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THE MECHANISM OF DEPOLYMERIZATION OF PARALDEHYDE CATALYZED BY SOLID ACID

By

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Initial velocity v of catalyzed depolymerization of paraldehyde in the presence of heterogeneous catalyst was observed at various initial concentrations of substrate [S]. It has been shown that a linear relationship between $1/v$ and $1/[S]$ does exist for a definite milli equivalent of acid sites on solid catalyst. It was concluded from the result that the reaction involves an intermediate paraldehyde-solid acid complex just as enzymatic process generally involves substrate-enzyme complex as intermediate. The kinetics, hence the mechanism inferred is thus different from that of usual acid-catalyzed reaction.

Introduction

The depolymerization of paraldehyde catalyzed by hydrogen chloride or carboxylic acids in non-aqueous solvents has been widely studied by BELL et al.[1] The mechanism of the homogeneous acid-catalyzed reaction is considered an acid-catalyzed prototropic change.

It has been recently found that paraldehyde in benzene is depolymerized also by solid acid catalysts such as nickel sulfate, cupric sulfate, manganous sulfate etc. and some kinetic studies have been made of the heterogeneous acid-catalyzed reaction[2]. Since a kinetic comparison of the heterogeneous reaction with the homogeneous one revealed appreciable differences of rate constant and energy of activation[3], it has seemed desirable to us to pursue further experiments for elucidating the mechanism of the heterogeneous reaction. In the present work we have observed the initial velocity of depolymerization at various initial concentrations of paraldehyde. For this purpose, benzene was employed as solvent and nickel sulfate as solid acid catalyst. For comparison, the catalytic activity for the reaction of silica-alumina, a well-known solid acid, was also examined. The mechanism of the solid acid-catalyzed depolymerization is discussed in the light of the observed results.

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Experimental

Reagents and materials : Paraldehyde and benzene were purified as described previously[2]. Nickel sulfate (NiSO₄7H₂O guaranteed reagent, Kanto Chemical Co., Tokyo, Japan) and silica-alumina (MS–FI $SiO_2 \cdot Al_2O_3$ supplied by Davison Co., Baltimore, Md., U.S.A.) were heated in an electric furnace attached with a thermocouple for about 3 hours at $350 \pm 10°C$ and cooled in an evacuated desiccator before use. The 120~325 mesh powder was used as catalyst[*].

Kinetic runs : A 50 mℓ of paraldehyde solution in benzene (0.0075~0.150 mol/ℓ) was pipetted into a 100 mℓ stoppered Erlenmeyer flask, about 0.5 g of solid acid added and shaken briskly by a shaking machine as in the previous work[3] in a thermostat maintained at $30 \pm 0.2°C$. At an appropriate time interval, the flask was cooled by cold water, the catalyst filtered off and 10 mℓ of the filtrate was pipetted into an excess of potassium bisulfite solution[**]. After the excess of bisulfite was removed by adding an equivalent amount of standard iodine solution using starch solution as an indicator, about 1 g of sodium bicarbonate was added and the bisulfite liberated from acetaldehyde-sulfurous acid compound was titrated with iodine solution[4]. The amount of acetaldehyde formed due to depolymerization of paraldehyde was thus determined.

Measurement of acidity of solid acid : The acid sites of solid acid were determined by using the amine titration method developed by JOHNSON[5]. The acidity is expressed in units of meq/g calculated from the titre of 0.1 N *n*-butylamine required for the amount of solid catalyst as described previously[6].

TABLE 1. Depolymerization of paraldehyde in benzene.

Reaction temperature : 30.2°C
Concentration of paraldehyde : 0.0150 mol/ℓ
Catalyst : 0.5 g of NiSO₄ heated for 3 hours at $352 \pm 10°C$,
the acidity 0.148 meq/g

Time	Sample analyzed	Ca. 0.1 N KHSO₃ added	0.0498 M iodine required[†]	Acetaldehyde formed	Initial velocity v
min	mℓ	mℓ	mℓ	mol/ℓ, meq	mol/ℓ, meq, min
15	15	10	2.63	0.118	
30	10	10	3.58	0.240	0.0081
45	10	10	4.75	0.320	

*) Since the catalytic activity as well as the acidity of the solid acids are diminished by moisture in air, dried catalysts were avoided to expose to air as possible.

