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## DEPOLYMERIZATION OF PARALDEHYDE CATALYZED BY METAL SULFATES

By

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### Abstract

First order rate constants for the depolymerization with cupric sulfate, aluminum sulfate and manganous sulfate were determined and found greater than those with silica-alumina and a homogeneous acid catalyst. Arrhenius activation energies with aluminum sulfate and cupric sulfate were found to be 25.6 and 21.7 kcal/mol respectively, both being smaller than the value (26.9) with nickel sulfate and higher than that (14.3) with trichloroacetic acid. Acidity and acid strength of cupric sulfate heat-treated at various temperatures ranging from 100 to 600°C were measured and the acidity maxima at any acid strengths were found for the sulfate heated at 300°C. It was also found that the catalytic activity of cupric sulfate best correlates with the number of acid sites having acid strength  $pK_a \leq -3$  and that the sulfate poisoned with dicinnamalacetone shows no catalytic activity. These results led us to conclude that the acid sites having  $pK_a \leq -3$  are catalytically active. Since the observed kinetic data with cupric sulfate fit Michaelis-Menten's equation, the catalytic action of the sulfate is considered similar to enzymatic action.

### Introduction

We have previously reported that metal sulfates such as nickel sulfate, aluminum sulfate, cupric sulfate and manganous sulfate catalyze the depolymerization of paraldehyde in benzene<sup>1)</sup>. As for nickel sulfate, correlation of the catalytic activity with the surface acidity<sup>2)</sup> and the mechanism of the reaction<sup>3)</sup> were studied in detail. Since, however, not much kinetic work has been made of other sulfates, the present work has been initiated.

### Experimental

**Catalysts and Reagents:** Cupric sulfate ( $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ , guaranteed reagent of Kanto Chemical Co., Tokyo) was heated in an electric furnace for 3 hours at various temperatures ranging from 100 to 600°C and cooled in an evacuated desiccator before use. Aluminum sulfate ( $\text{Al}_2(\text{SO}_4)_3 \cdot 18\text{H}_2\text{O}$ , extra pure reagent of Kojima Kagaku Co.) was heat-treated at 300°C for 3 hours and manganous

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sulfate ( $\text{MnSO}_4 \cdot 7\text{H}_2\text{O}$ , guaranteed reagent of Kanto Chemical Co.) at  $400^\circ\text{C}$  for 4 hours. The powdered catalysts collected between 100 and 200 mesh sieves were used. In some runs, cupric sulfate and nickel sulfate whose acid sites having acid strength  $pK_a \leq -3$  were poisoned with a basic indicator, dicinnamalacetone were used as catalysts.

Paraldehyde was purified as described previously<sup>1)</sup>. Benzene and *n*-butylamine used were a guaranteed reagent, the product of Kanto Chemical Co. and an extra pure reagent, the product of Tokyo Chemical Industry Co. respectively. All indicators used for the determination of acidic property were of the same preparations as those described in our previous work<sup>2)</sup>. Those indicators are neutral red ( $pK_a = +6.8$ ), methyl red ( $pK_a = +4.8$ ), phenylazo- $\alpha$ -naphthylamine ( $pK_a = +4.0$ ), *p*-dimethylamino-azo-benzene ( $pK_a = +3.3$ ), benzeneazodiphenylamine ( $pK_a = +1.5$ ) and dicinnamalacetone ( $pK_a = -3$ ).

**Measurements of Acidity and Acid Strength<sup>2)</sup>:** The amount of acid sites per unit weight or surface area (acidity) of the catalysts having various acid strengths were measured by titrating with a solution of 0.1 N *n*-butylamine in benzene, using various indicators of different  $pK_a$  values mentioned above.

**Determination of Surface Area:** Surface area of heat-treated cupric sulfate were measured by the Brunauer-Emmett-Teller method<sup>4)</sup> using nitrogen as an adsorbate. The surface area changes, as illustrated in Fig. 1, with increasing

