$$V/V_0 = 1 + \beta U_{max} - [(U_{max} - U)/(U_{max} - U_{min})]^{\frac{1}{n}}$$

where U_{max} and U_{min} are the maximum and minimum fluidized gas velosity respectively and a, b, C, β, and n, are constants concerning the diameter, density, and shape of particles.

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31. On the Mechanism of Vinyl-Acetate Synthesis

Junji Furukawa and *Hideo Ozasa*

(Oda Laboratory)

On the vapor-phase synthesis of vinylacetate, it was found that the reaction velocity was proportional to the partial pressure of acetylene and the chemisorption of acetylene on the catalyst (zinc acetate on the active carbon) was the rate determining step for the reaction. We measured then the velocity of chemisorption of acetylene on the catalyst at the constant pressure of acetylene, raising the temperature at the constant rate. From this experiment, we evaluated the activation energy E, and the constant A of chemisorption according to the following equation;

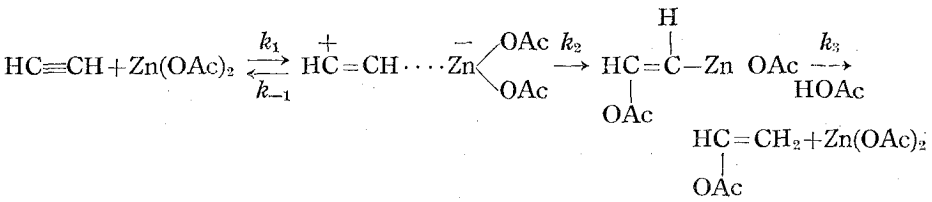
$$\log V = \log A + \log T - \log a - 0434E/RT$$

where V is the volume of acetylene adsorbed at any time or any temperature T, and a is the rate of raising the temperature. The observed activation energy is about 18 to 20 Kcal/mol which is in accordance with the date obtained from the experiment on the reaction between acetylene and acetic acid vapor.

The reaction did not occured by zinc acetate or active carbon alone below 240°C.

Zinc chloride had also activity at 250°C, after it had turned to zinc acetate as seen from the analytical date.

From these facts we assumed the following mechanism,

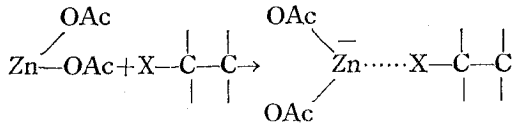


where k_1, k_{-1}, k_2 and k_3 are constants of reaction velocity. k_1 will be probably small in comparison with k_2 and k_3 except for the case at high temp. For the latter case k_{-1} predominate and E becomes small.

About the action of active carbon, we regard that the active carbon forms

the complex compound with zinc acetate to increase the activity of zinc acetate for acetylene.

The negative part of active carbon which is shown by the symbol X, will probably be united with zinc acetate as follows.



32. X-ray Studies on the Reaction between Polyvinyl Alocohol and Boric Acid

Noboru Okada and *Ichiro Sakurada*

(Sakurada Laboratory)

It was found recently in this laboratory, that a small ammount of boric acid reduces enormously the effect of heat treatment of polyvinyl alcohol fibers. X-ray studies were therefore carried out to elucidate the mechanism of this disturbing effect of boric acid.

Reaction between aqueous solutions of polyvinyl alcohol and boric acid of various concentrations was at first studied. Above 3% (conce. of boric acid) polyvinyl alcohol was no more soluble and precipitation occured. The precipitate showed, even after complete drying or heat treatment, no characteristic crystalline diagram of polyvinyl alcohol. With increasing concentration of boric acid, all interference rings became broader, A_1(d=7.98A) of polyvinyl alcohol disappeared, and intensity of A_3 decreased while that of A_4 increased. Spacing of A_3 decreased from 4.52Å to 4.26Å, while that of A_4 increased from 3.79Å to 4.11Å. The typical X-ray diagram of the precipitate, obtained from 10% boric acid solution was an amorphous one.

Films or fibers of polyvinyl alcohol which had been subjected to heat treatment were immersed in boric acid solutions of various concentrations; above 7.5% crystalline interferences disappeared and only amorphous ones remained.

It may be concluded from these observations that polyvinyl alcohol reacts as a polyalcohol with boric acid to form a complex and random cross linkages are formed between fiber molecules, which disturbs crystallization of polyvinyl alcohol and reduces the effect of the heat treatment.