**) In order to ensure the formation of acetaldehyde-sulfurous acid compound, the mixed solution was allowed to stand for 15 minutes with occasional shaking by hand.

Reaction temperature : 30.1°C
Concentration of paraldehyde : 0.0752 mol/ℓ
Catalyst : 0.5 g NiSO$_4$ heated for 3 hours at 348±6°C, the
acidity 0.2 meq/g

Time	Sample analyzed	Ca. 0.1 N KHSO$_3$ added	0.0498 M iodine required†)	Acetaldehyde formed	Initial velocity v
min	mℓ	mℓ	mℓ	mol/ℓ. meq	mol/ℓ, meq, min
12	10	10	5.58	0.279	
31	10	20	13.10	0.655	0.022
45	10	25	18.13	0.907	

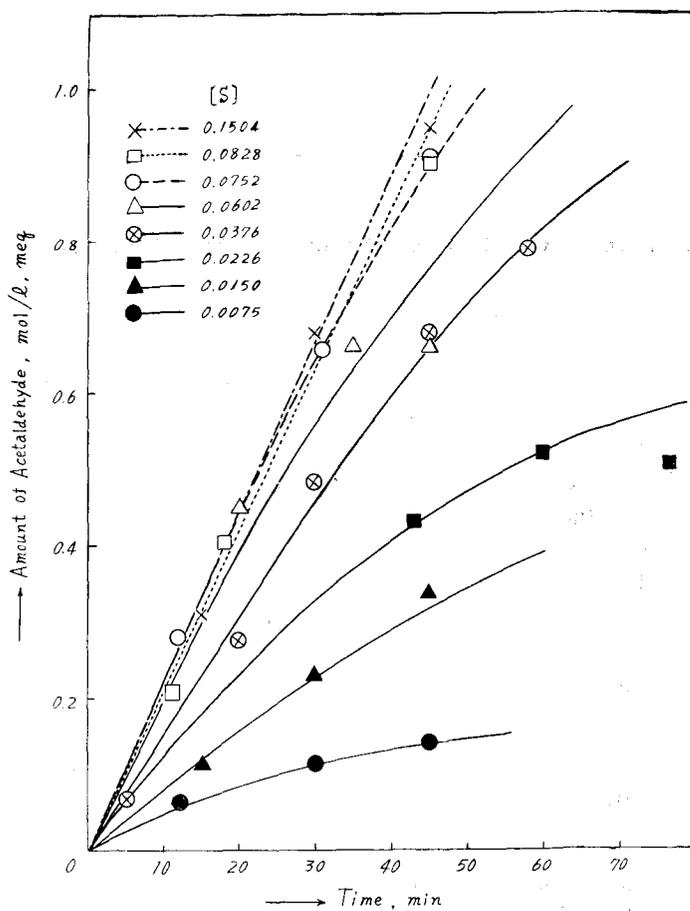†) Titre required after the addition of sodium bicarbonate.

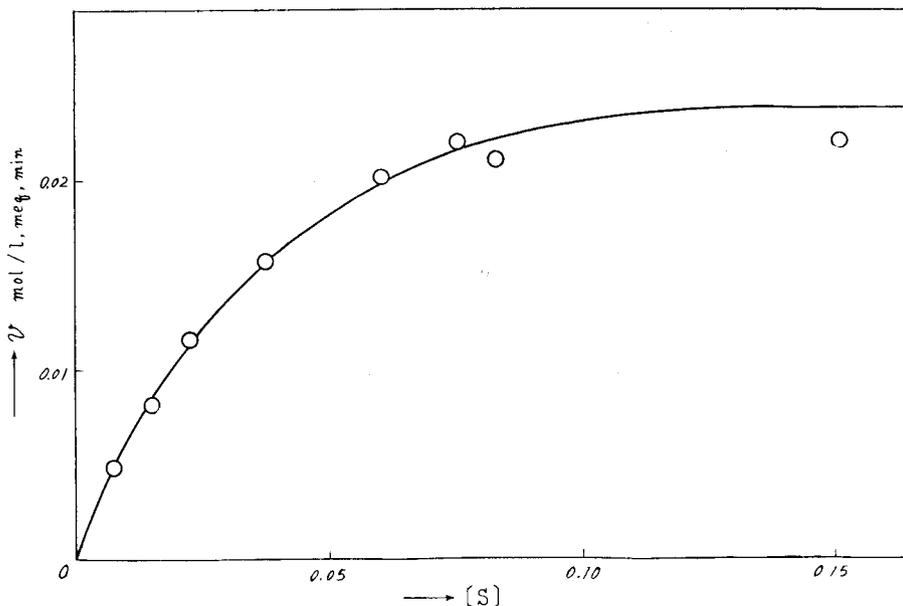**Fig. 1.** Depolymerization of paraldehyde at 30°C.

