BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN, VOL. 44, 3123—3126 (1971)

Carboxylation of Phenol Derivatives. XX. Syntheses of Phenolpolycarboxylic Acids by the Carboxylation of Alkali Phenoxide in the Presence of Alkali Alkyl Carbonate[1]

Taketoshi Kito and Ichiro Hirao
Laboratory of Industrial Chemistry, Department of Chemical Engineering,
Kyushu Institute of Technology, Tobata-ku, Kita-kyushu

(Received April 30, 1971)

Phenolpolycarboxylic acids, especially hydroxytrimesic acid, were obtained in good yields by heating alkali phenoxide under a carbon dioxide pressure in the presence of alkali alkyl carbonate. Hydroxytrimesic acid was obtained in the best yield by the reaction of potassium phenoxide and potassium alkyl carbonate. In this reaction, neither a superatmospheric pressure nor a high reaction temperature was needed. The formation processes of phenolcarboxylic acids are also discussed.

Phenolcarboxylic acids are usually prepared by heating alkali phenoxide under a carbon dioxide pressure. In this reaction, salicylic acid (SA) is produced mainly from the sodium salt, and *p*-hydroxybenzoic acid (POB) mainly from potassium salt, while 4-hydroxyisophthalic acid (4-OIP) is formed only as a minor product from both the salts.[2]

Although phenolcarboxylic acids are also obtained from the reaction of alkali phenoxide and alkali alkyl carbonate in an atmosphere of nitrogen or carbon dioxide, 4-OIP is similarly a minor product.[3,4]

On the other hand, the methods to produce 4-OIP and hydroxytrimesic acid (OT) have been reported.[5,6] For example, 4-OIP is obtained when dipotassium salicylate or dipotassium salt of POB is heated under a superatmospheric pressure of carbon dioxide at temperatures from 300° to 500°C, and OT is obtained when phenol, SA, POB, 4-OIP, or 2-hydroxyisophthalic acid (2-OIP) or alkali salts of these compounds are heated at carbon dioxide pressures greater than 100 atm at temperatures higher than 250°C in the presence of potassium carbonate. By these methods, phenolpolycarboxylic acids are obtained in good yields, but a high pressure and a high temperature are needed.

However, it has now been found that when the carboxylation of alkali phenoxide is carried out in the presence of an excess of alkali alkyl carbonate, phenolpolycarboxylic acids, such as 4-OIP and OT, are obtained in good yields under mild conditions. The present investigation deals with this newer method for preparing phenolpolycarboxylic acids, especially OT.

Experimental

Alkali Alkyl Carbonate. Carbon dioxide was vigorously introduced into a solution of alkali alcoholate, derived from pure aliphatic alcohol and alkali metal. From the resulting mixture, the excess alcohol was distilled off in a vacuum at a temperature lower than 120°C.

Reaction of Alkali Phenoxide and Alkali Alkyl Carbonate. In a 300-m*l* autoclave, equipped with an electromagnetic stirrer, we placed 0.02 mol of alkali phenoxide, the prescribed amount of alkali alkyl carbonate, and 100 m*l* of a light oil (bp$>$250°C). After the air had been replaced by carbon dioxide (unless otherwise mentioned, the carbon dioxide pressure means the starting pressure), the autoclave was heated to the prescribed temperature. This took about 30 min. When the reaction was carried out in a flask, a 300-m*l* three-necked flask, equipped with a mechanical stirrer, a thermometer, a gas inlet-tube, and a 10-cm glass tube whose top was connected to a gas-flow meter, was used in place of an autoclave. The flow rate of carbon dioxide was regulated at about 25 *l*/h. After reaction had been stopped, 200 m*l* of water was added and a light oil was separated from the aqueous solution. The aqueous solution was

---

[1] This paper was presented at the 24th Annual Meeting of the Chemical Society of Japan, Osaka, 1971.

[2] A. S. Lindsey and H. Jeskey, *Chem. Rev.*, **57**, 583 (1957).

[3] J. I. Jones, *Chem. Ind.* (London), **1958**, 228.

[4] T. Kito, T. Kondo, H. Ago, S. Yamamoto, and I. Hirao, *Kogyo Kagaku Zasshi*, **73**, 742 (1970).

[5] J. C. Wygant, U. S. 3089905 (1963).

[6] Henkel, Brit. 968829 (1963).

adjusted to pH 7 with hydrochloric acid and washed with ether. Then, phenolcarboxylic acids were acidified with hydrochloric acid and extracted with ether. After the removal of the ether, SA, POB, 4-OIP, 2-OIP, and OT were found to be present in the residue.

