BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN, VOL. 46, 3617—3618 (1973)

Rearrangement of Potassium *o*-Hydroxybenzoate as Revealed by Microthermal Analyses

Koki OTA

Department of Chemistry, Kyushu Institute of Technology, Sensui-cho, Tobata-ku, Kitakyushu 804

(Received June 5, 1972)

It is well-known that potassium *o*-hydroxybenzoate (mono-potassium salicylate, SA–K), the main product of the Kolbe-Schmitt reaction, undergoes rearrangement ultimately to di-potassium *p*-hydroxybenzoate (POB–K_2).[1]

$$2\text{SA–K} \longrightarrow \text{POB–K}_2 + \text{PhOH} + \text{CO}_2 \qquad (1)$$

The following reaction schemes were suggested by Ueno and Muramoto for the thermal behavior of SA–K.[2]

$$\begin{aligned} &\text{SA–K} \longrightarrow \text{PhOK} + \text{CO}_2 \\ &\text{SA–K} + \text{PhOK} \longrightarrow \text{SA–K}_2 + \text{PhOH} \qquad (2) \\ &\text{SA–K}_2 \longrightarrow \text{POB–K}_2 \end{aligned}$$

However, we found by means of microthermal analysis that the thermal reaction of SA–K cannot be satisfactorily interpreted by the above schemes and a hydroxy dicarboxylic acid exists as an intermediate of the rearrangement reaction.

We undertook to elucidate the mechanism of the rearrangement by a combination of micro differential thermal analysis (DTA), detection and analysis of evolved gas, thermogravimetry (TG), and UV analysis.

Measurements were carried out in a stream of N_2. The results of thermal analyses are shown in Fig. 1.

Small, sharp DTA peaks 1, 2, and 3 in a large endothermic background and the three corresponding peaks of generated gases were observed. The amounts of CO_2 and PhOH simultaneously evolved were determined. It is evident from the analysis of the residues that peak 1 is partly due to the formation of 4-hydroxy isophthalic acid (4-OIP).

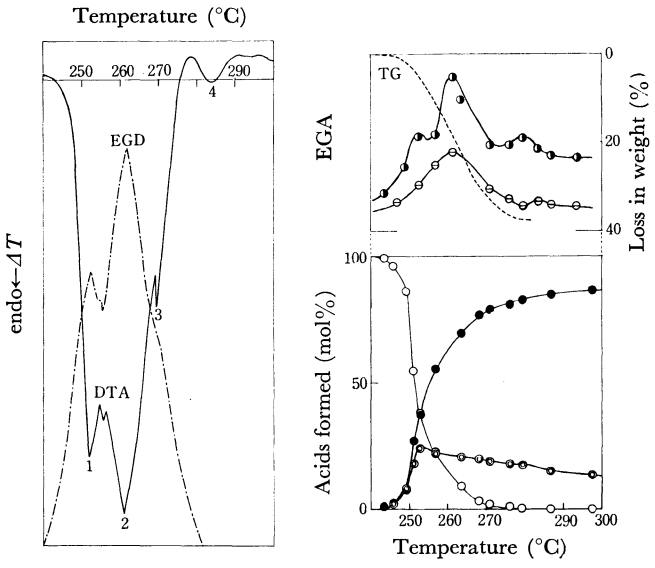


Fig. 1. Rearrangement of SA–K in N_2 stream.
⊖ CO_2, ◑ PhOH, ○ SA, ● POB, ◎ 4-OIP

The formation rate of POB increases greatly at temperatures between peaks 1 and 2. CO_2 and gaseous

1) C. A. Buehler and W. E. Cate, "Organic Synthesis," Coll. Vol. II, (1950), p. 341.

2) R. Ueno and Y. Muramoto, *Kogyo Kagaku Zasshi*, **64**, 1317 (1961).

