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Author(s)	TANABE, Kozo
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THE CATALYTIC ACTIVITY OF SOME SOLID ACIDS FOR DEPOLYMERIZATION OF PARALDEHYDE*)

By

Kozo Tanabe**)

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Introduction

It has been reported that many inorganic chemicals such as metal oxides, sulfates, chlorides *etc.* show acidic property on the surfaces[1)2)] and that the acidity of some solids is changed by heating in air or in vacuum[2)].

In the present work an attempt has been made to use some of these solid acids instead of ordinary mineral acids as the catalyst of acid-catalyzed reaction. For this purpose, cupric sulfate, aluminum sulfate, manganous sulfate and nickel sulfate were chosen as catalysts because of their strong acidity[2)] and depolymerization of paraldehyde as a test reaction, since the reaction is known to be catalyzed by mineral acids or carboxylic acids in non-aqueous solvent and can be followed by an accurate and easy method of analysis[3)]. Since the solids are soluble in water, benzene dried as carefully as paraldehyde was employed as a solvent. The amount of acetaldehyde formed was determined by the bisulfite method[4)], which was shown by preliminary tests to give accurate results in the presence of paraldehyde and benzene, provided that the catalysts were filtered off before analysis.

It has been found that cupric sulfate, aluminum sulfate, manganous sulfate do catalyze the reaction at room temperature and that the catalytic activity of the solid acids are increased remarkably when the catalysts are heated before use.

Results

Some results of the preliminary experiment are shown in Table 1. An experiment in the absence of catalyst showed that solution of paraldehyde in benzene was completely stable for about 4 days at 30°C By the addition of 1.96 g of anhydrous cupric sulfate, however, twenty three per cent of paralde-

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**) Research Institute for Catalysis, Hokkaido University.

TABLE 1. Depolymerization of paraldehyde.
Concentration of paraldehyde: 0.0378 mol/ℓ
Volume of reaction mixture : 50 mℓ

Run	Catalysts	Reaction temperature °C	Reaction time min	% of reacted paraldehyde
1.	absent	30	5880	0
2.	1.96 g $CuSO_4$	26	2920	23
3.	1.84 g $CuSO_4$ (1.27 mℓ of water was added)	26	2920	0
4.	2.08 g $CuSO_4$ heated for a week at 175°C	24	1630	58
5.	2.0 g $CuSO_4$ heated for 4 hrs at 300°C	30	50	18
6.	4.0 g $CuSO_4$ heated for 4 hrs at 300°C	30	40	28
7.	4.0 g $Al_2(SO_4)_3 \cdot 18H_2O$	30	162	0
8.	4.0 g $Al_2(SO_4)_3$ heated for 4 hrs at 300°C	30	58	68
9.	4.0 g $MnSO_4$ heated for 4 hrs at 300°C	30	61	33
10.	2 g $NiSO_4$ heated for 3 hrs at 325°C	30	15	22
11.	1.49 g Cl_3CCOOH (0.182 N)	30	78	35

hyde was depolymerized for about 2 days at lower temperature.

In Run 3, where the reaction was carried out under almost the same condition as in Run 2 except that a small amount of water sufficient to dissolve the solid was added, no reaction was observed. This indicates that cupric or sulfate ion has no catalytic activity for the reaction, *i.e.*, the existence of solid phase is necessary for the activity. It is also evident that the catalytic activity is not due to any impurities such as mineral acids.

In order to see whether or not catalytic activity is changed by heating, cupric sulfate was heated in an electric furnace at various temperatures in Run 4~6. The results show that the activity is increased remarkably by heating. Aluminum sulfate and manganous sulfate showed also high activity when heated for 4 hrs at 300°C, though no reaction was observed in the case of *hydrated* aluminum sulfate as shown in Run 7. Nickel sulfate showed highest activity of all sulfates employed here, *i.e.*, 2 g of nickel sulfate heated for 4 hrs at 325°C depolymerized 22% of paraldehyde in 15 mins at 30°C. For a comparison,

the reaction in the presence of 1.49 g trichloroacetic acid was run in Run 11. It is seen that the catalytic activity of the heated solid acids is higher than that of trichloroacetic acid.