Analysis of the Products by the Ultraviolet Technique. After the removal of the SA by washing with chloroform, the residue was dissolved in water; the solution was then buffered at pH 11 with disodium hydrogen phosphate and sodium hydroxide and at pH 2.8 with disodium hydrogen citrate and sodium hydroxide. The absorptivities of the components are given in Table 1. By using the four key wavelengths the amounts of POB, 4-OIP, 2-OIP, and OT may be determined. The SA can also be determined by the ultraviolet technique after the evaporation of the chloroform from the chloroform solution.

Table 1. Absorptivities of components

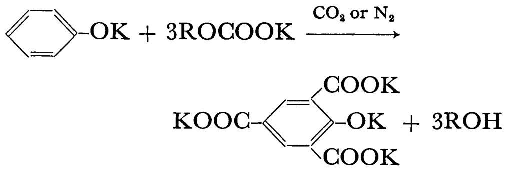
Wavelength (mμ)	231	252	280	300	340
Slit width (mμ)	0.26	0.24	0.24	0.24	0.24
pH	11.0	11.0	11.0	2.8	2.8
Components	Absorptivity[a]				
SA	4.764	0.310	1.370	2.453	0
POB	1.860	4.055	12.46	0	0
4-OIP	5.820	5.040	1.000	1.382	0
2-OIP	4.785	1.238	0.777	1.637	1.532
OT	10.03	4.181	0.623	1.045	1.698

a) Concentration; 100 γ/m*l*.

Results and Discussion

Phenolcarboxylic acids are formed by heating potassium phenoxide and an equimolar quantity of potassium alkyl carbonate in an atmosphere of nitrogen or carbon dioxide, but the main product is always POB or SA.

We have further investigated this reaction in the presence of an excess amount of potassium aklyl carbonate. The results are summarized in Table 2. In this reaction, one of the most remarkable features is that considerable amounts of OT and 4-OIP are obtained under mild conditions. Although the latter compound is also obtained from the reaction of potassium phenoxide and carbon dioxide or an equimolar quantity of potassium alkyl carbonate, it is always a minor product. However, by the reaction of potassium phenoxide and potassium 1-pentyl carbonate in a 1 : 3 molar ratio at 220°C for 2 hr, 4-OIP was formed in a 36% yield even at an atmospheric pressure. The total yield of phenolcarboxylic acids (POB+SA+4-OIP+2-OIP+OT) was nearly independent of the reaction temperature and the molar ratio of potassium alkyl carbonate to potassium phenoxide, that is, the carbonate ratio. On the contrary, the carboxylation yield, which is defined as the mole per cent of carbon dioxide introduced into a phenyl nucleus, increased with a rise in the reaction temperature or with an increase in the carbonate ratio. If the reaction proceeds according to Eq. (1), the theoretical values of the carbonate ratio



(1)

and of the carboxylation yield must be 3 and 300% respectively. However, the maximum carboxylation yield was only 198% (66% of the theoretical value), even at a carbonate ratio of 5 : 1 and at 240°C.

The reaction was again examined in an autoclave under carbon dioxide pressure. The results are summarized in Table 3. From the results shown in Tables 2 and 3, it is evident that the reaction temperature, the carbonate ratio, and the carbon dioxide pressure have a great effect on both the composition of phenolcarboxylic acids and the carboxylation yield. For example, the carboxylation yield amounted to 284% in the reaction of potassium phenoxide and three times as much potassium 1-pentyl carbonate at 260°C and 5 kg/cm^2 of carbon dioxide; in other words, OT was nearly the only product. Although other kinds of potassium alkyl carbonates, such as potassium ethyl-, *n*-butyl-, and *n*-octyl carbonate, were used in place of potassium 1-pentyl carbonate (Table 3), no remarkable effects of the alkyl group on the yield of OT was observed. Moreover, the superatmospheric pressure of carbon dioxide was not needed in this reaction.

The effect of the atmosphere was also examined (Table 4). It has been reported that potassium alkyl carbonate reacts with potassium phenoxide to yield phenolcarboxylic acids, especially POB, in good yields. In this reaction, the carbonate is regarded as a car-

Table 2. Reactions in a stream of carbon dioxide

Carbonate (ROCOOK) R	Carbonate (ROCOOK) ratio[a]	Reaction temp.[b] (°C)	Total yield of acids (%)	Carboxylation yield (%)	Yield of each acid (%) POB	SA	4-OIP	2-OIP	OT
C_2H_5	2	240	96	151	45	6	28	7	10
n-C_5H_{11}	1	240	80	104	45	11	24	0	0
n-C_5H_{11}	2	240	82	135	34	8	27	0	13
n-C_5H_{11}	3	180	98	130	18	50	28	0	2
n-C_5H_{11}	3	200	86	146	22	18	30	2	14
n-C_5H_{11}	3	220	86	160	15	14	36	4	17
*n-C_5H_{11}[c]	3	240	85	174	19	5	33	0	28
n-C_5H_{11}	5	240	85	198	10	12	13	0	50

a) ROCOOK/PhOK (mol/mol). b) Reaction time; 2 hr. c) Compare with the asterisked result in Table 4.

