Table 3. The influence of synthesis conditions on the yield of products of the potassium phenoxide carboxylation reaction with potassium alkyl carbonates [25]

ROCOOK		Reaction conditions			Total yield of hydroxyacids, %	Rate of carboxylation, %	Yields of hydroxyacids, wt %				
R	ratio[a]	p, MPa	$T^{b)}$, °C				I	II	III	IV	V
–	0	5	240		34	38	7	23	3	0	1
C_2H_5	3	5	240		84	244	4	0	0	80	0
$n\text{-}C_4H_9$	3	5	240		89	263	2	0	0	87	0
$n\text{-}C_5H_{11}$	1	5	240		67	98	5	41	9	10	2
$n\text{-}C_5H_{11}$	2	5	240		81	198	4	12	13	52	0
$n\text{-}C_5H_{11}$	3	5	220		88	195	13	4	28	36	7
$n\text{-}C_5H_{11}$	3	5	240		88	262	1	0	0	87	0
$n\text{-}C_5H_{11}$	3	5	260		96	284	2	0	0	94	0
$n\text{-}C_5H_{11}$	3	50	240		97	287	2	0	0	95	0
$n\text{-}C_8H_{17}$	3	5	240		88	256	4	0	0	84	0

[a] ROCOOK/PhOK (mol/mol); [b] duration, 2 h.

Table 4. Carboxylation of potassium phenoxide with potassium alkyl carbonates at atmospheric pressure of nitrogen [25]

ROCOOK		$T^{b)}$, °C	Total yield of hydroxyac-ids, %	Rate of carboxy-lation, %	Yields of individual hydroxyacids, wt %				
R	ratio[a]				I	II	III	IV	V
C_2H_5	1	220	76	81	5	66	5	0	0
$n\text{-}C_5H_{11}$	1	220	78	89	12	55	11	0	0
C_2H_5	3	240	96	138	2	63	18	11	2
$n\text{-}C_5H_{11}$	3	240	82	183	3	11	31	33	4

[a] ROCOOK/PhOK (mol/mol), [b] duration, 2 h.

uct of the reaction under these conditions; the nature of the alkyl groups in the reactant potassium alkyl carbonates barely affects its yield [25].

But, the nature of the gas medium substantially affects the yield of products of the potassium phenoxide carboxylation reaction with potassium alkyl carbonates. A comparison of the data in Tables 2 and 4 shows that the yield of carboxylation products in a CO_2 atmosphere is higher than that in a nitrogen medium (especially for hydroxytrimesic acid) [25].

Kito and Hirao [25] suggest nine routes for the formation of hydroxybenzoic acids, of which routes (a)–(c)–(e), (a)–(f), and (b)–(e) are most likely for 4-hydroxyisophthalic acid, and route (i) is most likely for hydroxytrimesic acid (scheme 1, where SA is salicylic acid, POB is p-hydroxybenzoic acid, 2-OIP is 2-hydroxyisophthalic acid, 4-OIP is 4-hydroxyisophthalic acid, and OT is hydroxytrimesic acid):
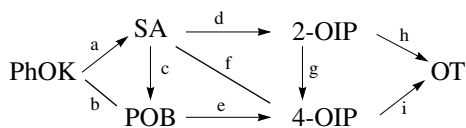
Scheme 1.

In addition, the cited authors of [25] studied the influence of the nature of alkali metals in the reactant phenoxides ($PhOM_1$) and metal alkyl carbonates ($ROCOOM_2$) on the course of the reaction. It was shown that the best yield of hydroxytrimesic acid was achieved when M_1 and M_2 were potassium atoms. As is seen from Table 5, the activity of potassium phenoxide in the carboxylation reaction is usually higher than that of sodium phenoxide. The COONa group is a stronger electron-withdrawing substituent than the COOK group, and it stronger inactivates the phenyl ring; therefore, the degree of carboxylation with sodium pentyl carbonate is lower than in the case of the corresponding potassium salt (Table 5).

The synthesis of 2,5-dihydroxybenzoic acid via the carboxylation of hydroquinone and its alkali metal salts with ROC(O)OM (M is an alkali metal) in a medium of organic solvents, including C_2–C_8 alcohols and aprotic polar compounds, in a carbon dioxide atmosphere has been patented [26]. 2,5-Dihydroxyterephthalic acid was formed as a by-product.