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A KINETIC COMPARISON OF HETEROGENEOUS ACID-CATALYZED DEPOLYMERIZATION OF PARALDEHYDE WITH HOMOGENEOUS ONE

By

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Depolymerization of paraldehyde with nickel sulfate catalyst has been studied in benzene. It has been found that the reaction is first order with respect to paraldehyde concentration and that the rate constant of the reaction varies remarkably with increase of temperature at which the catalyst is heated. The energy of activation was determined to be 23.9 kcal/mole for the 20~30°C temperature interval. A kinetic comparison of this heterogeneous reaction with homogeneous one has been made. It has been found that the rate of the heterogeneous reaction is 200 or 500 times larger than that of homogeneous reaction catalyzed by trichloroacetic acid at 20 or 30°C, while the energy of activation is 15 kcal/mole higher in heterogeneous reaction.

Introduction

Depolymerization of paraldehyde in homogeneous phase has been studied by BELL, LIDWELL and VAUGHAM-JACKSON[1] and found to be catalyzed by carboxylic acids and hydrogen chloride in non-aqueous solvents. It has been reported by one of the present authors that the reaction is catalyzed even by some solid acids in benzene[2]. In the present work we have studied the reaction more in detail by using nickel sulfate as catalyst and made a kinetic comparison of the heterogeneous acid-catalyzed reaction with the homogeneous one.

Experimental

Reagents and materials: Paraldehyde and benzene were purified as described previously[3]. Nickel sulfate ($NiSO_4 \cdot 7H_2O$ guaranteed reagent, Kanto Chemical Co.) was dried for about 3 hours at a desired temperature and cooled in an evacuated desiccator before use. The 100~250 mesh powder was used as catalyst**).

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**) Since the catalytic activity as well as the acidity of nickel sulfate decreases by adsorbing moisture in air, dried catalyst was avoided to expose in air as possible.

Kinetic runs: A 50 mℓ of paraldehyde solution in benzene (0.0374 mole/ℓ) was pipetted into a 100 mℓ stoppered ERLENMEYER flask, 1～3 g of nickel sulfate (100～250 mesh powder) added and shaken up and down (350 times per miunte) by a shaking machine in a thermostat maintained at 30 ± 0.02°C. After a recorded time, the catalyst was filtered off and 10 mℓ of the filtrate was pipetted into an excess of potassium bisulfite solution and titrated with a standard iodine solution similary as in the previous work[3]. The amount of acetaldehyde formed was thus determined.

Preliminary experiments showed, as expected, that the rate of reaction depends on the shaking condition. Therefore, the experiments were carried out under the condition where the rate was independent of the shaking. Constant rate was obtained when the reaction mixture was shaken 300, 320, 350 and 400 times per min respectively.

Results and Discussions

Kinetic order of the reaction: It was reported in the foregoing paper

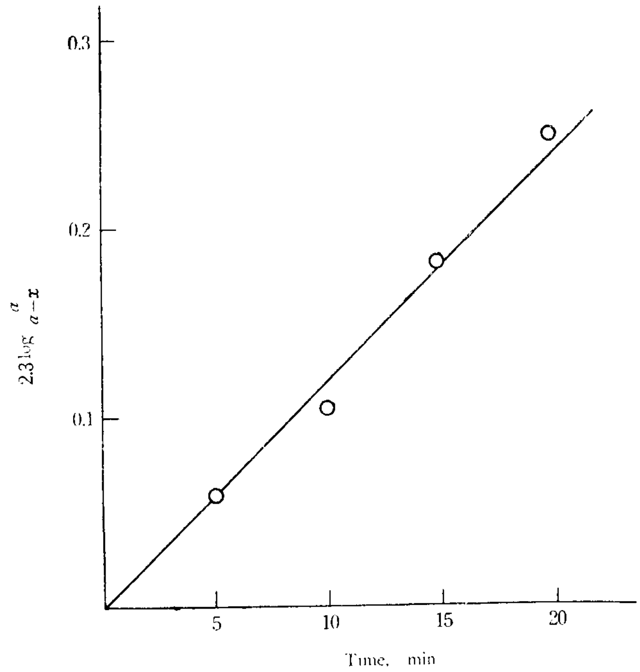

Fig. 1. Depolymerization of paraldehyde at 30°C. Concentration of paraldehyde: 0.0374 mol/ℓ. Volume of reaction mixture: 50 mℓ. Catalyst: 2 g of $NiSO_4$ heated for 3 hours at 300°C.

that the rate of depolymization of paraldehyde catalyzed by cupric sulfate is first order with respect to paraldehyde concentration[2] as in the case of the homogeneous reaction catalyzed by carboylic acids and hydrogen chloride[1]. In this investigation it has been found that the reaction with nickel sulfate catalyst is also first order with respect to paraldehyde concentration. It is shown in Fig. 1 that the plot of $2.303 \log \frac{a}{a-x}$ against time t lies on a 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 k determined from the slope of the line was found to be $1.23 \times 10^{-2}\,\mathrm{min}^{-1}$. The plot of the rate constant *vs.* the amount of catalyst is shown in Fig. 2.