BELL *et al.* found that the rate of depolymerization of paraldehyde in homogeneous solution is first order with respect to paraldehyde concentration[3]. It was found that the reaction in heterogeneous phase is also first order with respect to paraldehyde concentration. In Fig. 1, $2.303 \log \frac{a}{a-x}$, where $a = [(CH_3CHO)_3]_0$ and $x = \Delta[(CH_3CHO)_3]_t$, was plotted against time, straight

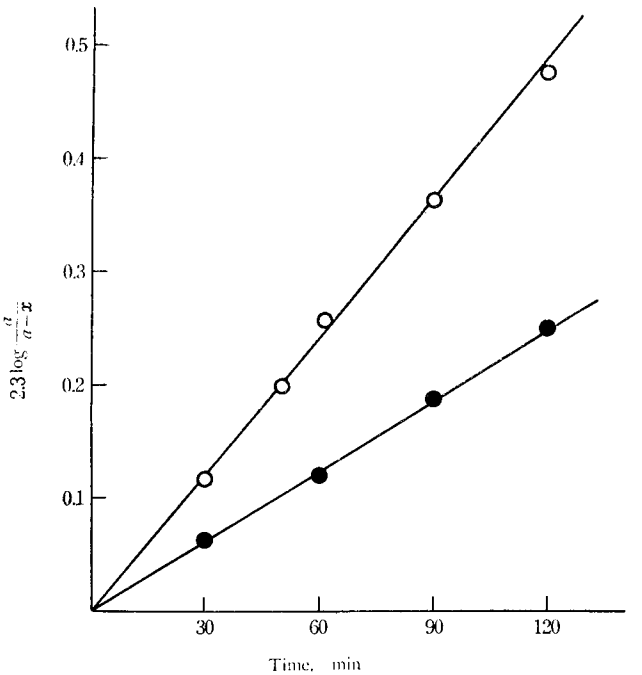

Fig. 1. Depolymerization of paraldehyde at 30°C. Concentration of paraldehyde: 0.0376 mol/ℓ, Volume of reaction mixture: 50 mℓ, Catalyst: ○ 2 g $CuSO_4$ heated for 4 hours at 300°C, ● 2.5 g $CuSO_4$ heated for 4 hours at 450°C.

lines being obtained. The first order rate constant k was determined from the slope of the best line through the points, the values being 4.05×10^{-3} min^{-1} when 2 g of $CuSO_4$ heated for 4 hrs. at 300°C was used as catalyst and 2.07×10^{-3} min^{-1} when 2.5 g of $CuSO_4$ heated for 4 hrs at 450°C was used respectively. Fig. 2 shows that the plots of the rate constant *vs.* the amount of catalyst lie on almost straight lines.

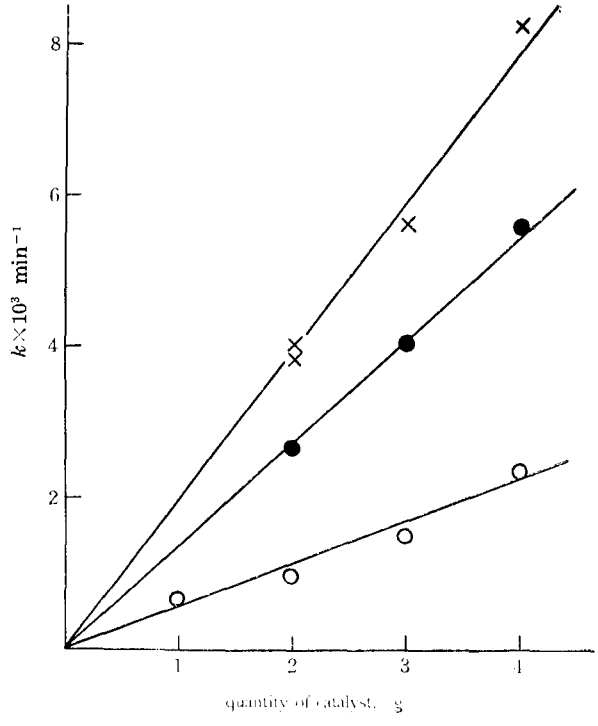

Fig. 2. Depolymerization of paraldehyde at 30°C. Concentration of paraldehyde: 0.0376 mol/ℓ, Volume of reaction mixture: 50 mℓ, Catalyst: × $CuSO_4$ heated for 4 hours at 300°C, △ at 400°C, ○ at 500°C.

