A METHOD FOR PRODUCING HYDROXYBENZOIC ACIDS DIRECTLY FROM THE ALKALI FUSION MIXTURE OF SODIUM BENZENESULFONATE

by

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Synopsis

The reaction mixture from alkali fusion of sodium benzenesulfonate (SBS) cannot be used as starting material for the carboxylation of the alkali phenoxide, because of residual excess alkali. It was found that hydroxybenzoic acids were obtained in good yield by the reaction of carbon dioxide with the treated alkali fusion mass, in which the residual alkali hydroxide was completely converted to alkali alkoxide by the reaction with some aliphatic alcohols ($C_4 \sim C_5$) under the removal of the formed water as an azeotrope with the alcohol. For example, p-hydroxybenzoic acid was obtained in 66 % yield (70 % based on phenol) from the reaction product from the alkali fusion of SBS with potassium hydroxide in a 1 : 3 molar ratio.

This method is very convenient for the preparation of hydroxybenzoic acids from the mixture of phenol and alkali hydroxide with continuous treatment without preparation of alkali alkylcarbonates and alkali phenoxides separately, although this method is essentially the reaction of carboxylation of the latter in the presence of the former.
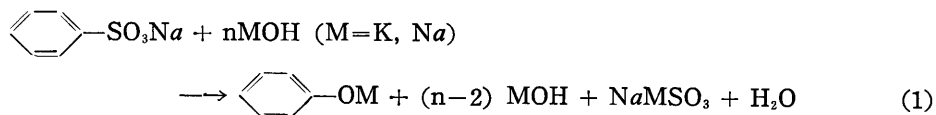
1. INTRODUCTION

Aromatic hydroxy acids, such as p-hydroxybenzoic acid, are obtained mainly by the carboxylation of alkali phenoxide. This reaction, which we have often reported, can be roughly divided as follows ; (i) the reaction of alkali phenoxide with carbon dioxide in the solid-gas phases, (ii) the reaction in aprotic polar solvents in liquid phase[1], (iii) the reaction of alkali phenoxide suspended in nonpolar solvents such as kerosene with carbon dioxide[2], (iv) the reaction of alkali phenoxide with alkali alkyl carbonates[3]. The main products formed from these reactions are p-hydroxybenzoic acid (POB) and salicylic acid (SA), the latter being obtained from sodium phenoxide quantitatively. Usually POB is obtained from either the thermal rearrengement of dipotassium salt of SA or the reaction of potassium phenoxide with carbon dioxide at high temperatures.

By the latter method the yield of POB, however, does not exceed more than 50% because the reaction proceeds via SA as medium.[4] When the potassium is used as alkali in the reaction (iv), POB is obtained more than 80 % in yield, but usually it is obtained in 50~60 % based on potassium used, whose value is considerably lower than that of SA from sodium salt. Since in both cases, however, the alkali phenoxides are used as a starting material to obtain the hydroxy acids by carboxylation, the effective use of alkali, particularly potassium, must be considered (although POB is obtained mainly also from sodium phenoxide in aprotic polar solvents,[1] the yield is not so good). By the way, the alkali phenoxides used in these reactions are prepared by mixing equimolar amounts of phenol and alkali hydroxide in water and evaporating to dryness.

On the other hand, the conventional synthetic method of phenol was the alkali fusion of benzensulfonate. When sodium salt is used as the sulfonate, the reaction will follow the equation (1).

$$\text{C}_6\text{H}_5\text{--SO}_3\text{N}a + n\text{MOH} \quad (M=K, Na)$$

$$\longrightarrow \text{C}_6\text{H}_5\text{--OM} + (n-2)\ \text{MOH} + Na\text{MSO}_3 + \text{H}_2\text{O} \tag{1}$$

From this reaction phenol is usually obtained in a free form and alkali is recovered as carbonates or sulfites by introducing CO_2 or SO_2 into the reaction mixture after alkali fusion is over. In this case, as phenol exists as the alkali salts in the fusion mass, the direct use of them as a starting material for carboxylation not only brings about effective use of alkalis but also shortens the process. However, it is difficult to obtain hydroxy acids in good yields acting carbon dioxide directly on the fusion mass because of the residual excess alkali. We now report the effective method to use the alkali phenoxide contained in the alkali fusion mass directly.

2. EXPERIMENTAL

2. 1 Alkali fusion

The alkali fusion of 1 mol of sodium benzenesulfonate was carried out in a 500-ml. stainless steel beaker in a stream of nitrogen. After the reaction was over, the reaction mixture was taken out with hot water, filtered and washed with ether, followed by dilution to 1 l. for convenience of the experiment. The alkali fusion reaction is expressed by (1). The alkali ratio is defined as the molar ratio of alkali hyroxide used to 1 mol of SBS (K-ratio and Na-ratio refer to potassium hydroxide and sodium hydroxide, respectively).