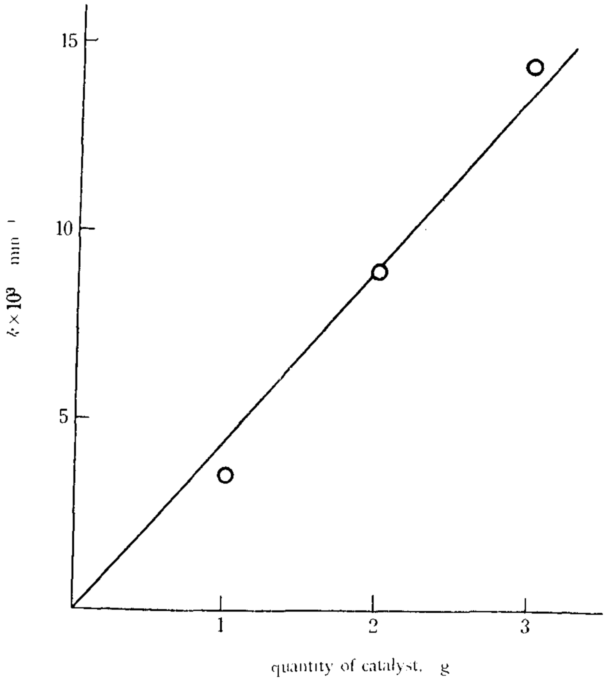

Fig. 2. Depolymerization of paraldehyde at 30°C. Concentration of paraldehyde: 0.0374 mol/ℓ. Volume of reaction mixture: 50 mℓ. Catalyst: NiSO$_4$ heated for 3 hours at 400°C.

BELL *et al.* reported that homogeneous acid-catalyzed depolymerization goes almost to completion to give acetaldehyde in benzene, anisole and nitrobenzene[1]. In the reaction with nickel sulfate catalyst, however, the percentage of acetaldehyde formed did not exceed 70%. The percentage was decreased slowly after it attained to the maximum value (70%). This seems to indicate that heterogeneous reaction is accompanied by the irreversible polymerization of acetaldehyde to give aldol, croton-aldehyde and other products in later stage of the reaction.

Temperature dependence of depolymerization: The results of depolymerization carried out at 20, 30 and 40°C are shown in Table 1. Catalyst was 2 g of 100∼250 mesh nickel sulfate which was prepared under strictly the same condition throughout all the experiments. The energy of activation was calculated from the equation

TABLE. 1. Temperature dependence of depolymerization rate.
Concentration of paraldehyde: 0.0374 mole/ℓ
Volume of reaction mixture: 50 mℓ
Catalyst: 2.0 g. $NiSO_4$ heated for 3 hours at 325°C

Reaction temp. °C	Reaction time min	% of acetaldehyde formed	$k \times 10^3$ min^{-1}
20.0	15	5.91	4.02
〃	〃	5.91	4.02
30.1	15	21.8	16.4
〃	〃	21.9	16.5
40.0	5	34.8	85.4
〃	10	52.6	74.6*)

*) This value seems less reliable because of the measurement at later stage of the reaction

$$E = 2.303\,R\,\frac{T_1 \times T_2}{T_1 - T_2}\log\frac{k_1}{k_2}\ ,$$

where k_1 and k_2 are rate constauts at T_1 and T_2 respectively. The values were found to be 23.9 kcal/mole for the 20∼30° temperature interval and 29.8 kcal/mole for the 30∼40° interval.

Acidity and depolymerization activity of nickel sulfate catalyst: Fig. 3 shows that the depolymerization activity increases with increase of temperature at which the catalyst is heated in air before use, attains to a maximum near 325°C and then decreases sharply. The varitions of the acidity of nickel sulfate with temperature which was determined by amine titration in the previous work[3] is shown by a dotted line in the same figure. It is seen that the variation of acidity against temperature runs parallel with that of depolymerization rate. This suggests that acid sites of the surface of nickel sulfate may play a catalytic role for the depolymerization.