The temperature dependence of catalytic activity is shown in Fig. 3, where k was plotted against temperatures at which cupric sulfate was heated. The catalytic activity (first order rate constant k) increases with increasing temperature of heating, attains to a maximum near 300°C and then decreases. That no catalytic activity was observed at 650°C, *i.e.* the decomposition temperature of cupric sulfate, indicates that cupric oxide has no activity for the depolymerization of paraldehyde.

The catalytic activity of metal sulfates is changed remarkably by heating in air and their acidity is changed also by heating[2]. From these observations and the fact that depolymerization of paraldehyde is catalyzed by acids such as acetic acid, hydrogen chloride and trichloroacetic acid[3], it appears likely that the catalytic action of the solids is mainly due to acid sites on their surfaces.

The present work suggests that a kinetic comparison of homogeneous acid-catalyzed reaction in solution with heterogeneous one is possible. Some results

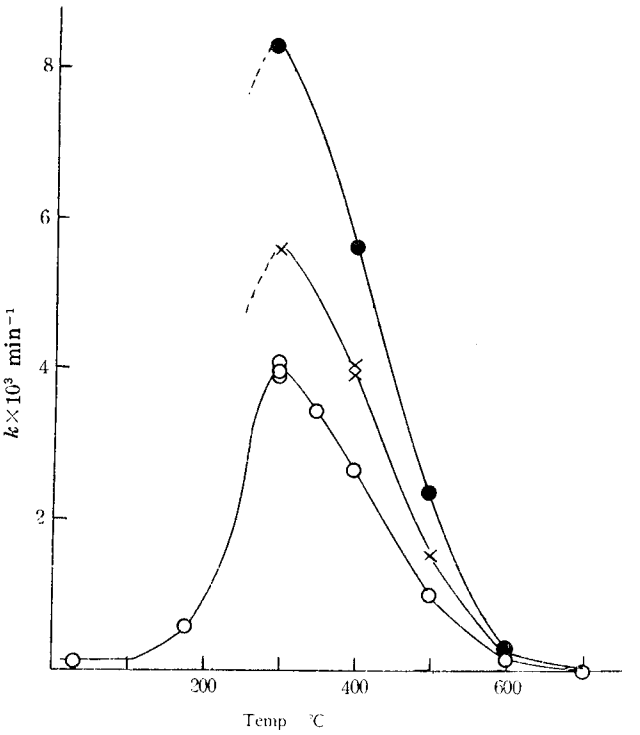

Fig. 3. Depolymerization of paraldehyde at 30°C. Concentration of paraldehyde: 0.0376 mol/ℓ, Volume of reaction mixture: 50 mℓ, Catalyst: ● 4 g of $CuSO_4$, × 3 g of $CuSO_4$, ○ 2 g of $CuSO_4$.

of the kinetic comparison will be reported in the following paper.

Experimental

Materials: Paraldehyde was dried over sodium and redistilled. Benzene was dried over sodium and fractionally distilled. Solid acids ground in a mortar were heated in an electric furnace attached with a thermocouple at desired temperature and cooled to room temperature in a desiccator before use. Solid acids used are $CuSO_4$ (Purif. Anhyd. Baker Chemical Co.), $Al_2(SO_4)_3\cdot18H_2O$ (C. P. Cryst. Baker Chemical Co.), $MnSO_4\cdot H_2O$ (C. P. Baker Chemical Co.) and $NiSO_4\cdot7H_2O$ (guaranteed reagent, Kanto Chemical Co.).

Kinetic Runs: In a typical run, 50 mℓ of paraldehyde solution in benzene was pipetted into a 100 mℓ volumetric flask, about 2 g of cupric sulfate added and stirred by a magnetic stirrer at room temperature. At a recorded time, the solid was filtered off and 10 mℓ of the filtrate (whole filtrate in some

experiments including Run 3) was pipetted into an excess of 0.0971 M potassium bisulfite solution and titrated with 0.0520 M standard iodine solution by using starch solution as an indicator, the excess of bisulfite being thus removed. About 1 g of sodium bicarbonate was then added and the bisulfite liberated from the acetaldehyde-bisulfite compound[4] was titrated again with the iodine solution.

The reaction was carried out under dry nitrogen for some experiments but this treatment had no effect on the results. The temperature variations did not exceed 1 C. Since the reaction is heterogeneous so that the rate depends upon efficiency of stirring condition, the experiments were carried out under the condition where the efficiency was constant.

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