2. 2 The quantitative analysis of phenol.

Ten ml. aqueous solution of the alkali fusion mass was acidified with H_2SO_4

then the phenol was distilled by steam. After the distillate was buffered at pH 11, the phenol contained was determined by the ultraviolet absorption method (λ_{max} 234 $m\mu$, ε_{max}8930). The reaction conditions and the yields of phenol were shown in Table 1.

Table 1. Alkali fusion.

Alkali ratio		Fusion condition		Yield of phenol
K-ratio	Na-ratio	Temp. (°C)	Time (hr)	(%)
3	0	260	1	94.0
2.5	0	260	1	94.8
2	0	260	1	92.7
2	1	280	1	92.1
0	2.5	300	0.25	85.1

2. 3 Carboxylation.

(Method A)

In a 500 m*l.* four-necked flask was placed 150 m*l.* of light oil and the fusion mass which was obtained from alkali fusion of 0.1 mol of SBS. Carbon dioxide was introduced in it under vigorous stirring at 220°C for two hours.

(Method B)

In a 500 m*l.* four-necked flask, equipped with a thermometer, gas inlet-tube and water separator,[*4] were placed 100 ml. of aliphatic alcohols, 150 m*l.* of light oil (b. p. > 240°C) and 100 ml. of the aqueous solution of alkali fusion mass. The mixture was stirred vigorously under refluxing in a stream of nitrogen and the water formed was removed by a water separator in which water was separated from the organic layer. When the water was no longer separated from the organic layer, nitrogen was replaced by carbon dioxide (flow rate, 25*l*/h.), and then the temperature was raised for 40 minutes and fixed the prescribed temparature (shown in Table 3). After the reaction was completed, the light oil was separated by adding water to the reaction mixture. The aqueous layer was adjusted to pH 7 and the unchanged phenol was extracted with ether. Then, the aqueous layer was adjusted to pH 1 or below with hydrochloric acid and the hydroxy acids formed were extracted with ether. They were analysed according to the method previously reported.[1]

2. 4 The reaction of alkoxide with benzylchloride and the analysis of the products.

In the apparatus, as was mentioned in the method B, were placed 150 m*l.* of 1-pentanol and 0.05 mol of sodium hydroxide. The mixture was stirred vigorously under refluxing for 1 hr. after the water was no longer separated in the water

separator. Then 0.05 mol of benzylchloride was added to the mixture and reaction was continued at the same temperature for 1 hr.[5] After the reaction was completed, water was added to the reaction mixture and allowed to stand over night. The organic layer was separated, and the aqueous layer was washed with benzene. The benzene layer was added to the organic layer and the mixture was dried with anhydrous sodium sulfate. After 1-pentanol and benzene had been distilled out as much as possible, the residue was analysed by a gas chromatograph (Yanagimoto GCG–550 T ; column : PEG 20 M 2.25 m, 220°C ; carrier ; He 17.5 ml/min.). Each peak in gas chromatogram was assigned by comparing the retention time of the standard sample, but benzylchloride was not detected.

2. 5 The quantitative analysis of the recovered alcohol.

The recoverd alcohol was determined by gas chromatograph using internal standards. The condition of analysis was the same as that of in 2.4 (but column temperature was at 100°C). Cumene and p-xylene were employed as the internal standards for the analysis of 1-butanol and 1-pentanol, respectively.

3. RESULTS AND DISCUSSION

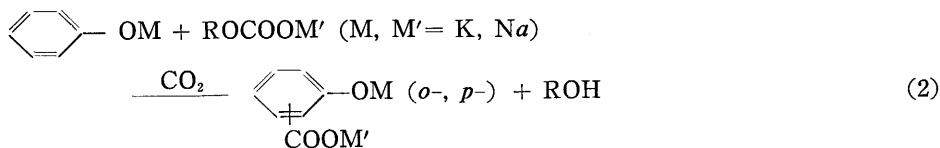### 3. 1 Carboxylation by the method A.

The carboxylation of the alkali phenoxide contained in the alkali fusion mass was carried out by the method A, but only a small amount of hydroxy acids was obtained (Table 2). The reason seems to be that the alkali hydroxide contained in the alkali fusion mass interfered with the carboxylation. Exp. 5 in Teble 4, which is the result of the carboxylation at 200°C for 2 hrs in the presence of potassium hydroxide, shows the fact that only 10 mol % excess potassium hydroxide lowers the yield of hydroxy acids greatly.

