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Author(s)	TANABE, Kozo; NAGATA, Akiko; TAKESHITA, Tsuneichi
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## Note

### The Catalytic Activity of Solid Acids for the Mutarotation of $\alpha$ -D-Tetramethylglucose in Benzene Solution

By

Kozo TANABE<sup>\*</sup>), Akiko NAGATA<sup>\*</sup>)  
and Tsuneichi TAKESHITA<sup>\*\*</sup>)

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The mutarotation of  $\alpha$ -D-tetramethylglucose in benzene solution is known to be remarkably catalyzed by an acid-base bifunctional catalyst. A catalyst on which two active groups (one basic and one acidic) are properly oriented is capable of giving powerful and specific catalysis even though it contains only relatively mild groups.<sup>1,2)</sup>

The catalytic activities for various reactions of solid acids such as nickel sulfate, silica-alumina, phosphoric acid mounted on diatomaceous earth have been extensively studied and correlated with their acidic property. Only a few works suggest the existence of acid-base bifunctional catalysis of the solid acids; metal sulfates for the isomerization of butene-1 to butene-2<sup>3)</sup> and silica-alumina for the double bond isomerization of *n*-pentene<sup>4)</sup>. In this work, the catalytic activity of those solid acids for the mutarotation of tetramethylglucose are examined.

The results are given in Table 1. Nickel sulfate, solid phosphoric acid and silica-alumina do catalyze the mutarotation<sup>\*\*\*)</sup>. Table 2 shows the acidity and acid strength of those catalysts. The observed catalytic activity seems to depend on the acidic property of the catalyst. Silica-alumina which has the strongest acid strength and the highest acidity shows the greatest catalytic activity. Since, however, silica-alumina was found to have almost the same number of basic sites as that of acidic sites<sup>5)</sup> and nickel sulfate is also considered to have basic sites (oxygen of sulfate)<sup>6)</sup>, their possibilities of acting as bifunctional catalysts cannot be excluded

<sup>\*</sup>) Department of Chemistry, Faculty of Science, Hokkaido University, Sapporo.

<sup>\*\*</sup>) Research Institute for Catalysis, Hokkaido University. Present address: Elastomer Chemicals Department, Research Division, Experimental Station, E. I. du Pont de Nemours & Co., Inc., Wilmington, Del. 19898, U.S.A.

<sup>\*\*\*</sup>) In the cases of silica-alumina and solid phosphoric acid, the specific rotations  $[\alpha]_D^{25}$  after the reaction were below the equilibrium value of the mutarotation of  $\alpha$ -D-tetramethylglucose to the  $\beta$ -D-isomer. Some other reaction takes place together with the mutarotation in these cases.

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TABLE 1. Mutarotation of Tetramethylglucose with Solid Acid Catalysts

Concentration of tetramethylglucose: 2% in benzene,  $[\alpha]_D$  before reaction: 115°

No. of Run	Catalysts and the Amounts	Volume of Solution (ml)	Reaction Temp. (°C)	Time of Reaction (min)	$[\alpha]_D^{25}$ after Reaction
1	none	25	25	5	115
2	none	25	23–26	40	114
3	none	25	25 ± 0.2	180	114
4	none	25	25 ± 0.2	200	114
5	none	25	room temp.	1500	105
6	NiSO <sub>4</sub> *) 3.7 g	50	25 ± 1.5	150	94.0
7	NiSO <sub>4</sub> *) 3.7 g	50	25 ± 0.2	180	94.6
8	NiSO <sub>4</sub> *) 3.7 g	50	room temp.	5880	91.0
9	NiSO <sub>4</sub> ***) 3.7 g	50	25 ± 0.2	180	99.2
10	SiO <sub>2</sub> ·Al <sub>2</sub> O <sub>3</sub> 0.40 g	10	25 ± 0.2	180	74.6
11	Solid H <sub>3</sub> PO <sub>4</sub> 0.40 g	10	25 ± 0.05	180	84.9
12	CCl <sub>3</sub> COOH 0.027 g	10	27	7	105
13	CCl <sub>3</sub> COOH 0.028 g	10	25 ± 0.2	180	96.1

\*) Heat-treated at 250°C. \*\*) Heat-treated at 350°C.

TABLE 2. Acidity and Acid Strength of Catalysts

Catalyst	Acidity (mmol/g)				
	$pK_a = +3.3$	$pK_a = +1.5$	$pK_a = -3$	$pK_a = -5.6$	$pK_a = -8.2$
NiSO <sub>4</sub> *)	0.084	0.078	0.029	—	—
NiSO <sub>4</sub> ***)	0.11	0.11	0.059	—	—
Solid H <sub>3</sub> PO <sub>4</sub>	0.61	0.30	0.076	0	—
SiO <sub>2</sub> ·Al <sub>2</sub> O <sub>3</sub>	0.74	—	0.47	0.042	0

\*) Heat-treated at 250°C. \*\*) Heat-treated at 350°C.

completely from this semi-quantitative experiment.

Nickel sulfate heat-treated at 250°C (Run 7) showed higher catalytic activity than that heat-treated at 350°C (Run 9), despite that the former acidity is less than the latter one (see Table 2). This seems to indicate that the catalytically active acid sites on the catalyst surface are BRÖNSTED type, but not LEWIS type, since the observed acidity is only the sum of the acid sites of both types and BRÖNSTED's acidity is considered to be higher, according to the mechanism of the formation of BRÖNSTED acid site<sup>6)</sup>, than LEWIS' one for the catalyst heat-treated at lower temperature.

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### Experimental

Materials: Tetramethylglucose was prepared by the "Organic Syntheses" procedure<sup>7</sup>). The sample had specific rotation ( $[\alpha]_D^{25}$ ) of 115 (2% solution in benzene) and melting point of 82~86°C\*). Benzene used was a guaranteed reagent, the product of the Junsei Pure Chem. Co. Ltd., Tokyo.

Roughly ground nickel sulfate ( $\text{NiSO}_4 \cdot 7\text{H}_2\text{O}$ , guaranteed reagent of Kanto Chemical Co., Tokyo) was heated at 250 or 350°C for three hours and cooled in an evacuated desiccator. The finely ground powder was used for acidity measurement and as catalyst. Solid phosphoric acid (N 501) and silica-alumina (N 631) of Nikki Chemical Co. were finely ground and used as catalysts. Their acid properties which were measured by the method described below are shown in Table 2. Trichloroacetic acid was a guaranteed reagent of Kanto Chemical Co. Inc. The indicators used for acidity measurement are as follows<sup>9</sup>): *p*-dimethylamino-azobenzene with  $pK_a = +3.3$ , benzeneazodiphenylamine with  $pK_a = +1.5$ , dicinnamalacetone with  $pK_a = -3$ , benzalacetophenone with  $pK_a = -5.6$  and anthraquinone with  $pK_a = -8.2$ .

Measurement of Acidity and Acid Strength: The acidity (the number of acid sites) having an acid strength  $H_0$  equal to or lower than the  $pK_a$  value of the indicator used was determined by using amine titration method<sup>8,9</sup>) developed by JOHNSON.

Kinetic Runs: A weighed amount of solid catalyst was added into 2% benzene solution of tetramethylglucose placed in a stoppered Erlenmeyer flask and stirred by a magnetic stirrer at about 25°C (see Table 1). At a recorded time, the catalyst was filtered off, the filtrate transferred to a 10 cm polarimeter tube and readings commenced.

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\*) In order to obtain the value of  $[\alpha]_D$  at equilibrium, the mutarotation was run in a pure water at room temperature. The equilibrium value was found to be 91.

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