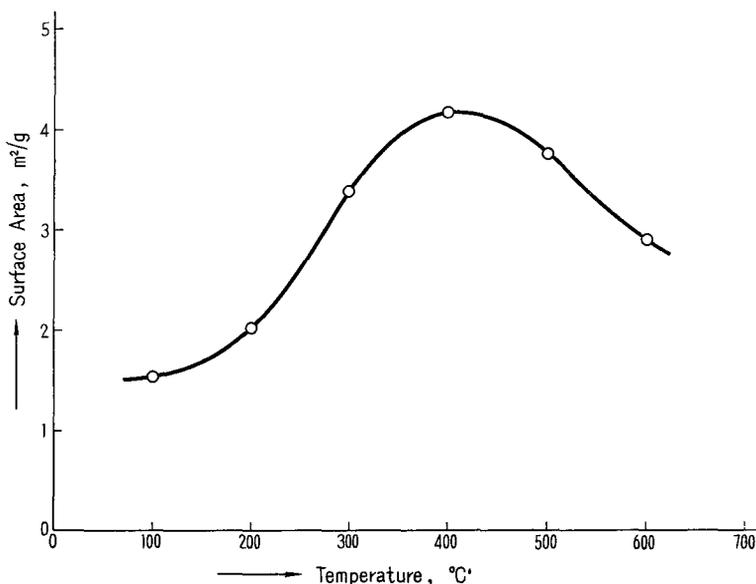


Fig. 1. Change of surface area of cupric sulfate on heat-treatment.

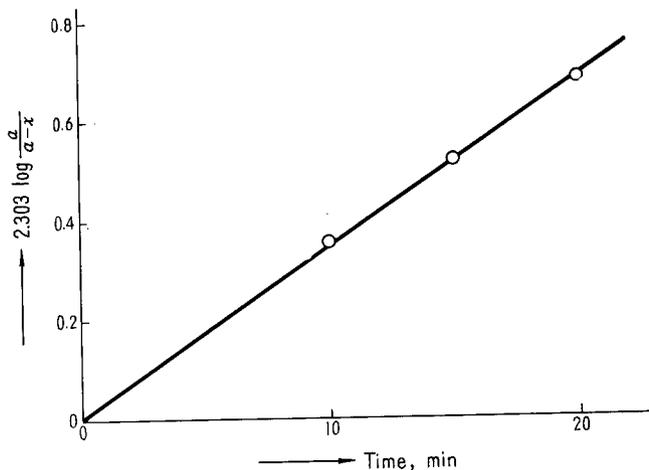
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temperature of heat-treatment, the maximum value of 4.2 m<sup>2</sup>/g being observed on the sample heated at 400°C.

**Kinetic Runs:** Fifty ml of paraldehyde solution in benzene (0.0090~0.301 mol/l) was pipetted into a 100 ml stoppered Erlenmeyer flask and 0.5~1 g of catalysts was added and shaken briskly by a shaking machine as in the previous work<sup>5)</sup> in a thermostat maintained at desired temperatures ( $\pm 0.02^\circ\text{C}$ ). After a recorded time, the catalyst was filtered off and the filtrate was analyzed for acetaldehyde formed by the bisulfite method<sup>6)</sup> as described previously<sup>3,5)</sup>.

### Results and Discussion

**Kinetic Order of the Reaction:** It was reported in our previous papers<sup>1,5)</sup> that the rate of the depolymerization of paraldehyde catalyzed by cupric sulfate or nickel sulfate is first order with respect to paraldehyde concentration as in the case of the homogeneous reaction catalyzed by carboxylic acids or hydrogen chloride<sup>7)</sup>. The reaction with aluminum sulfate was also found to be first



**Fig. 2.** Depolymerization of paraldehyde at 30°C. Concentration of paraldehyde; 0.1078 mol/l, Volume of reaction mixture; 50 ml, Catalyst; 1 g Al<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub> heated for 3 hours at 300°C.

order in paraldehyde concentration. It is shown in Fig. 2 that the plot of  $2.303 \log a/(a-x)$  against time  $t$  lies on a good straight line, where  $a$  is the initial concentration of paraldehyde and  $x$  the concentration of reacted paraldehyde at time  $t$ . The value of the first order rate constant determined from the slope of the line is given in the last column of Table 1.

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TABLE 1. Depolymerization of Paraldehyde at 30°C.  
(cf. Fig. 2)

Time of Reaction min.	Aldehyde Formed mol/l	$2.303 \log \frac{a}{a-x}$	$k$ min. <sup>-1</sup>
10	0.0962	0.353	} 0.035
15	0.130	0.514	
20	0.161	0.688	

All experiments for obtaining rate constants were carried out at an early stage of the reaction. Paraldehyde does not depolymerize more than about 76% at 30°C, where the reaction attains equilibrium, as shown in Fig. 3. The percentage decreases slowly after it attained the maximum. This seems to indicate that acetaldehyde formed is consumed by some side reactions such as formation of crotonaldehyde or aldol condensation.