Table 2. Carboxylation by the method A
Reaction Condition : 220°C, 2hr

Alkali ratio		Yield of hydroxy acid (%)
K-ratio	Na-ratio	
3	0	trace
2.5	0	trace
2	0	10

3. 2 Carboxylation by the method B.

Hydroxy acids are obtained in good yields by the carboxylation of alkali phenoxide in the presence of alkali alkyl carbonates (equation 2). They act as a carboxylating reagent when the reaction is carried out in a nitrogen atmosphere.[3] By the way, alkali alkylcarbonates are obtained from the reactions of carbon

$$\text{⟨benzene⟩— OM + ROCOOM' (M, M' = K, N}a)$$

$$\xrightarrow{CO_2} \text{⟨benzene⟩—OM } (o\text{-}, p\text{-}) + \text{ROH} \quad\text{(with COOM')} \tag{2}$$

dioxide and alkali alkoxides, the latter being generally prepared acting potassium or sodium metal on alcohols. Although alkali alkoxide fomed from alkali hydroxide and alcohol according to the equation (3), it is difficult to take them out because the equilibrium lies so far to the left. But Kyrides reported that alkali

$$\text{ROH} + \text{MOH (M=K, N}a) \rightleftarrows \text{ROM} + H_2O \tag{3}$$
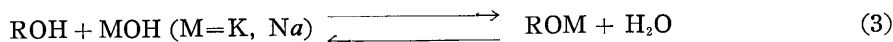
alkoxide can be prepared by adding benzene and alcohols to alkali hydroxide, followed by the separation of the water formed as an azeotrope with the benzene.[6] Therefore, it seems to be possible to obtaine hydroxy acids by the carboxylation of alkali fusion mass in which the residual alkali hydroxides were completely converted to alkali alkoxide by the method of Kyrides. As alkali hydroxides, as mentioned above, seriously interfere with the carboxylation, the residual alkali hydroxides in the alkali fusion mass must react with alcohols quantitatively by this method. Then, to choose appropriate alcohols for forming alkoxides, the carboxylation was carried out by the method B of using nine alcohols,[7] that is methanol (b. p. 65°C), ethanol (79°C), 2-propyl alcohol (82°C), 1-propyl alcohol (97°C), 1-butylalcohol (118°C), isoamylalcohol (132°C), 1-pentanol (138°C), 1-hexanol (158。C) and 1-octanol (195°C). But the mixture of 0.05 mol of potassium phenoxide prepared by another method and 0.05 mol potassium hydroxide were used in place of alkali fusion mass. To the mixture 50 m*l*. of benzene was added as an azeotrope. Fig. 1 shows the relation of the boiling points of alcohols against the yields of hydroxy acids. As can be seen from it, relatively low boiling alcohols such as methanol, ethanol and 2-propylalcohol and relatively high boiling alcohols such as 1-hexanol and 1-octanol did not give good results. The reason for the low boiling alcohols seems to be due to the difficulty of separating the water from the azeotrope composed of alcohol-benzene-water because of the free miscibility of water and alcohol (although 1-propylalcohol is also miscible with water, but it was easily separated from the azeotrope), and the reason for the high boiling alcohols due to the slower formation of alkoxides than the lower boiling ones such as 1-pentanol (it may be difficult to remove alcohols because of their high boiling points and the remainders may prevent the carboxylation, but this idea is denied by the Ex. 6 in Table 4). Further examination showed that it is rather convenient to carry out the removal of the water formed in the absence of benzene because this procedure results in shorter time reguired to remove the water. Since the higher boiling alcohols are employed, the more water contains
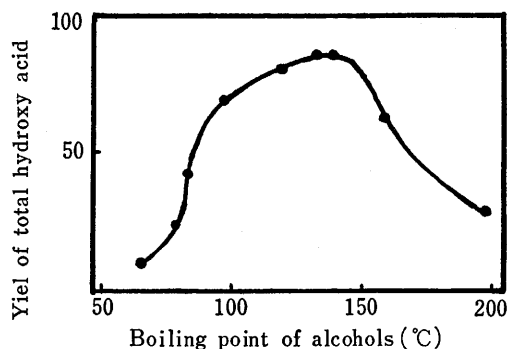
Fig. 1. Effect of Alcohols
PhOK : 0.05 mol, KOH : 0.05 mol,
Alcohol : 100 ml, Benzene : 50 ml,
Light oil : 150 ml, at 220°C for 2 hr in a stream of CO_2

in azeotropic mixture, 1-pentanol seems to be the most suitable (azeotropic point with water : 95.8°C, the water content in the azeotrope : 54.4 wt %).[8]

3. 3 The carboxylatton of alkali phenoxide in alkali fusion mass.