Table 3. Reactions under carbon dioxide pressure

Carbonate (ROCOOK)		Conditions		Total yield of acids (%)	Carboxylation yield (%)	Yield of acid (%)				
R	ratio[a]	press.[b] (kg/cm^2)	temp.[c] (°C)			POB	SA	4-OIP	2-OIP	OT
—	0	5[d]	240	34	38	23	7	3	1	0
C_2H_5	3	5	240	84	244	0	4	0	0	80
n-C_4H_9	3	5	240	89	263	0	2	0	0	87
n-C_5H_{11}	1	5	240	67	98	41	5	9	2	10
n-C_5H_{11}	2	5	240	81	198	12	4	13	0	52
n-C_5H_{11}	3	5	220	88	195	4	13	28	7	36
n-C_5H_{11}	3	5	240	88	262	0	1	0	0	87
n-C_5H_{11}	3	5	260	96	284	0	2	0	0	94
n-C_5H_{11}	3	50[e]	240	97	287	0	2	0	0	95
n-C_8H_{17}	3	5	240	88	256	0	4	0	0	84

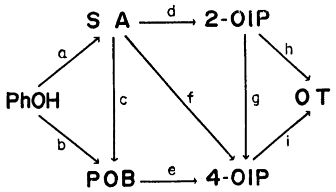
a), c) See Table 1. b) Starting pressure of CO_2. d) Reaction pressure; about 15 kg/cm^2 at 240°C.
e) Reaction pressure; 195 kg/cm^2.

Table 4. Reactions in an atmosphere of nitrogen

Carbonate (ROCOOK)		Reaction temp. (°C)[b]	Total yield of acids (%)	Carboxylation yield (%)	Yield of each acid (%)				
R	ratio[a]				POB	SA	4-OIP	2-OIP	OT
C_2H_5	1	220	76	81	66	5	5	0	0
n-C_5H_{11}	1	220	78	89	55	12	11	0	0
C_2H_5	3	240	96	138	63	2	18	2	11
*n-C_5H_{11}	3	240	82	183	11	3	31	4	33

a) b) See Table 2.

boxylating agent. The results listed in Table 4 are consistent with the above idea. However, it must be a weak carboxylating agent. In other words, the first carboxy group is easily introduced into the *ortho* or *para* position to the hydroxy group, but it is difficult to introduce the third one. Although the best-known carboxylating agent is carbon dioxide, the asterisked result in Table 2 is somewhat analogous to the asterisked one in Table 4. Therefore, carbon dioxide is also a weak carboxylating agent, but the yield of OT increased considerably when the carboxylation reaction was carried out under a carbon dioxide pressure. Consequently, in the reactions under a carbon dioxide pressure potassium alkyl carbonate may act as an alkali supplying agent rather than as a carboxylating agent to the carboxy groups introduced.



Scheme 1

There are nine routes that are considered to be possible formation processes of the five kinds of acids (Scheme 1). Potassium phenoxide, on being heated for 2 hr in the presence of an equimolar quantity of potassium 1-pentyl carbonate in a stream of carbon dioxide, gave 31% of POB and 48% of SA at 180°C, together with minor amounts of 4-OIP, but it gave 57% of POB, 11% of SA, and 12% of 4-OIP at 220°C. The increase in the amount of POB at 220°C must be due to the rearrangement of the dipotassium salicylate to the dipotassium salt of POB, which is known to be an important process in producing POB. The rearrangement of the tripotassium salt of 2-OIP to the tripotassium salt of 4-OIP may similarly occur at high temperatures. Then, the tripotassium salt of 2-OIP was heated at 180°C or 240°C for 2 hr in an atmosphere of nitrogen; the resulting solid was analysed by the ultraviolet spectral technique, whereas 4-OIP was not obtained even at 240°C. Consequently, the (g) route can be disregarded.

