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Preparation of Naphthalene-2,3,6,7-tetracarboxylic Acid

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In the presence of sodium iodide and cadmium oxide, sodium 1-naphthoate was effectively converted into naphthalene-2,3,6,7-tetracarboxylate at 480 °C under carbon dioxide pressure. The minor product was naphthalene-2,6-dicarboxylate. Also in the rearrangement of sodium 2-naphthoate, the addition effect of sodium iodide was observed.

Raecke[1,2] found that potassium 1- and 2-naphthoates were catalytically converted into naphthalene-2,6-dicarboxylate under carbon dioxide pressure and at high temperatures. On the other hand, Mc Nelis,[3] Patton and Son,[4] and Dozen[5] reported that sodium 1- and 2-naphthoates could be transformed into naphthalene-2,3-dicarboxylate. It was thought that such difference resulted from the difference in orientation in the disproportionation between potassium and sodium salts of naphthoic acids.[5,6]

Recently more detailed studies on the rearrangement of potassium 1- and 2-naphthoates were undertaken, and a very small proportion of naphthalene-2,3,6,7-tetracarboxylate was detected in the reaction products.[7] As naphthalene-2,3,6,7-tetracarboxylic acid is expected to be a useful raw material for a heat-resistant polyimide, polyester etc., we have widely investigated the rearrangement of sodium naphthoates with a view to preparing the above tetracarboxylic acid in reasonable yields. It was found that sodium 1-naphthoate was effectively converted into naphthalene-2,3,6,7-tetracarboxylate when the rearrangement was carried out in the presence of sodium iodide.

A typical experimental procedure was described below. Sodium 1-naphthoate(1.40 g), sodium iodide(0.70 g), and cadmium oxide(0.07 g) were thoroughly mixed in a mortar and dried at 150 °C. The autoclave charged with the above mixture was initially pressurized at 3.0 MPa with carbon dioxide, and heated at 480 °C for 1 h. After cooling, the reaction mixture was taken out, and dissolved in hot water(30 ml) in a flask equipped with an air condenser. The insoluble matter(R_1; cadmium oxide, naphthalene, carbonized matter etc.) was removed by filtration, and excess silver nitrate(3.0 g) dissolved in a small portion of water was added to the filtrate(the solution of sodium iodide and naphthalenecarboxylates). The resulting suspension was warmed on a water bath for 1 h. After cooling, the precipitate(R_2; silver salts of naphthalenecarboxylic acids and silver iodide) was separated by filtration, dried under vacuum, and powdered.

R_2 was suspended in benzene(100 ml) and methyliodide(2 ml), and the suspension was warmed on a water bath for 8 h. Silver iodide was removed by filtration, and the filtrate(the solution of methyl esters of naphthalenecarboxylic acids) was gaschromatographed on Shimadzu capillary column HiCap CBP 10-M50-025 (column temperature 220-300 °C, heating rate 10 °C/min, N_2 flow rate 0.3 ml/min).

Naphthalene-2,3,6,7-tetracarboxylic acid and naphthalene-2,6-dicarboxylic acid were obtained in 53.2 and 34.6 mol % yields, respectively. These product yields were calculated assuming that 1 mol of the tetracarboxylate was produced from 4 mol of 1-naphthoate, and 1 mol of the dicarboxylate was produced from 2 mol of 1-naphthoate. Small amounts of 2-naphthoic acid(1.7 mol %), naphthalene-2,3-dicarboxylic acid(2.2 mol %) and naphthalene-2,3,6-tricarboxylic acid(5.0 mol %) were also detected. The total yield of naphthalenecarboxylic acids was 97.0 mol %. The results suggest that the direct substitution of carbon dioxide on naphthalene nucleus does not take place. On the other hand, R_1 was extracted with benzene. After the evaporation of benzene, naphthalene 0.33 g (36 mol % on naphthoate) was recovered. The low recovery of naphthalene may be due to an unsuitable work-up procedure.

Other experiments were carried out changing the amount of sodium iodide to be added to 1-naphthoate. The results were shown in Fig. 1. The maxium yield of naphthalene-2,3,6,7-tetracarboxylic acid was obtained at a sodium iodide amount of ca. 50 wt % with respect to 1-naphthoate.

The authers have already reported that, in the rearrangement of dipotassium phthalate, benzoate and various benzenepolycarboxylates are initially produced, but these carboxylates decrease in the course of reaction rapidly, and simultaneously terephthalate increases. The driving force of the formation of terephthalate is assumed to be its poor fusibility: Since terephthalate has a high melting point (above 500 °C), it easily deposits from the reaction mixture, resulting in an equilibrium favorable to the formation of terephthalate.8)

Melting points of sodium salts of naphthoic acids, naphthalene-2,6-dicarboxylic acid, and 2,3,6,7-tetracarboxylic acid were measured by use of a sealed aluminium cell connected to a differential scanning calorimetor. As shown in Table 1, naphthoates have relatively low melting points, but 2,3,6,7-tetracarboxylate and 2,6-dicarboxylate have high melting points above 520 °C. In the rearrangement of sodium 1-naphthoate, 2,3,6,7-tetracarboxylate and 2,6-dicarboxylate have a tendency to deposit from the reaction mixture, and such tendecy may be enhanced by the presence of sodium iodide. Further work is under way to elucidate the mechanism of this rearrangement.