Fig. 2. Initial velocity v vs. initial concentration of paraldehyde [S].

Results and Discussion

Typical kinetic data are shown in Table 1. In Fig. 1, the amount of acetaldehyde formed for unit milli equivalent of acid sites was plotted against time over the range of various initial concentrations of paraldehyde from 0.0075 to 0.150 mol/ℓ. Initial velocity v given in the sixth column of Table 1 was obtained from the tangent at the initial state of the curve in Fig. 1.[*] In Fig. 2 is shown the plot of the initial velocity v against the initial concentration of paraldehyde [S]. The initial velocity for unit meq of acid site increases with increasing initial substrate concentration, approaching asymptotically a constant value. This incorporated with the above independence of v on the amount of acid sites is quite analogous to the most characteristic feature of enzymatic reactions as seen in the hydrolysis of lactose by emulsin, the hydrolysis of sucrose by saccharase, the digestion of casein by trypsin etc[7].

We shall now consider the kinetics of enzymatic reactions. If E denotes free enzyme, S free substrate, (ES) the enzyme-substrate complex and P the

[*] Because of the proportionality of the depolymerization rate to the amount of the acid site as found in a previous work,[3] initial velocity v for unit meq of acid site was used in the present work.

reaction product, the enzymatic reaction may be represented by

$$E + S \underset{k_2}{\overset{k_1}{\rightleftharpoons}} (ES) \overset{k_3}{\longrightarrow} E + P , \tag{1}$$

where k_1, k_2 and k_3 are the velocity constants for the steps denoted respectively by the annexed arrows. According to the stationary state hypothesis, the derivation of the well-known MICHAELIS-MENTEN's law is given by the following equation,

$$v = -d[S]/dt = \frac{k_3 [S][E]}{K_m + [S]} , \tag{2}$$

where MICHAELIS constant is $K_m = \dfrac{k_2 + k_3}{k_1}$. Since, according to mass law, the concentration of (ES) increases as [S] is increased, equation (2) shows that v approaches with increase of substrate concentration to value $V_{max} = k_3[E]$ or that

$$v = \frac{V_{max}[S]}{K_m + [S]} . \tag{3}$$

We have from equation (3) immediately

$$\frac{1}{v} = \frac{K_m}{V_{max}} \cdot \frac{1}{[S]} + \frac{1}{V_{max}} , \tag{4}$$

the slope of the straight line being K_m/V_{max} and the ordinate intercept $1/V_{max}$.

The reciprocal of depolymerization velocity $1/v$ in the present work was now plotted against the reciprocal of initial concentration of paraldehyde $1/[S]$. As shown in Fig. 3 the plots lie on a good straight line. According to equation (4), the values of constants corresponding to K_m/V_{max} and $1/V_{max}$ are determined from Fig. 3 to be 1.34 and 29.5 respectively, the "MICHAELIS constant" in this case being calculated to be 4.5×10^{-2} mol/ℓ from those values.