There are three routes, that is, (d)—(h), (e)—(i), and (f)—(i), for yielding OT. Therefore, the dipotassium salt of POB or dipotassium salicylate was heated with twice as much potassium ethyl carbonate at 200° or 240°C for 2 hr in an autoclave at 5 kg/cm^2 of carbon dioxide. The results were as follows; 1 mol of dipotassium salt of POB gave, at 240°C, 0.89 mol of OT and 0.01 mol of POB, and at 200°C, 0.76 mol of POB, 0.20 mol of 4-OIP, and 0.02 mol of OT, while 1 mol of dipotassium salicylate gave, at 240°C, 0.81 mol of OT and 0.09 mol of SA, and at 200°C, 0.53 mol of SA, 0.28 mol of 4-OIP, and 0.14 mol of 2-OIP. From these results, it was found that neither the dipotassium salt of POB nor dipotassium salicylate give OT at temperatures lower than 200°C, although they give OT as the main product in a good yield at high temperatures. In these reactions, OT must be formed predominantly *via* Route (i), because dipotassium salt of POB can not give 2-OIP and dipotassium salicylate rearranges to dipotassium salt of POB or is carboxylated mainly at the position *para* to the hydroxy group rather than at

Table 5. Reactions in the various combinations of alkali salts

PhOM$_1$ Carbonate (n-$C_5H_{11}OCOOM_2$)			Reaction temp. (°C)[b]	Total yield of acids (%)	Carboxylation yield (%)	Yield of each acid (%)				
M$_1$	M$_2$	ratio[a]				POB	SA	4-OIP	2-OIP	OT
K	K	2	220	82	178	17	9	12	4	40
Na	K	2	220	84	189	1	10	35	6	32
K	Na	2	220	76	140	4	24	20	12	16
Na	Na	2	220	81	122	0	49	11	12	9
K	K	3	240	88	262	0	1	0	0	87
Na	K	3	240	75	219	0	3	0	0	72
K	Na	3	240	71	186	0	6	15	0	50
Na	Na	3	240	71	152	0	17	17	10	27

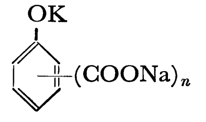
a) n-$C_5H_{11}OCOOM_2/PhOM_1$ (mol/mol), where M_1 and M_2 refer to Kand Na, respectively.
b) Reaction time; 2 hr.
Starting pressure of CO_2; 5 kg/cm^2.

the position *ortho*. Then, it became clear that both the dipotassium salt of POB and dipotassium salicylate give 4-OIP, which is further carboxylated to OT at high temperatures.

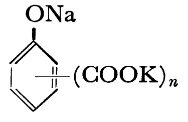
SA gives 4-OIP *via* two routes. It is known that dipotassium salicylate rearranges to the dipotassium salt of POB,[7] but the rearrangement is influenced by the presence of carbon dioxide. For example, although dipotassium salicylate, on being heated at 240°C and 5 kg/cm^2 of carbon dioxide, rearranges to give 24% of POB and 28% of 4-OIP, 46% of the starting material, dipotassium salicylate, remains unreacted. Therefore, Route (f) is also of importance as the process for yielding 4-OPI. On the other hand, both the tripotassium salt of 2-OIP and that of 4-OIP, on being heated at 240°C and 5 kg/cm^2 of carbon dioxide in the presence of twice as much potassium ethyl carbonate, gives OT in a good yield, but 2-OIP was a minor product in any of the reactions listed in Tables 2, 3, and 4.

On the basis of these data, it seems that the main processes for 4-OIP are the (a)—(c)—(e), (a)—(f), and (b)—(e) routes and that the main process for OT is Route (i).

Sodium salt was used in place of potassium phenoxide or potassium 1-pentyl carbonate. The results are summarized in Table 5. OT was obtained in the best yield when both M$_1$ and M$_2$ were potassium. The yield of OT was lowered when either M$_1$ or M$_2$ was replaced by sodium, but better results were obtained in the reactions using sodium phenoxide (M$_1$=sodium). The structures of the products are designated (I) when potassium phenoxide is used and (II) when sodium phenoxide.



(I)



(II)

The reactivity of potassium phenoxide is generally greater than that of sodium phenoxide in the carboxylation of alkali phenoxide. On the other hand, as the COONa group is a more powerful electron attractor than the COOK group, the former makes the phenyl nucleus inactive to a greater extent than the latter. Consequently, the carboxylation yields in the reactions using sodium 1-pentyl carbonate are lower than that in the reactions using the potassium salt of the corresponding carbonate.

Thanks are due to Mr. Y. Hokamura for his assistance in the experimental work.

---

[7] A. J. Rostron and A. M. Spivey, *J. Chem. Soc.*, **1964**, 3092.