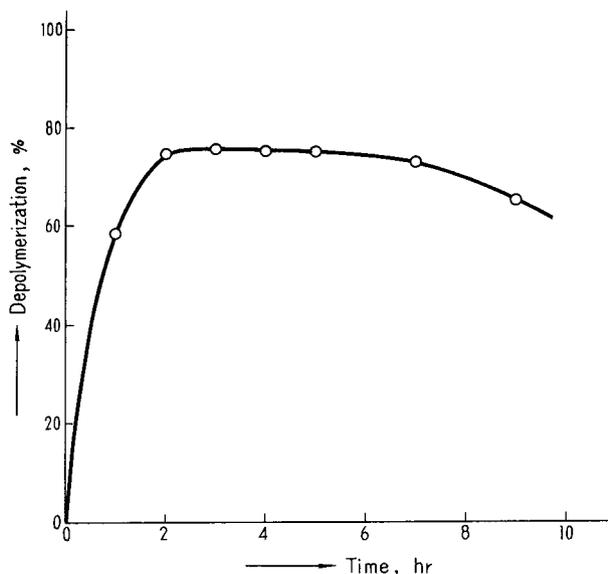


Fig. 3. Depolymerization of paraldehyde at 30°C. Decomposition % vs. time of reaction. Concentration of paraldehyde; 0.101 mol/l, Catalyst;  $\text{Al}_2(\text{SO}_4)_3$  heated for 3 hours at 300°C.

**Comparison of Catalytic Activity:** The catalytic activities (first order rate constants) of metal sulfates, silica-alumina and trichloroacetic acid are shown in Table 2. The catalytic activity is higher in solid acids than in liquid acid,

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partly because trichloroacetic acid is a weaker acid. Of all solid acids, the rate constant per milli equivalent of acid sites is smallest in silica-alumina. However, such a high catalytic activity of metal sulfates could be attributed to that analogous to enzymatic one as described in a later section.

TABLE 2. Catalytic activity of heterogeneous and homogeneous catalysts at 30°C.  $k$ ; first order rate constants, Volume of reaction mixture; 50 ml.

	NiSO <sub>4</sub> <sup>*)</sup>	Al <sub>2</sub> (SO <sub>4</sub> ) <sub>3</sub>	CuSO <sub>4</sub>	MnSO <sub>4</sub>	SiO <sub>2</sub> Al <sub>2</sub> O <sub>3</sub> <sup>**)</sup>	CCl <sub>3</sub> COOH <sup>***)</sup>
Acidity <sup>****)</sup> meq/g	0.09	0.53	0.19	0.11	0.50	24 mmol/l
$k \times 10^3$ min <sup>-1</sup> , g <sup>-1</sup>	6.2	35	2.2	0.05	0.10	—
$k \times 10^3$ min <sup>-1</sup> , meq <sup>-1</sup>	68	65	12	0.45	0.20	0.10

\* ) Taken from ref. 5), \*\* ) from ref. 3), \*\*\* ) from ref. 7)

\*\*\*\* ) Acidity at acid strength  $pK_a \leq +3.3$ .

**Temperature Dependence of Depolymerization:** The results with aluminum sulfate and cupric sulfate are given in Table 3 and 4.

TABLE 3. Temperature dependence of depolymerization rate. Concentration of paraldehyde; 0.1014 mol/l, Volume of reaction mixture; 50 ml, Catalyst; 0.5 g Al<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub> heated for 3 hours at 300 °C.

Reaction temp. °C	Reaction time min	Paraldehyde depolymerized mol/l × 10 <sup>3</sup>	$k \times 10^3$ min <sup>-1</sup> , g <sup>-1</sup>
20	20	6.44	6.59
25	15	8.86	12.3
30	15	18.2	26.4
35	15	36.3	59.7
40	15	55.9	107

Arrhenius activation energies obtained from the plots of  $\log k$  vs.  $1/T$  as shown in Fig. 4 are given in Table 5, with those for nickel sulfate<sup>5)</sup> and trichloroacetic acid<sup>7)</sup> for comparison.

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TABLE 4. Temperature dependence of depolymerization rate. Concentration of paraldehyde; 0.0376 mol/l, Volume of reaction mixture; 50 ml, Catalyst; CuSO<sub>4</sub>, heated for 4 hours at 300°C.