Kinetic comparison of heterogeneous reaction with homogeneous one:

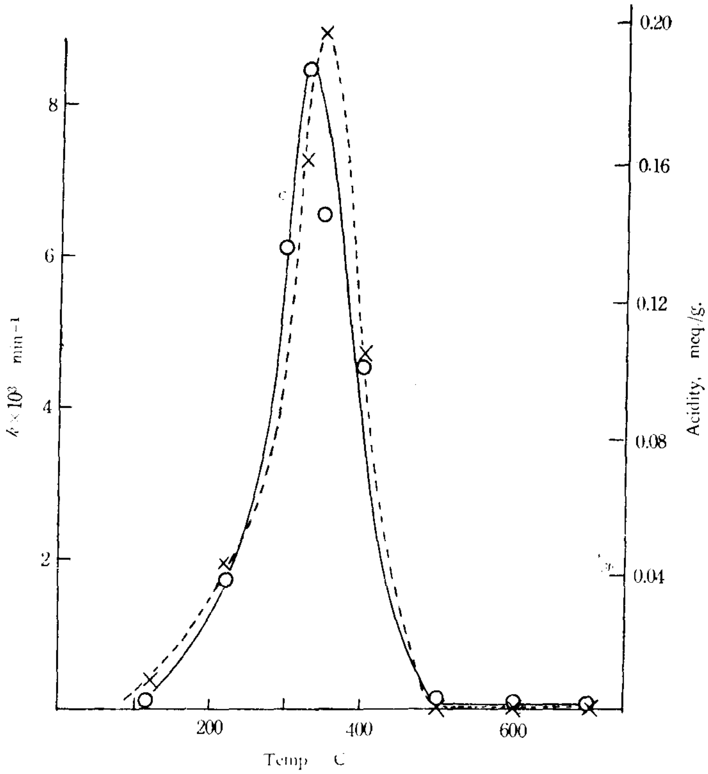

Fig. 3. Depolymerization rate and acidity of $NiSO_4$. Open circles show the rate constants of the reaction with 1 g of $NiSO_4$ at 30°C. Crosses show the acidity of 1 g of $NiSO_4$.

The kinetic comparison has been made of the following three points.

(I) *The first order rate constant*: Since the total number of acid sites on the surface of nickel sulfate is known, it is possible to compare the first order rate constant of heterogeneous reaction with homogeneous one. The rate constant of depolymerization catalyzed by nickel sulfate is 4.02×10^{-3} or 16.4×10^{-3} min^{-1} at 20 or 30.1°C as shown in Table 1 where 2.0 g of $NiSO_4$ heated for 3 hours at 325°C was used. The acidity of the nickel sulfate heated under the same condition was determined to be 0.16 meq./g. in the previous work[3]. Since 2 g of nickel sulfate was used for 50 mℓ of reaction mixture, the concentration of acid sites on the solid surface at which the above rate was determined is estimated to be 0.0064 eq/ℓ. On the other hand, first order rate constants in homogeneous reaction catalyzed by trichloroacetic acid and dichloroacetic acid at 20 and 30°C are available from the data obtained by BELL *et al.*[1] Those are shown in Table 2. The linear relation between rate constant and the amount

TABLE 2. Heterogeneous and homogeneous depolymerization of paraldehyde.

		Heterogenous reaction	Homogeneous reaction		
Catalyst		$NiSO_4$	CCl_3COOH		$CHCl_2COOH$
Solvent		benzene	benzene		benzene
Concentration of catalyst		0.0064 eq/ℓ	0.0209 mole/ℓ	0.0240 mole/ℓ	0.131 mole/ℓ
$k \times 10^3$ min^{-1}	20 °C	4.02	0.076	—	
	30 °C	16.5	—	0.120	0.104

of catalyst in the case of $NiSO_4$ is not so accurate as shown in Fig. 2, but assuming the linear relation, the rate constant of the heterogeneous reaction can be estimated at the same concentration as that in the case of the homogeneous reaction. Thus, at the same concentration of catalyst, the rate constant of the heterogeneous reaction is 197 times or 516 times larger than that of the trichloroacetic acid-catalyzed reaction at 20°C or 30°C respectively and 3250 times larger than that of the reaction catalyzed by dichloroacetic acid at 30°C.

(II) *Energy of activation*: Energy of activation of the trichloroacetic acid-catalyzed reaction in benzene was calculated from the data of BELL *et al.*1) The value was found to be 14.3 kcal/mole for the 20∼30°C temperature range. The energy of activation in heterogenous reaction is 15.5 kcal/mole higher than that in homogeneous one for the 20∼30°C temperature interval.

(III) As described above, depolymerization of paraldehyde in homogeneous phase goes almost to completion to give acetaldehyde, while the reaction with nickel sulfate catalyst does not form acetaldehyde more than 70% and the percentage of acetaldehyde decreases slowly after it attained to the 70% maximum.

Acknowledgments

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