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The Conversion Reaction of Alkali 4-Hydroxyisophthalates into Hydroxybenzoic Acids

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Synopsis. When alkali 4-hydroxyisophthalates are heated with phenol or alkali phenolates, *p*-hydroxybenzoic acid is formed from potassium salts and salicylic acid is formed from sodium salts preferentially.

Although the Kolbe-Schmidt reaction has long been studied from the synthetic point of view, the complete elucidation of this reaction mechanism has not yet been given and 4-hydroxyisophthalic acid (4-OIP) has been regarded as an unimportant by-product, because its yield was extremely poor.

In a preceding paper,1) though, it was reported that 4-OIP was formed in a good yield when the rearrangement of monopotassium *o*-hydroxybenzoate (SA-K) to dipotassium *p*-hydroxybenzoate (POB-K$_2$) was investigated in detail by means of microthermal analyses.

4-OIP may be the dominant product which holds the key to the Kolbe-Schmidt reaction scheme. Therefore, the thermal behavior of 4-OIP under various conditions was examined.

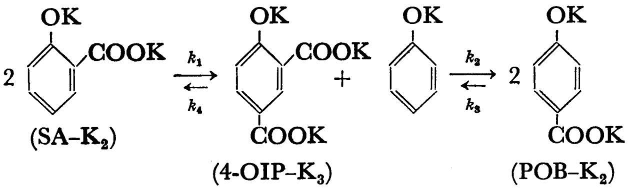
Experimental

Samples. The disodium, trisodium, dipotassium, and tripotassium 4-hydroxyisophthalates (4-OIP–Na$_2$, –Na$_3$, –K$_2$, and –K$_3$) were prepared as has been reported previously1) from commercial 4-OIP (Tokyo Kasei Kogyo, Ltd.).

Methods. The reader should refer to the previous paper1,2) for a description of the methods and the apparatus. When the experiment was carried out at increased pressures, a tubular resistance3) was connected to the apparatus in order to maintain the sample vessel at 3.85 atm.

Results and Discussion

Rostron *et al.*4) have proposed the following scheme for the reaction of 4-OIP–K$_3$ with potassium phenolate (PhOK),



This reaction was at first re-investigated by using a mixture of 4-OIP–K$_3$ and PhOK (4-OIP–K$_3$: PhOK= 1: 1) at 300 °C under a N$_2$ atmosphere. As PhOK reacts with CO$_2$, this reaction in a CO$_2$ atmosphere was not examined.

The amount of evolved gases (PhOH+CO$_2$) leads to a decrease in the sample; this decrease was evaluated by subtracting the product's weight from the anhydrous sample's weight, as has been described in the previous paper.1) PhOK is fairly stable in a N$_2$ atmosphere, even at elevated temperatures.

TABLE 1. REACTIONS OF 4-OIP–K$_3$ WITH PhOK OR PhOH AT 300°C a)

Atmospheric condition	Decrement b) (%)	Purity c) (%)	Composition of acids (mol%)		
			POB d)	SA e)	4-OIP f)
With PhOK					
N$_2$ stream g)	10.9	94.1	6	0	94
N$_2$ stream	13.2	89.1	16	16	68
N$_2$ 3.85 atm g)	10.0	90.0	3	0	97
N$_2$ 3.85 atm	14.1	91.8	16	6	78
With PhOH					
N$_2$ stream	3.6 h)	94.2	22	18	60
N$_2$ 3.85 atm	2.4 h)	83.3	41	14	45
CO$_2$ stream	3.1 h)	95.0	23	18	59
CO$_2$ 3.85 atm	5.0 h)	80.7	32	13	55

a) Reaction period=10 s (Raised the temperature continuously at the rate of 10°C/min from 30°C to the fixed temperature). b) (Decrease in weight/Original weight) × 100. c) [K salts of the total acid/(The product—PhOK)] × 100. d) *p*-Hydroxybenzoic acid. e) Salicylic acid. f) 4-Hydroxyisophthalic acid. g) The sample was sealed into a small Al vessel to suppress the evolution of gases. h) (Decrease in weight/Original weight of 4-OIP–K$_3$) × 100.

As is shown in Table 1, a mixture is converted into POB and SA with an increase in the decrement, regardless of the variation in the N$_2$ pressure. The rate of conversion decreases in this order: $k_2>k_4$. The conversion of 4-OIP–K$_3$ is affected more remarkably in the presence of PhOH than in the presence of PhOK, as was revealed by the previous results.

On the bases of these results, we carried out the reaction of 4-OIP–K$_3$ with PhOH under N$_2$ and CO$_2$ (Table 1). As expected, the conversion took place more rapidly in the presence of PhOH and the yield of POB was higher than that of SA. 4-OIP–K$_3$ itself was very stable upon heating in the absence of PhOK or PhOH and was more stable than 4-OIP–K$_2$ at 300 °C, as is shown in Table 2.

It seems that the formation of a large amount of 4-OIP conflicts with the poor yield of 4-OIP obtained from the same reaction carried out in an autoclave.5)

This can be explained as follows: the fair amounts of both 4-OIP–K$_2$ and –K$_3$ produced are consumed in their interaction with the PhOH which is simultaneously formed and can not be removed from an autoclave. Therefore, the reaction of 4-OIP–K$_2$ with PhOH was examined under N$_2$ or CO$_2$ (PhOH/4-OIP–K$_2$=1.2 mol/mol). The results are shown in Table 3.