As it was found that the carboxylation of potassium phenoxide was pos-sible by the method B, even in the presence of potassium hydroxide, the procedure was applied to the carboxylation of alkali phenoxide in alkali fusion mass. Since the alkali fusion of SBS needs theoretically at least 2 mols of alkali hydroxide to 1 mol of SBS (alkali ratio 2), the carboxylations were carried out using the alkali fusion mass which was obtained under potassium ratio 3, 2.5, 2, alkali mixture of potassium ratio 2 and sodium ratio 1 (alkali ratio 3) and sodium ratio 3 by the method B. The results are shown in Table 3.

Table 3. Carboxylation of Alkali Fusion Mass by the Method B

Ex.	Alkali ratio		Conditions		Total yield of acids (%)	Ratio of hydroxy acids (mol %)		
	K-ratio	Na-ratio	Temp. (°C)	Time (hr)		POB	SA	4-OIP
1			180	2	85	36	57	7
2			200	2	83	59	33	8
3	3	0	220	2	83	72	18	10
4			220	5	81	87	5	8
5			240	2	80	82	7	11
6	2.5	0	200	2	68	59	35	6
7			240	2	67	89	3	8
8	2	0	200	2	46	59	31	10
9			240	2	40	84	7	9
10			180	2	66	32	54	14
11	2	1	220	2	60	43	21	36
12			240	2	56	52	13	35
13	0	3	220	2	60	6	90	4

a) Total acid=POB+SA+4-OIP
b) Yield is based on phenol formed in the alkali fusion.

Table 4. Carboxylations by Various Combinations

Ex.	PhOM 0.05mol M	Additions and its amount (mol)	Temp. (°C)	Total yield of acids (%)	Ratio of hydrox acids (mol %)		
					POB	SA	4-OIP
1	K	—	220	41	71	12	17
2	K	—	240	41	86	6	8
3	K	0.05a)	220	86	70	13	17
4	K	0.05a)	240	84	78	7	15
5	K	0.005b)	220	15	87	9	4
6	K	0.05c) 100ml	220	76	50	16	34
7	K	0.05e)	240	83	47	42	11
8	Na	0.05a)	240	83	47	38	15
9	K	f)	240	55	58	17	25
10	Na	0.05e)	220	80	2	95	3

a) $CH_3(CH_2)_4OCOOK$
b) KOH (85 %)
c) $CH_3(CH_2)_7OCOOK$
d) $CH_3(CH_2)_7OH$
e) $CH_3(CH_2)_4OCOONa$
f) Carboxylation was carried out by the method B by using 0.05 mol of PhOK, 0.05 mol of NaOH, 100 ml of $CH_3(CH_2)_4OH$ and 150 ml of ilght oil.

Since the yield of phenol was considerably better as can be seen in Table 1, which was obtained by varying the potassium ratio, the reaction under potassium ratio 2 will correspond to the carboxylation of potassium phenoxide by carbon dioxide, and potassium ratio 3 to the reaction in the equation (2) in which M and M′ are refer to K. For comparison, experiments 1∼4 were carried out by use of potassium phenoxide and 1-pentyl potassium carbonate[9] which were prepared separately. As can be seen by comparing the results in Table 4 with the ones in Table 3, both reactions agreed with each other closely, and it was found that the same result was obtained from both the carboxylation of alkali fusion mass using potassium hydroxide by method B, and of potassium phenoxied.

Appreciably different results were obtained when some amount of potassium hydroxide was replaced by sodium hydroxide. Thus, by comparing the results (Ex. 10-12 in Table 3) from the reaction using the mixture of potassium ratio of 2 and of sodium ratio 1 (total alkali ratio 3) with those from the reaction using the potassium ratio of 3, it was found that the total yield of hydroxy acids from the latter reaction and the ratio of POB to the total hydroxy acids decreased against the increases of the yields of SA and 4-OIP.

