

Preparation of Crystalline Polyaldehydes

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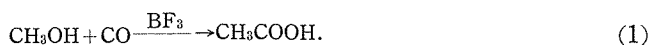
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We found that some organometallic compounds and metal alkoxides polymerized aldehydes including acetaldehyde, propionaldehyde and trichloroacetaldehyde (anhydrous chloral) to give crystalline polyaldehydes. Crystalline polyacetaldehyde was much less soluble in organic solvents than the amorphous one.

Active species of this polymerization was supposed to be metal alkoxide and the mechanism of polymerization was considered in connection with several synthetic organic reactions which involve metal alkoxides and carbonyl compounds. It was assumed that the coordination of aldehyde to the metal alkoxide was essential in propagation reaction which determined the stereospecificity of the polymer produced.

**BF₃-Catalyzed High Pressure Synthesis of Acetic Acid
from Methanol and Carbon Monoxide**
Yoshimasa TAKEZAKI, Tsuneo KAWATANI, Nobuyuki SUGITA,
Sachio YUASA, Minoru OSUGI and Yoshiko SUZUKI*Bulletin of the Japan Petroleum Institute*, **2**, 94 (1960)

The reaction of acetic acid synthesis from MeOH and CO has been investigated kinetically in the presence of BF₃·4H₂O as catalyst, as shown by



The following results have been found out:

1) Preliminary experiments on the system BF₃/H₂O/MeOH/AcOH: On atmospheric distillation of the mixture MeOH/BF₃/H₂O/AcOH (mole ratio 1/0.25/1/0.8) with a Widmer column, AcOH, MeOH and H₂O are distilled out until 106°C and the residue is of the composition (0/0.5/1/0.1).

When the mixture of MeOH/BF₃/H₂O(1/0.5/1) is heated in the autoclave up to 335°C, vapor pressure reaches 66 atm., and both of BF₃ and H₂O remain in the liquid phase, and free MeOH is in the dehydration equilibrium with MeOMe and each gaseous component (MeOH and MeOMe) is also in equilibrium with each dissolved in the liquid phase. The dehydration equilibrium constant K and Henry's constants, K'_m and K'_e , have been obtained at 335°C as below:

$$\text{CH}_3\text{OH} \rightleftharpoons \frac{1}{2}\text{MeOMe} + \frac{1}{2}\text{H}_2\text{O}_2 \text{ (gas phase)}, K = P_e^{1/2} P_{\text{H}_2\text{O}}^{1/2} / P_m = 2.13 \quad (2)$$

$$M'_m/V_l = k'_m P, \quad k'_m = 4.56 \times 10^{-4} \text{ (mol. c.c.}^{-1} \text{ atm.}^{-1}) \quad (3)$$

$$M'_e/V_l = k'_e P, \quad k'_e = 7.25 \times 10^{-5} \text{ (mol.c.c.}^{-1} \text{ atm.}^{-1}) \quad (4)$$

where, suffix m stands for MeOH and e for MeOMe.

M' = moles in liq., V_l = liq. volume, P = pressure.