carbonic acids ROC(O)OM (M = Na, K; R = Me, Et) in a nitrogen or CO_2 atmosphere on the yields of salicylic, *p*-hydroxybenzoic, and 4-hydroxyisophthalic (III) acids was studied [23]:



When ROC(O)OK (R = Me, Et) and potassium phenoxide in equimolar quantities are heated in a nitrogen atmosphere (2 h), an increase in temperature from 140 up to 220–260°C results in an increase in the total yield of hydroxyaromatic acids I–III to 70–80%. In this case, the yield of salicylic acid at high temperatures decreases and *p*-hydroxybenzoic acid becomes the main product. The ratio of hydroxy acids I, II, and III in the mixture of products does not depend on the nature of ROC(O)OK (R = Me, Et), but their total yield is 5–15% higher in the case of MeOC(O)OK.

An increase in the duration of heating an equimolar mixture of PhOK with MeOC(O)OK at 220°C in a nitrogen atmosphere increases the total yield of hydroxyacids; their maximum yield (70–75%) was achieved in 4–6 h. *p*-Hydroxybenzoic acid makes up 80–90% of the total quantity of the acids in the product

Table 1. The influence of the nature of solvents on the yield of products of potassium phenoxide carboxylation with potassium methyl carbonate [24]

Solvent	Total yield of hydroxyac- ids, wt %	Yields of hydroxyacids, wt %		
		II	Ι	III
White oil	85	98	2	0
o-Cl-C ₆ H ₄ Cl	83	94	2	4
n-Cl-C ₆ H ₄ Cl	81	96	0	4
$(C_6H_5)_2O$	77	93	4	3
Kerosene	73	99	0	1
$(C_6H_5)_2$	73	93	4	3
C ₆ H ₅ Cl	73	87	5	8
C ₆ H ₅ OCH ₃	71	85	4	11
Methylcyclohexane	70	93	1	6
$(C_2H_5)_2O$	70	89	5	6
$(C_2H_5)_3N$	69	98	1	1
N-Methyl-2-pyrroli-	68	87	9	4
done				
Solvent-free	68	84	11	5
$C_6H_5N(CH_3)_2$	65	75	5	20
DMF	6	65	27	8

Note: The reaction was run in 40 g of a solvent in the presence of 50 mmol of C_6H_5OK and 50 mmol of CH_3OCOOK at a temperature of 220°C for 2 h in an N₂ atmosphere.

in as early as 1 h. An increase in the CO_2 pressure from 0 up to 10 atm does not lead to an increase in the yield of hydroxyacids (81–84%), but it results in a reduction in the proportion of *p*-hydroxybenzoic acid and a lower content of salicylic and 4-hydroxyisophthalic acids in the mixture.

In the reaction of PhOK with ROC(O)OK (R = Me, Et) in a CO₂ atmosphere (2 h), an increase in temperature from 140 to 260°C results in an increase in the total yield of hydroxybenzoic acids by 10–12%; in the case of EtOC(O)OK at 220°C, the mixture of hydroxyacids is formed with a yield of ~100%. The proportion of *p*-hydroxybenzoic acid in the product mixture increases, and that of hydroxyacids I and III decreases.

Under the same conditions, the presence of CO_2 causes an increase in the total yield of hydroxybenzoic acids, as in the case of the reaction of sodium phenoxide with MeOC(O)ONa, but the increment is smaller than that with the use of MeOC(O)OK. Here, the yield of *p*-hydroxybenzoic acid remains practically unchanged, while the yields of 4-salicylic and hydroxyisophthalic acids increase.

Thus, it was shown that the carboxylation of alkali metal salts of alkyl carbonic acids ROC(O)OM (M = Na, K; R = Me, Et) with sodium and potassium phenoxides proceeds with the formation of monocarboxylation (salicylic and *p*-hydroxybenzoic acids) and dicarboxylation (4-hydroxyisophthalic acid) products, with the product ratio depending both on the conditions of the process and the nature of the alkali metal.

Kito et al. [24] studied the carboxylation of potassium phenoxide with potassium alkyl carbonates in 20 various solvents in a nitrogen flow. The results presented in Table 1 show that *p*-hydroxybenzoic, salicylic, and 4-hydroxyisophthalic acids are formed in the reaction of equimolar quantities of potassium phenoxide and potassium methyl carbonate. The total yield of hydroxyacids increases from 68% (without a solvent) to 81-85% in dichlorobenzene and white oil; the use of dimethylformamide (DMF) sharply reduces the yield. In all cases, the main product was *p*-hydroxybenzoic acid.

Running the reaction in a CO_2 atmosphere increases the yield of hydroxyacids: the yields in DMF (220°C,

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