

**Preparation of Crystalline Polyaldehydes**

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*Makromol. Chem.* **44-46**, 398 (1961)

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.

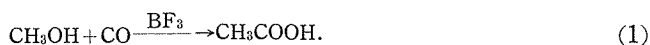
Active species of this polymerization was supposed to be metal alkoxide and the mechanism of polymerization was considered in connection with several synthetic organic reactions which involve metal alkoxides and carbonyl compounds. It was assumed that the coordination of aldehyde to the metal alkoxide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

**BF<sub>3</sub>-Catalyzed High Pressure Synthesis of Acetic Acid  
from Methanol and Carbon Monoxide**

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*Bulletin of the Japan Petroleum Institute*, **2**, 94 (1960)

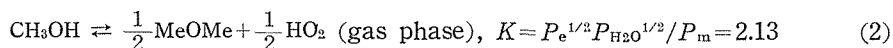
The reaction of acetic acid synthesis from MeOH and CO has been investigated kinetically in the presence of BF<sub>3</sub>·4H<sub>2</sub>O as catalyst, as shown by



The following results have been found out:

1) Preliminary experiments on the system BF<sub>3</sub>/H<sub>2</sub>O/MeOH/AcOH: On atmospheric distillation of the mixture MeOH/BF<sub>3</sub>/H<sub>2</sub>O/AcOH (mole ratio 1/0.25/1/0.8) with a Widmer column, AcOH, MeOH and H<sub>2</sub>O are distilled out until 106°C and the residue is of the composition (0/0.5/1/0.1).

When the mixture of MeOH/BF<sub>3</sub>/H<sub>2</sub>O(1/0.5/1) is heated in the autoclave up to 335°C, vapor pressure reaches 66 atm., and both of BF<sub>3</sub> and H<sub>2</sub>O 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'*<sub>m</sub> and *K'*<sub>e</sub>, have been obtained at 335°C as below:



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

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

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

*M'* = moles in liq., *V<sub>l</sub>* = liq. volume, *P* = pressure.

## ABSTRACTS

2) Effect of CO pressure (560~1030 atm., MeOH 0.5M, BF<sub>3</sub>·4H<sub>2</sub>O 0.125M, 335°C):

The initial rate is proportional to the fugacity of CO, and the yield is over the stoichiometrical amount of BF<sub>3</sub>, for instance 0.4M of AcOH is produced under 860 atm. of CO and 0.125M of BF<sub>3</sub> in 2 hrs.

3) Effect of temperature (320~360°C, CO 800atm., MeOH 0.5M, BF<sub>3</sub>·4H<sub>2</sub>O 0.125M): Initial velocities  $(dx/dt)_{t=0} \times 10^3$ , are 26.2 at 360°C, 10.6 at 340°C and 4.4 at 320°C.

4) Effect of MeOH charge amount: Under the fixed conditions of 335°C, 800~850 atm. and BF<sub>3</sub> 0.125 M, the yield drops the charge of MeOH is raised, for instance 97% yield for charged MeOH 0.5M and 1 hr., but only 10% for charged MeOH 1.0 M in a reactor of 130 c.c.

The linear relationship is obtained between the initial velocity and MeOH equilibrium concentration in the liquid.

5) From the above-mentioned results, the initial rate equation has been obtained as shown next:

$$(dx/dt)_{t=0} = (kf_{co}k'_m/4aeV_f) [-(m/M_0) + \{(m/M_0)^2 + (8ae/M)^{1/2}\}]$$

where,  $x$  = produced AcOH/charged MeOH ( $M/M$ ),

$$a = K^2RT/P_{H_2O}V_f, \quad b = RTV_i/V_f, \quad m = 1 + k'_mb,$$

$$e = 1 + k'_eb, \quad a = 9060/V_f, \quad b = 49900/V_f,$$

$M$  = charged MeOH ( $M$ ),  $V$  = free space of autoclave.

Rate constants  $k$ 's have been calculated to be  $3.97 \times 10^{-5}$  (atm<sup>-1</sup>. min<sup>-1</sup>.) at 350°C,  $2.37 \times 10^{-5}$  at 335°C and  $1.62 \times 10^{-5}$  at 320°C. The activation energy of 22Kcal./mol. has been obtained.

### Synthesis of Dimethylformamide from Methanol, Ammonia and Carbon Monoxide under High Pressure

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Japan, Industrial Chemistry Section), 63, 1739 (1960)*

The effects of reaction conditions on the one step synthesis of dimethylformamide from MeOH, NH<sub>3</sub> and CO have been studied under high pressure in the presence of AcOK as a catalyst. Stoichiometrically the reaction is represented as below, but it is very interesting to know whether the reaction proceeds in one step or in two steps, i. e. methylation followed by formylation.



1) The effect of reaction temperature (220~340°C): The increase of DMA yield and the decrease of MMF and DMF above 280°C are due to the instability