That the kinetic data for depolymerization of paraldehyde fitted to equation (4) indicates that the depolymerization may be represented by the following scheme involving an intermediate paraldehyde-nickel sulfate complex as in equation (1).

$$\text{Paraldehyde} + \text{Nickel sulfate} \underset{k_2}{\overset{k_1}{\rightleftharpoons}} (\text{Paraldehyde} \cdot \text{Nickel sulfate})$$
$$\downarrow k_3$$
$$\text{Acetaldehyde} + \text{Nickel sulfate}$$
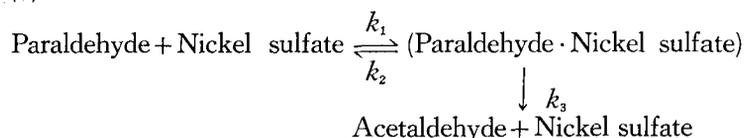
It is of interest that solid nickel sulfate and enzyme behave very similarly.

Apart from the reaction mechanism, the following two features are pointed out in general as characteristic of enzymatic reaction in comparison with usual acid-base catalyzed prototropic reaction.
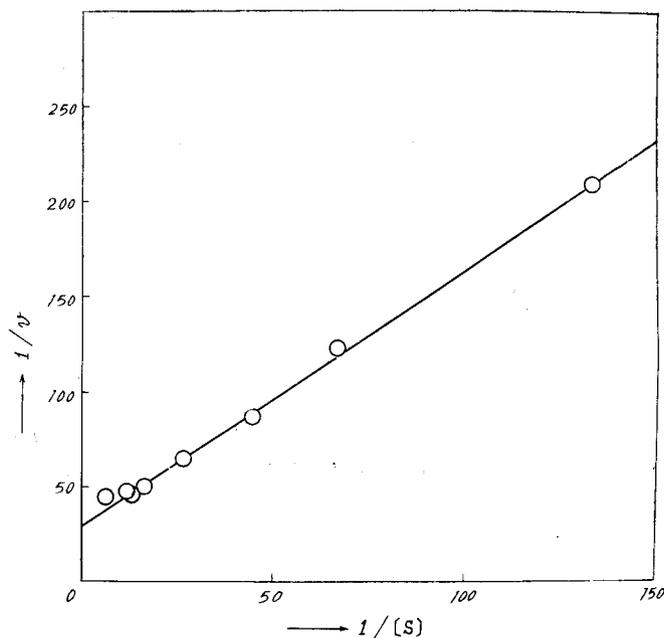
Fig. 3. Plot of $1/v$ *vs.* $1/[S]$.

A) Energies of activation and of entropy are lower in enzyme reaction[8)9)].

B) The reaction of enzyme with substrate is selective[10)], whereas the selectivity of that kind is never seen in homogeneous acid-base catalysis.
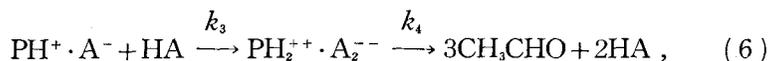
In depolymerization of paraldehyde, the energy of activation is 15 kcal/mol higher in the heterogeneous reaction[3)*]. Present experimental results show now that the reaction of paraldehyde is selective for solid acid. A well-known solid acid, silica-alumina whose acidity is much stronger than nickel sulfate**) was found to be much less catalytically active***) than the latter for depolymerization of paraldehyde. The only difference between enzyme and solid acid-catalyzed reaction consists thus in energy of activation.

Comparison with the mechanism of homogeneous reaction.

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*) It is of interest to note that the first order rate constant of solid acid-catalyzed reaction is 500 times as large as that of the homogeneous trichloroacetic acid-catalyzed reaction at the same catalyst concentration, where the catalyst concentration in heterogeneous reaction was taken as meq of acid site per unit volume of solution[3)].

**) The acidity of silica-alumina was determined to be 0.5 meq/g, being five times higher than the acidity of nickel sulfate 0.10 meq/g.

***) The first order rate constant in the case of silica-alumina is less than 1×10^{-4} min^{-1}, while that in the case of nickel sulfate is 2.5×10^{-3} min^{-1} under the same experimental condition.