Reaction temp. °C	Reaction time min	% of paraldehyde depolymerized	$k \times 10^3$ min <sup>-1</sup> , g <sup>-1</sup>
25.9	30	3.87	1.33
25.9	30	4.08	1.37
32.0	30	8.88	3.08
32.0	30	7.70	2.69
38.6	30	16.5	6.03
38.6	30	16.5	6.03

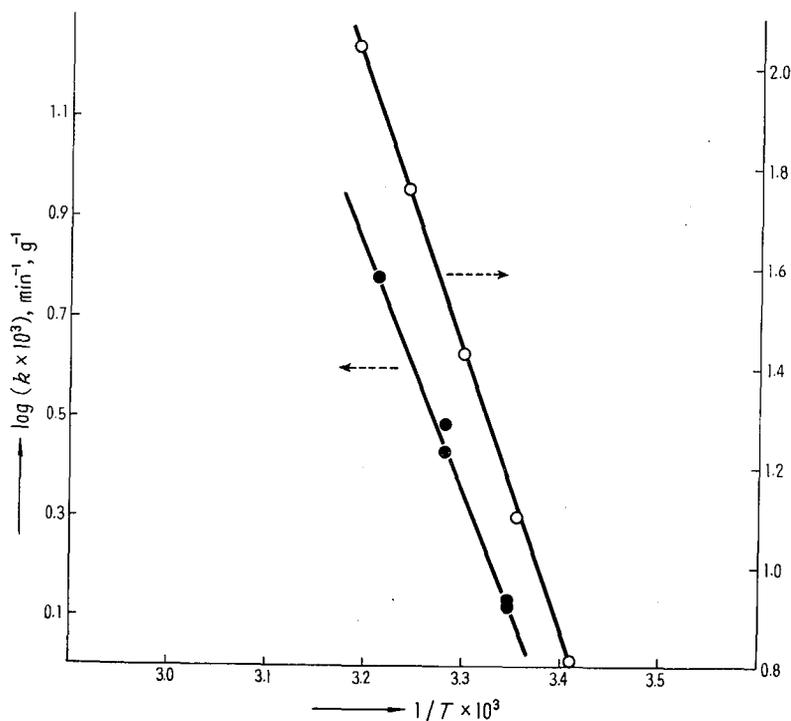


Fig. 4. Log  $k$  vs.  $1/T$ .

O; Al<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub>, ●; CuSO<sub>4</sub>.

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TABLE 5. Activation energy ( $E_a$ ) kcal/mol.

Catalyst	NiSO <sub>4</sub> *)	Al <sub>2</sub> (SO <sub>4</sub> ) <sub>3</sub>	CuSO <sub>4</sub>	CCl <sub>3</sub> COOH **)
$E_a$ kcal/mol	26.9	25.6	21.7	14.3

\*) from ref. 5). \*\*) from ref. 7)

**Acidic Property of Cupric Sulfate:** The acidity and acid strength of cupric sulfate heat-treated at various temperatures are shown in Table 6. The second column shows the surface areas measured by BET method mentioned in the section of experiment. In the next column are given *n*-butylamine titers (acidity) measured by using indicators having different  $pK_a$  values. The acidities per unit surface area are plotted against acid strengths in Fig. 5. In the case of nickel sulfate, the acid sites having mediate acid strength  $pK_a = +4.0 \sim +3.3$  increased remarkably on heating at higher temperatures<sup>9)</sup>, but such phenomena were not observed in this case. It is characteristic of cupric sulfate that greater number of acid sites having  $pK_a = +6.8 \sim +4.0$  appear on heating at relatively low temperature (100°C).