The conversion of 4-OIP–K$_2$ into POB and SA was

Table 2. Thermal stabilities of 4-OIP–K_2 and –K_3 at 300°C and those of 4-OIP–Na_2 and –Na_3 at 320°C a)

Reactant	Atmospheric condition	Decrement b) (%)	Purity c) (%)	Composition of acids (mol%)		
				POB d)	SA e)	4-OIP f)
4-OIP–K_2	N_2 stream	13.1	86.4	38	13	49
	N_2 3.85 atm	17.5	80.4	45	8	47
	CO_2 stream	18.2	87.8	32	13	55
	CO_2 3.85atm	18.7	81.3	33	11	56
4-OIP–K_3	N_2 stream	4.6	97.1	6	6	88
	N_2 3.85 atm	2.9	96.0	8	6	86
	CO_2 stream	4.8	94.5	6	8	86
	CO_2 3.85atm	3.0	93.3	5	1	94
4-OIP–Na_2	N_2 stream	24.8	88.9	13	17	70
	N_2 3.85 atm	25.0	80.2	15	18	67
	CO_2 stream	23.7	94.3	11	20	69
	CO_2 3.85atm	21.2	86.6	9	24	67
4-OIP–Na_3	N_2 stream	3.8	92.1	11	21	68
	N_2 3.85 atm	12.6	73.4	17	19	64
	CO_2 stream	5.4	91.2	10	26	64
	CO_2 3.85atm	11.3	78.0	11	26	63

a), b), c), d), e), f), See Table 1.
Every K in Eq. c) is replaced by Na in the case of Na salts.

Table 3. Reactions of 4-OIP–K_2 with PhOK or PhOH at 300°C a)

Atmospheric condition	Decrement b) (%)	Purity c) (%)	Composition of acids (mol%)		
			POB d)	SA e)	4-OIP f)
With PhOK					
N_2 stream	21.5	88.1	48	12	40
N_2 3.85 atm	21.1	96.6	52	11	37
N_2 3.85 atm g)	24.4	72.7	44	46	10
With PhOH					
N_2 stream g)	17.2 h)	84.3	55	7	38
N_2 3.85 atm g)	18.6 h)	78.1	85	5	10
CO_2 stream g)	17.7 h)	89.2	54	8	38
CO_2 3.85 atm g)	15.8 h)	84.0	90	3	7

a), b), c), d), e), f), g), See Table 1.
h) (Decrease in weight/Original weight of 4-OIP–K_2) × 100.

found to occur much more effectively in the presence of PhOH in a closed system than in the absence of PhOH. The reaction proceeded greatly and the 4-OIP–K_2 was almost completely converted into POB under increasing pressures. This suggests that a rather large quantity of PhOH remains in the reaction system and contributes to the formation of POB.

The reaction of 4-OIP–K_2 with PhOK instead of PhOH was carried out under N_2; the results are shown in Table 3. This reaction proceeded more rapidly than the reaction in the absence of PhOH (Table 2). Especially, the reaction with PhOK in a closed Al vessel resembled that with PhOH under the same conditions, but the compositions of the acids formed were different.

The thermal stabilities of 4-OIP–Na_2 and 4-OIP–Na_3 were examined at 320 °C (Table 2). 4-OIP–Na_2 was slightly more stable than 4-OIP–Na_3; this relation was the reverse of that of the corresponding potassium salts (4-OIP–K_2<4-OIP–K_3). The effects of the differences in atmosphere and pressure were hard to recognize in the conversion of both sodium salts into SA and POB.

Table 4. Reactions of both 4-OIP–Na_2 and 4-OIP–Na_3 with PhONa or PhOH at 340°C a)

Reactant	Atmospheric condition	Decrement b) (%)	Purity c) (%)	Composition of acids (mol%)		
				POB d)	SA e)	4-OIP f)
4-OIP–Na_2	With PhONa i)					
	N_2 3.85 atm g)	24.0	85.3	9	45	46
	With PhOH j)					
	N_2 3.85 atm g)	21.8 h)	80.7	10	45	45
	CO_2 3.85atm g)	20.9 h)	81.8	9	53	38
4-OIP–Na_3	With PhONa i)					
	N_2 3.85 atm g)	22.0	80.1	18	37	45
	With PhOH j)					
	N_2 3.85 atm g)	12.8 h)	68.5	12	43	45
	CO_2 3.85atm g)	12.1 h)	75.0	10	55	35

a), b), c), d), e), f), g), h), See Table 1, and also c), h), See Tables 2 and 3 (K is replaced by Na).
i) PhONa/4-OIP–$Na_{2(3)}$ = 1.2 mol/mol. j) PhOH/4-OIP–$Na_{2(3)}$ = 1.6 mol/mol.

The results of the reaction of 4-OIP–Na_2 with PhOH or sodium phenolate (PhONa) and that of 4-OIP–Na_3 with PhOH or PhONa are shown in Table 4. As may be seen in Table 4, both 4-OIP–Na_2 and –Na_3 were markedly converted into SA in the presence of PhOH or PhONa at 340 °C under an elevated gaseous pressure.

In conclusion, the difference in the orientation between PhOK and PhONa in the Kolbe-Schmidt reaction—that is, at high temperatures PhOK and PhONa give POB and SA respectively—may be caused by the difference in the degree of conversion between 4-OIP–K_α and 4-OIP–Na_α (α=2, 3).

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