The depolymerization of paraldehyde P catalyzed by Brönsted acid HA in non-aqueous solvents is represented according to BELL *et al.*[1] by the scheme,

$$P + HA \underset{k_2}{\overset{k_1}{\rightleftharpoons}} PH^+ \cdot A^- , \qquad (5)$$

$$PH^+ \cdot A^- + HA \overset{k_3}{\longrightarrow} PH_2^{++} \cdot A_2^{--} \overset{k_4}{\longrightarrow} 3CH_3CHO + 2HA , \qquad (6)$$

where $k_2 \gg k_1$, $k_3 \ll k_4$ and $k_3 \ll k_2$. The first step is then in equilibrium with the equilibrium constant $K = k_1/k_2$ and the velocity of the net reaction is given by

$$v = k_3 [PH^+ \cdot A^-][HA] = k_3 K [P][HA]^2 . \qquad (7)$$

Equation (7) explains amply the experimental facts that the homogeneous reaction is first order with respect to paraldehyde concentration and is approximately second order with respect to the concentration of Brönsted acid[1]. The difference of mechanism between the heterogeneous and homogeneous reaction is now clearly shown by comparing equation (2), which the heterogeneous reaction follows analogously, with equation (7).

The prototropic mechanism of equations (5) and (6) is given by BELL *et al.*[1]. in detail as involving the production of the enolic form of acetaldehyde.

$$\qquad (8)$$
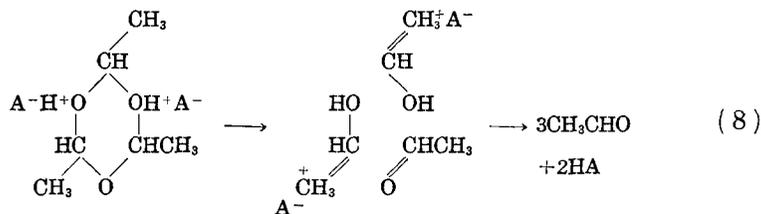
The transfer of a proton to one or more of the oxygen atoms in the paraldehyde molecule is considered to weaken the C—O bonds. Since it has been shown in the present work that solid acid behaves very similarly as enzyme does, it might be considered that the C—O bonds are weakened not only by the adsorption of oxygen atoms of paraldehyde on active center (probably Lewis acid) of the solid acid, but also by some interactions*[)] between a site other than the active center and any parts of $CH_3CH{<}$ of paraldehyde molecule.

Acknowledgments

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*) It is characteristic of enzyme action that there are some interactions between substrate and a site remote from the active center on enzyme, which accounts for the selectivity of enzyme action. The characteristic is shown in cases of α-chymotrypsin-catalyzed hydrolysis of benzoyl-L-phenylalanine ethyl ester[11], the hydrolysis of benzoyl-L-arginin-amide by papain[12], the myosin-catalyzed splitting of adenosine triphosphate[13] *etc.*

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References

1) R. P. BELL, O. M. LIDWELL and M. M. VAUGHAN-JACKSON, J. Chem. Soc. 1792 (1936).
2) K. TANABE, this Journal 7, 114 (1959).
3) K. TANABE and Y. WATANABE, *ibid.* 7, 120 (1959).
4) I. E. FRIEDMANN, M. COTONIO and G. A SCHAFFER, J. Biol. Chem. 73, 342 (1927).
5) O. JOHNSON, J. Phys. Chem. 59, 827 (1955).
6) K. TANABE and M. KATAYAMA, this Journal 7, 106 (1959).
7) E. A. MOELWYN-HUGHES, *The Kinetics of Reactions in Solution*, Oxford, Clarendon Press, p. 385 (1947).
8) S. L. FRIESS, J. Am. Chem. Soc. 76, 323 (1953).
9) D. D. ELEY, *Advances in Catalysis*, 9, 273 (1957).
10) N. NEURATH and G. W. SCHWERT, Chem. Rev. 46, 69 (1950).
11) M. L. BENDER and B. W. TURNQUEST, J. Am. Chem. Soc. 77, 4271 (1955).
12) A. STOCKELL and E. L. SMITH, J. Biol. Chem. 227, 313 (1957).
13) Y. TONOMURA and S. KITAGAWA, this Journal, to be published.