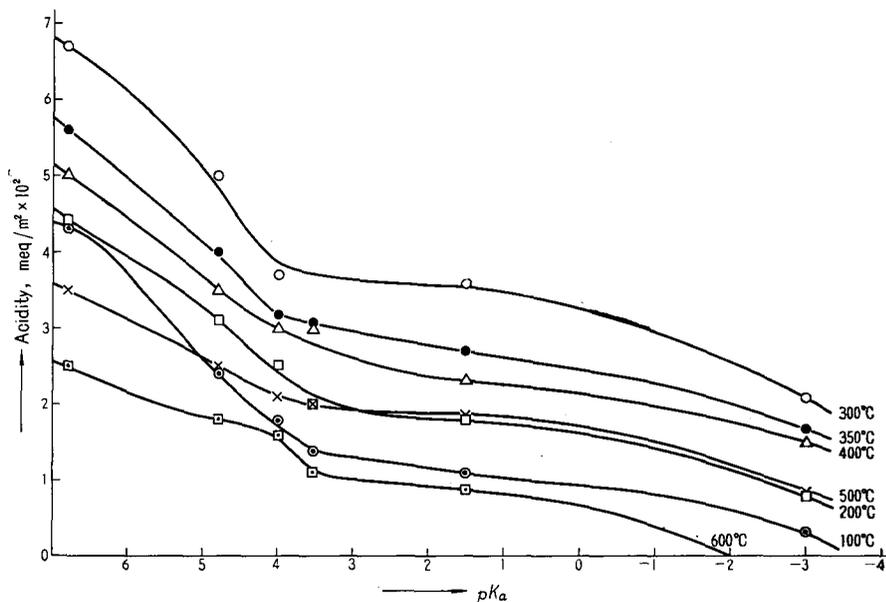


Fig. 5. Acidity vs. acid strength for cupric sulfate heat-treated at various temperature.

TABLE 6. Acid property of cupric surface heat-treated  
at various temperatures

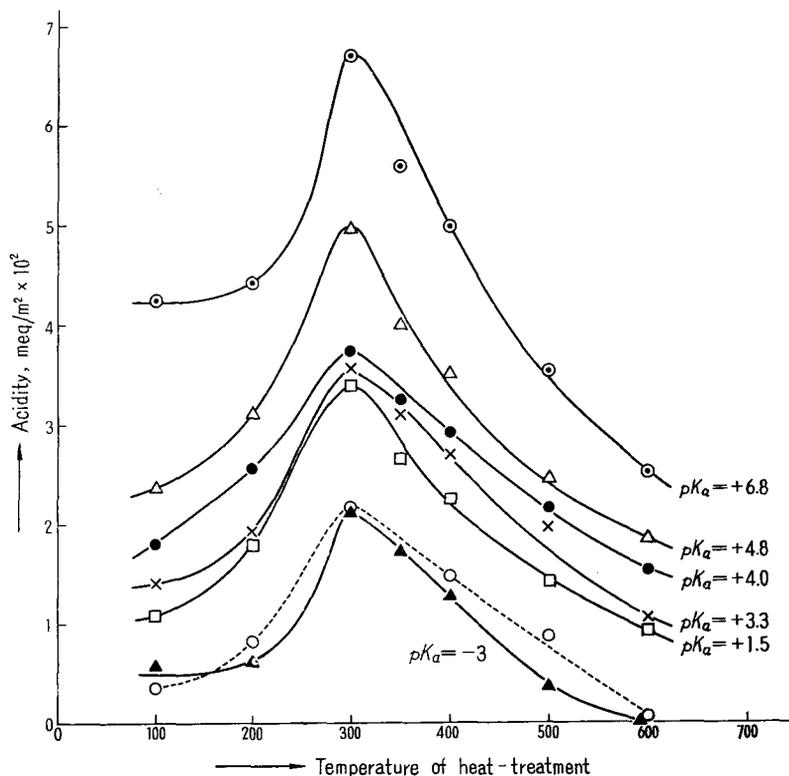
Temperature of Heat- treatment °C	Surface Area m <sup>2</sup> /g	Acidity, meq/g						$k \times 10^4$ min <sup>-1</sup> , g <sup>-1</sup>
		Neutral red $pKa = +6.8$	Methyl red $pKa = +4.8$	Benzene-azo- $\alpha$ -naphthyl- amine $pKa = +4.0$	<i>p</i> -Dimethyl- aminoazo- benzene $pKa = +3.3$	Benzeneazo- diphenylamine $pKa = +1.5$	Dicinnamal- acetone $pKa = -3$	
100	0.55	0.066	0.037	0.028	0.022	0.017	0.0052	4.1
200	2.02	0.089	0.063	0.051	0.039	0.036	0.0164	5.3
300	3.40	0.227	0.169	0.126	0.128	0.125	0.0724	32
350	—	0.219	0.157	0.128	0.122	0.104	0.0676	29.2
400	4.17	0.208	0.147	0.122	0.124	0.094	0.0615	21.7
500	3.14	0.080	0.057	0.049	0.033	0.029	0	0

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In Fig. 6 are plotted acidities per unit surface area of cupric sulfate at various acid strengths against the temperature of heat-treatment. The acidities at any acid strengths increase with increasing temperature of heat-treatment, attain to maxima at 300°C and then decrease. Such an acidity change is similar to that in the case of nickel sulfate, although the acidity maximum appears at 350° in the latter. The acidity change is considered to depend on development and collapse of vacant orbital on nickel ion by dehydration<sup>9</sup>).

