to the whole surface. Another speculation such as that only special attack of monomer is effective or only the special structure (surface defect or dislocation) is available for the reaction should always result in a rather small value of $A$. Then, for these speculations further speculation must be added in order to explain the experimental value of $A$.

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# BIOCHEMISTRY

## Enolase and Fluorophosphate

IT is commonly believed that the remarkable inhibition of the enzyme enolase by fluoride plus phosphate is due to the formation of fluorophosphate, a belief which is based on the hypothesis advanced by Warburg and Christian[1] to explain their interesting facts. This enzyme, now known as phosphopyruvate hydrolase, is numbered 4.2.1.11 by the Enzyme Commission and catalyses the step in glycolysis D-2-phosphoglycerate ⇄ phospho-enol-pyruvate + water.

During the course of some work on the plant enzyme, we had occasion to test the relative inhibitory effect of a mixture of fluoride plus phosphate and fluorophosphate, when we found to our surprise that fluorophosphate had no inhibitory action.

We, therefore, investigated the effects on crystalline enolase, from rabbit muscle (Boehringer). The reaction was followed in the recording Beckman spectrophotometer according to the technique described by Miller[2]; the effect of a mixture of fluoride plus phosphate, both $5 \times 10^{-3}$ M, was compared with that of fluorophosphate ($K_2F.PO_3$), also 5 mM (Table 1). Whereas almost complete inhibition

Table 1. ENOLASE (PHOSPHOPYRUVATE HYDRATASE)

Comparison of inhibitory activity of a mixture of fluoride and phosphate with that of fluorophosphate ($K_2F.PO_3$). (Enzyme present in all)

| Additions | Change in optical density at 240 mμ over 2 min |
|---|---|
| Nil (control) | 0·131 |
| $F^-$ + $PO_3^-$ (each 5·0 mM) | 0·007 |
| $F.PO_3^-$ 5 mM | 0·150 |
| $F.PO_3^-$ 10 mM | 0·153 |

Experiments were made in a Beckman recording spectrophotometer; the enzyme was added last. Cuvettes contained in 2·2 ml., *tris* buffer *p*H 8·0, 110 μmoles; 2-phosphoglycerate, 11 μmoles; $MgSO_4$, 2·2 μmoles; glycine, 66 μmoles; water or addition, 0·1 ml.; enzyme, 0·1 ml.
Note: The slight increase seen with $FPO_3$ appears to be some salt effect.