Also in the rearrangement of sodium 2-naphthoate, the addition effect of sodium iodide was observed (Fig. 1). Even in the presence of a considerable amount of sodium iodide (50 wt % on naphthoate), more than 20% of 2-naphthoate remained unreacted. Less reactivity of 2-naphthoate may be related to its higher melting point. On the other hand, 2,3-dicarboxylic acid was relatively abundantly produced(about 10 mol %). However, the difference of reactivity between 1- and 2-naphthoate is not sufficiently explicable at the present stage.

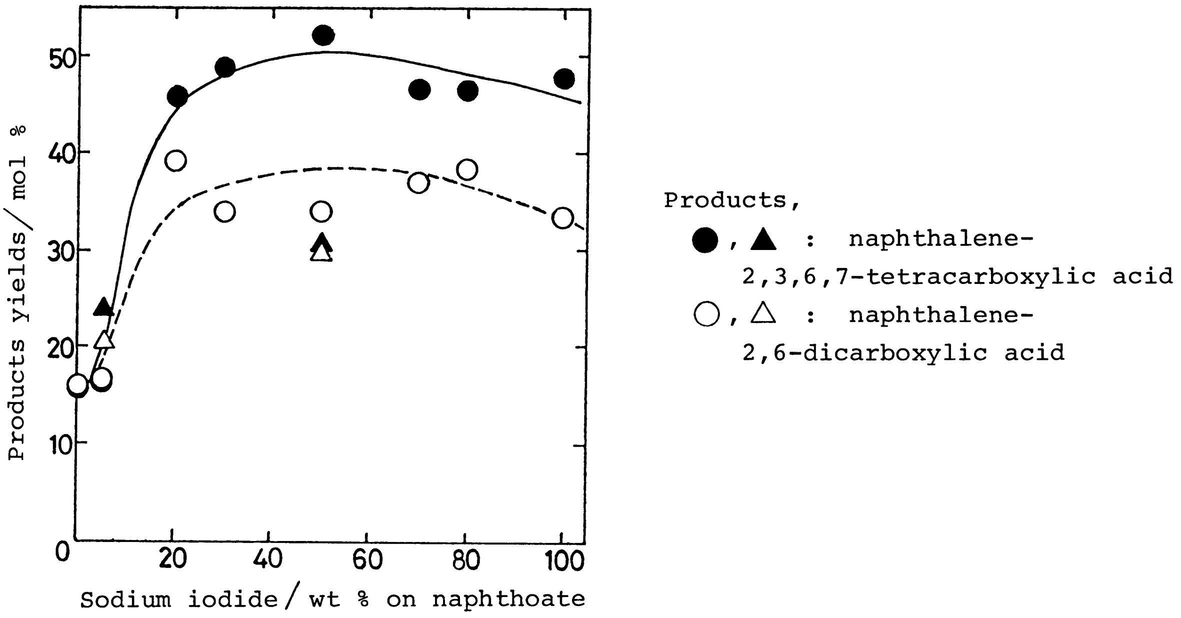

Fig. 1. The rearrangement of sodium 1-naphthoate (●, ○) and 2-naphthoate (▲, △).

Reaction conditions,
Catalyst : CdO 5 wt % on naphthoate
CO_2 : 3.0 M Pa (at room temperature)
Reaction temperature : 480 °C
Reaction time : 1 h

Table 1. Melting points of sodium salts of various naphthalenecarboxylic acids

Sodium salt	Melting point a) / °C
1-Naphthoate	387
2-Naphthoate	427
1,8-Dicarboxylate	415-440 b)
2,6-Dicarboxylate	above 520 c)
2,3,6,7-Tetracarboxylate	above 520 c)

a) The temperature at a peak in the endothermic curve.
b) The endothermic curve was broad.
c) The salt did not melt below 520 °C.

References

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7) K. Chiba, H. Tagaya, T. Watanabe, H. Kono, and M. Suzuki, Nippon Kagaku Kaishi, submitted. An example in the experimental results is described below. When potassium 1-naphthoate was heated at 460 °C for 1 h at the presence of cadmium oxide (5 wt % on naphthoate) under carbon dioxide pressure (initial pressure 3.0 MPa), naphthalene-2,6-dicarboxylic acid was obtained in 76.2 mol % yield, and 2,3,6,7-tetracarboxylic acid was simultaneously produced in about 2 mol % yield. These yields were calculated on the same base as described in the present letter.

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