**Correlation of Catalytic Activity with Acidic Property:** The depolymerization rate constants per unit surface area of cupric sulfate which is shown in the last column of Table 6 are plotted against temperature of heat-treatment in Fig. 6 (see a dotted curve). As seen in the figure, there exists a correlation between the acidity and the catalytic activity. More detailed survey of the figure reveals that the cupric sulfate heated at 600°C has a number of acid sites

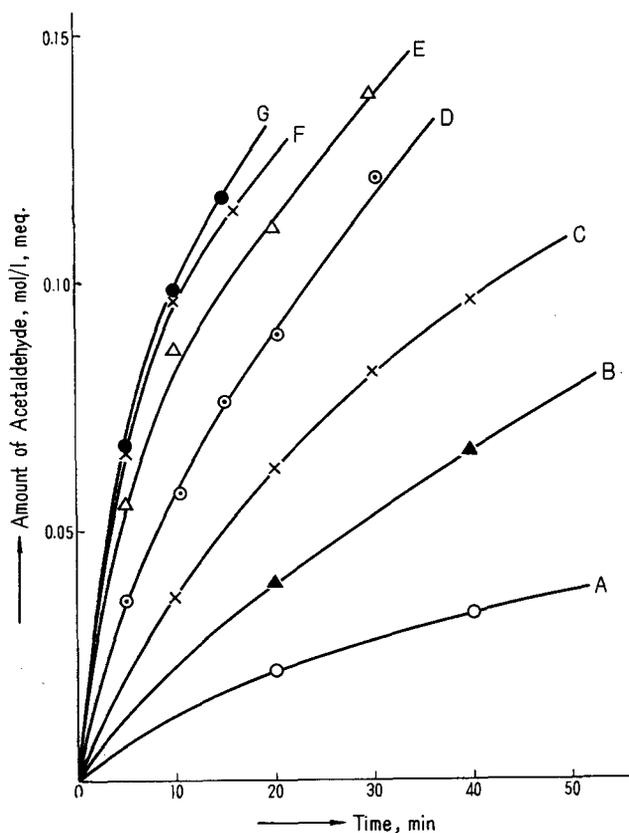


**Fig. 6.** Effect of heat-treatment on catalytic activity and acidic property of cupric sulfate.

--- ○ ---; catalytic activity.

having acid strength weaker than  $pKa = +1.5$ , but has no or little catalytic activity. Therefore, those relatively weak acid sites are considered to be catalytically inactive. The acid sites having acid strength stronger than  $pKa = -3$  best correlate with catalytic activity and are catalytically active for the depolymerization reaction. This conclusion is in accord with that obtained in the case of nickel sulfate<sup>2)</sup>.

**Depolymerization with Cupric Sulfate and Nickel Sulfate Poisoned with a Basic Indicator:** Cupric sulfate or nickel sulfate lost entirely the catalytic activity when the acid sites whose acid strength are equal to or lower than  $pKa = -3$  are poisoned with dicinnamalacetone. This indicates that the active sites having acid strength  $pKa \leq -3$  are catalytically active for the depolymerization in conformation with the conclusion obtained in the foregoing section.



**Fig. 7.** Depolymerization of paraldehyde at 30°C. Initial concentration of paraldehyde: A-0.0090 mol/l, B-0.0165, C-0.0240, D-0.0493, E-0.0981, F-0.198, G-0.301.