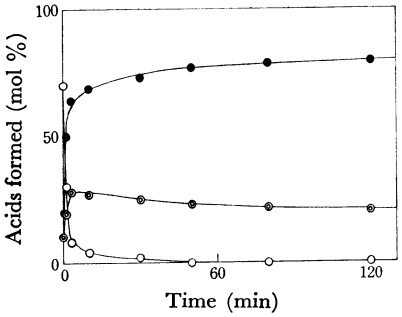


Fig. 2. Rearrangement of SA–K at 250 °C (N_2 stream).
○ SA, ● POB, ◎ 4-OIP

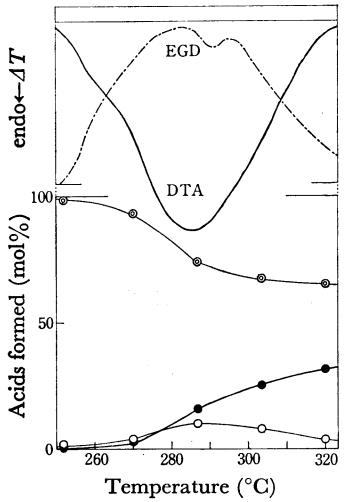


Fig. 3. Thermal reaction of 4-OIP–K_2 in N_2 stream.
○ SA, ● POB, ◎ 4-OIP

PhOH are evolved vigorously at about the same temperature (peak 2). These findings indicate that decarboxylation of SA takes place together with rearrangement of SA to POB. The changes of the DTA curve from peak 2 to peak 3 are characterized by the decrease in gases evolved, a loss in quantity of 4-OIP and the increasing amount of POB, suggesting a conversion of 4-OIP into POB. The curve TG shows that 37.0—37.4% of the original weight was lost (the theoretical value of Eq. (1) is 39.2%). This coincides with the result where acids formed contain 13—19% 4-OIP.

A small decrease in the TG curve at temperatures above 270 °C suggests that evolution of gases and the formation of POB are almost complete. When the DTA curve is restored to the initial level, the remaining amount of SA is about zero.

After this, the formation of POB occurs slightly from 4-OIP with small amounts of evolved gases as shown by evolved gas analysis and UV analysis.

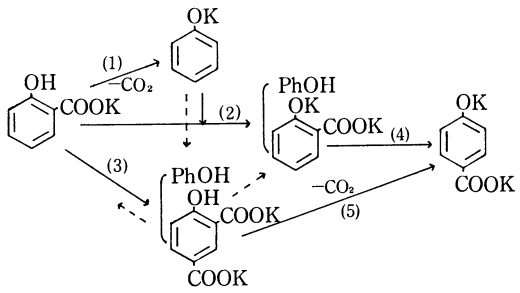
It seems that the rearrangement of SA–K proceeds partly through the formation of 4-OIP–K_2. For the sake of confirmation, the effect of reaction time at 250 °C on the reaction of SA–K was investigated.

The result is shown in Fig. 2.

At the initial stage of reaction, POB is formed and SA–K decomposes rapidly. This confirms the reaction route from SA–K to POB.[2] However, 4-OIP is also formed in this period and later slowly decomposes. This also confirms the view that the reaction proceeds from SA–K to POB *via* 4-OIP as a reaction intermediate, although 4-OIP is fairly stable under such conditions. It was confirmed that 4-OIP is formed in the thermal reaction of SA–K and is rearranged into POB at a lower rate.

The results for 4-OIP are shown in Fig. 3. We see that 4-OIP–K_2 undergoes rearrangement to POB and SA, and then SA–K_2 is converted into POB–K_2 at high temperatures. The amount of POB–K_2 formed nearly equals the loss of 4-OIP–K_2 (in weight). Evolution of a small amount of PhOH and excess CO_2 was observed (peak 4, Fig. 1).

The following reaction scheme is proposed.



The reaction rate of step (1) is high, step (2) being coupled with (1). Step (3) occurs in the earlier stage of reaction. The rate of rearrangement (4) is high, and that of (5) rather low. For the completion of reaction, it is necessary to remove PhOH and CO_2 formed.

Experimental

Sample. SA–K was prepared as reported previously[3] and 4-OIP–K_2 by purification of 4-OIP (Tokyo Kasei Kogyo Ltd.).

Apparatus. A Shimadzu EGD-20 and DT-GC system was used. TG was recorded with a TGC-20. Gas analysis was performed by gas-chromatography (GC). GC columns were packed with Shimalite-Q, MS-5A and active carbon for measurement of CO_2 and Shimalite-W (DEGS 10%+ H_3PO_4 1%) for PhOH.

QV-50 was used for UV analysis.

Methods. A sample (*ca.* 5 mg) was accurately weighed and set in an Al-sample holder. The heating rate was 10 °C/min.

The flow rate of gas was 30 ml/min, being regulated in the range 10—60 ml/min, when necessary.

The author would like to thank Dr. M. Senō, Tokyo University, for guidance and encouragement and Dr. T. Seiyama, Kyushu University, for advice.

3) K. Ota and I. Hirao, *Yuki Gosei Kagaku Kyokai Shi*, **28**, 426 (1970).