In the reaction (1), the sulfite produced as a by-product must exist as sodium-potassium salt because if it would exist in disodium salt, a result similar to that under potassium ratio of 3 should be obtained. Then, the reactions of Ex. 7, and 8 in Table 4 were carried out using the alkali salts prepared separately, but the yield of total acid was 83 %, this value being not analogous to the one of

Ex. 12 in Table 3. The reason can be considered as follows: the alkali fusion mass used in the Ex. 12 in Table 3 may be composed of an equimolar amount of potassium phenoxide, sodium hydroxide, sodium potassium sulfite and it should give a result similar to that of Ex. 7 in Table 4. However, sodium hydroxide remained in the reaction system because of its low reactivity to form an alkoxide and, as a result, it decrease the total yield. The fact that the yield from the sodium ratio of 3 is lower than that of Ex. 10 in Table 4 can be interpreted in the same way. Benzene as an azeotrope gave no desirable results in the reaction of sodium ratio of 3. To determine the amount of remainning alkali hydroxide, the mixure of 150 ml. of 1-pentanol and 0.05 mol of sodium hydroxide was dehydrated by azeotropic distillation. Reflux was continued for one hour after no more water separated (the reflux was continued for about 30 min. in the method B), then 0.05 mol of benzylchloride was added, followed by further reflux for one hour. If the sodium hydroxide does not convert into alkoxide completely, benzyl alcohol will be produced as a by-product with 1-pentylbenzylether. But only a trace amount of benzyl alcohol (less than 1 % for 1-pentylbenzylether) was detected. Since sufficient dehydration would be expected to lead a good yield, reflux was continued for 2 hours after water was no longer separated in the experiment of sodium ratio of 3. After the excess alcohol had been distilled out, the carboxylation was carried out according to the method B. The total yield of hydroxy acids became 72 %, the increment being 12 %.

By the way, a great difference in the yield of hydroxy acids is recognized between the experiment 9 in Table 4, which corresponds to experiment 12 in Table 3, and experiment 7 in the same Table. But in the former the yields (%) of POB, SA and 4-OIP are about 32, 9 and 14, while in the latter they are 39, 35 and 9, respectively. Accordingly, it was found that the difference was based on the decrease of the yield of SA. Although carboxylations were also carried out using 1-butanol and isoamylalcohol in the place of 1-pentanol under the condition of potassium ratio of 3 (220°C, 2 hr), almost the same result was obtained.

As mentioned above, hydroxy acids were obtained in good yields by the carboxylation of alkali phenoxide in alkali fusion mass by the method B. But it was found (i) the selection of alcohol was a very important factor and C_5 or C_6 aliphatic alcohols gave good results, (ii) the sulfite formed as a by-product in alkali fusion does not exchange the alkali metal with other salts or alkali hydroxides and therefore the composition of fusion mass is expressed in equation (1).

By the way, the alcohols used in this reaction are recovered from three layers, that is A, B and C. The distillate from the reaction mixture separates into the organic layer (A) and the aqueous one (B) by standing. More than 90 % of A is the alcohol used in the reaction, and the rest is the water and low

boiling materials which is contained in the light oil. Although the alcohol dissolved in the water is also recovered from the aqueous layer B, fortunately the solubilities in water of the most suitable alcohols such as 1-butanol, isoamylalcohol and 1-pentanol are very low, that is 7.8 (20°C), 2.0 (14°C) and 1.7 wt % (20°C),[10] respectively. When water is added to the reaction mixture and left to stand, it separates into water and light oil layers (C). Although the alcohols are recovered also from (C), the alkyl part of alkali alkyl carbonates used in the reaction are distilled off as an alcohol from the reaction system according to equation 2.

Then 1-butanol, isoamylalcohol and 1-pentanol were recovered as a result under the conditions shown in experiment 3 in Table 3. These alcohols were recovered in 94.3, 98.3, 97.1 % from A, in 4.0, 0.5, 0.1 % from B and in 0.2, 0.4, 1.0% from C, respectively. As shown above, almost all the amount of alcohol is recovered only by separating water from the distillate. And the alcohol recovered can be used in the next reaction without purification.

Furthermore the procedure of azeotropic dehydration can be applied not only to the direct synthesis of hydroxy acids from alkali fusion mass of SBS, but also to the continuous carboxylation of the mixture of phenol and alkali hydroxide (especially potassium) by the azeotropic dehydration, followed by the introducing of carbon dioxide as mentioned in 3.2. In that case, the variation of reaction conditions (reaction temp. and reaction time) have no effect on the result and the result is the same as that from the reaction (equation 2) using alkali salts prepared separately. There are some disadvantages in that the limitation encountered with alcohols and the yield of hydroxy acids was decreased when sodium hydroxide is used, but on the contrary, the following advantages were also recognized ; (i) alkali phenoxide is so hygroscopic that the treatment is troublesome, but the operation of the azeotropic dehydrating method is very easy, (ii) it takes much time to prepare both salts separately, but the azeotropic method reduces the time for dehydration and, moreover, this method does not need to fix the ratio of phenol to alkali hydroxide precisely, (iii) it needs anhydrous alcohol and metal alkali to prepare alkali alkylcarbonates, but the azeotropic method does not need both.

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