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**Michaelis-Menten's plot:** In Fig. 7, the amount of acetaldehyde formed for unit milli equivalent of acid sites having  $pKa \leq -3$  was plotted against time over the range of various initial concentrations of paraldehyde from 0.0090 to 0.301 mol/l. Initial velocity  $v$  was obtained from the tangent at the initial stages of the curves. The reciprocal of depolymerization velocity  $1/v$  was then plotted against the reciprocal of initial concentration of paraldehyde  $1/[S]$ . As

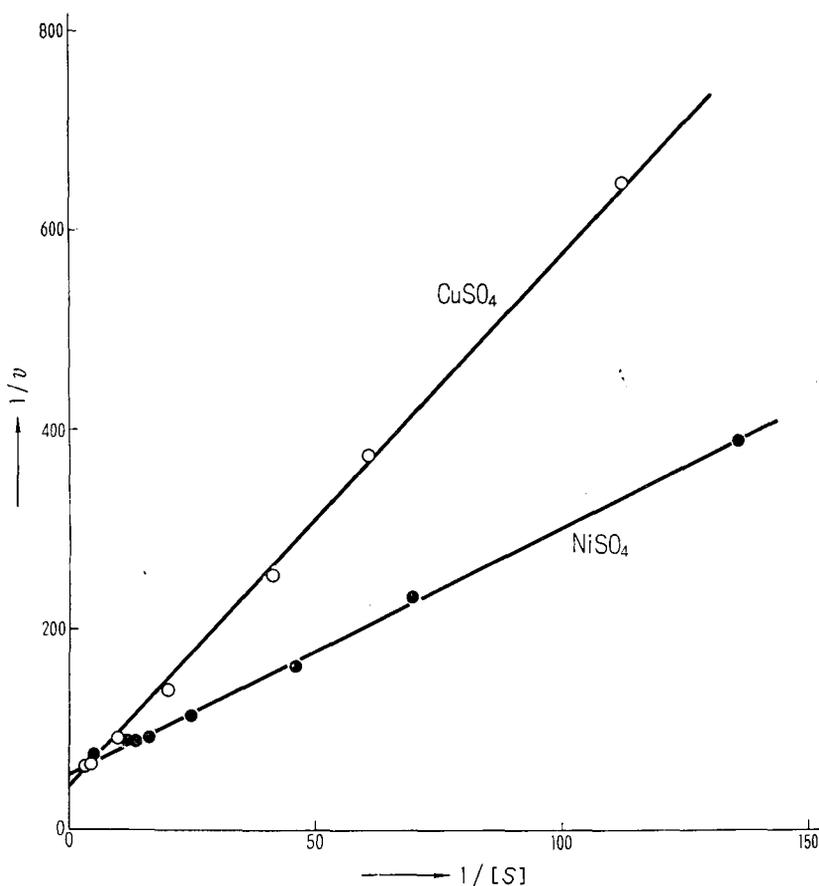


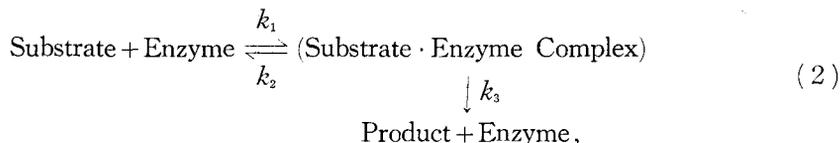
Fig. 8. Plot of  $1/v$  vs.  $1/[S]$ .

shown in Fig. 8, the plots lie on a good straight line, indicating that the observed kinetic data fit the well-known Michaelis-Menten's equation<sup>9)</sup>.

$$\frac{1}{v} = \frac{K_m}{V_{\max}} \cdot \frac{1}{[S]} + \frac{1}{V_{\max}}, \quad (1)$$

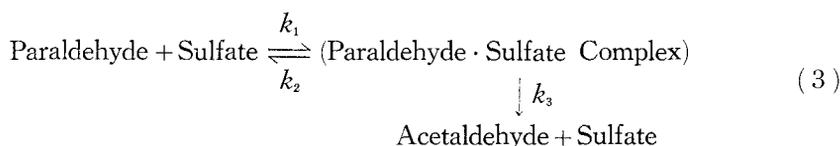
which is derived from the following scheme of enzymatic reaction.

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where  $K_m = (k_2 + k_3)/k_1$ ,  $V_{\max} = k_3 [\text{Enzyme}]$ .

Thus, the depolymerization with cupric sulfate may be presented by the analogous scheme to enzymatic reaction as shown below.



Michaelis constant was calculated to be 0.12 from  $K_m/V_{\max}$  and  $1/V_{\max}$ , which are obtained as inclination and intercept of the straight line in Fig. 8 respectively. This value is almost three times higher than that in the case of nickel sulfate<sup>9)</sup>.

#### Acknowledgment

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