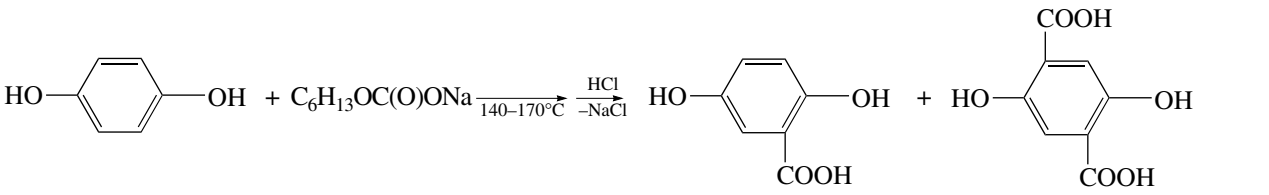
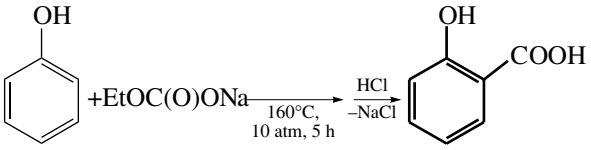


CARBOXYLATION OF PHENOL WITH ALKALI METAL SALTS OF ALKYL CARBONIC ACIDS

The qualitative composition of the products of phenol carboxylation with alkyl carbonates of alkali metals is similar to that obtained upon carboxylation with alkali metal salts. It follows from [23] that an increase in temperature from 140 to 220°C for the reaction of 0.05 mol of phenol with 0.1 mol of EtOC(O)OM (M = Na, K) in a nitrogen atmosphere results in an increase in the total yield of hydroxyacids. However, in contrast to the use of sodium salts, with an increase in temperature the yield of *p*-hydroxybenzoic acid increases, the yield of salicylic acid decreases, and that of 4-hydroxyisophthalic acid almost does not change. An increase in the quantity of the carboxylating reagent, potassium methyl carbonate, from 0.05 to 0.1 mol in the reaction with phenol in a nitrogen atmosphere (220°C, 2 h) results in an increase in the total yield of hydroxyacids from 53 up to 96%, and to an increase in the yield of each of them: *p*-hydroxybenzoic acid, from 49 to 71%; salicylic acid, from 4 to 20%; and 4-hydroxyisophthalic acid, from 0 to 5%. Under the same conditions, an increase in the amount of sodium methyl carbonate from 0.05 to 0.1 mol increases the total yield of hydroxyacids from 29 to up 50%, reduces the yield of *p*-hydroxybenzoic acid from 2 to 1% and the yield of 4-hydroxyisophthalic acid from 2 to 1%, and increases the yield of salicylic acid from 25 up to 48%.

An increase in the gas pressure from 1 to 10 atm in the reaction of 0.05 mol of phenol with 0.1 mol of sodium ethyl carbonate (220°C, 2 h) in a nitrogen atmosphere results in an increase in the total yield of hydroxyacids as compared to the reaction in a nitrogen atmosphere. In this case, the yield of 4-hydroxyisophthalic acid increases, the yield of salicylic acid decreases, and the yield of *p*-hydroxybenzoic acid remains almost unchanged [23].

The carboxylation of phenol with sodium and potassium alkyl carbonates in heterogeneous, solvent-free conditions was studied in [27–31]. It was shown, for example, that in the reaction of phenol with sodium ethyl carbonate in air, the yield of salicylic acid does not exceed 23–26%, presumably as a consequence of oxidative condensation processes. Under the same conditions but in a medium of argon or CO_2, it is possible to raise the yield of salicylic acid to 80–86% [30]:



86%

Temperature strongly affects the course of the carboxylation reaction. With an increase in temperature from 140 to 160°C (p_{CO_2} = 10 atm, τ = 3–5 h, [phenol] : [sodium ethyl carbonate] = 1 : 1.2), the yield of salicylic acid increases from 3 to 65% (Fig. 1). However, the further increase in temperature reduces the yield of the product (to 45% at 195°C). It has been found that *p*-hydroxybenzoic acid is formed as an impurity (detected by paper chromatography) in the range of 140–195°C. Its content in the product sharply increases (to 17%) with an increase in the temperature to 220°C; the yield of salicylic acid increases simultaneously (70%); the total yield of *o*- and *p*-hydroxybenzoic acids at a tem-

Table 5. The influence of the nature of alkali metal on the course of the carboxylation of alkali metal phenoxides with alkali metal salts of pentyl carbonic acid [25]

$PhOM_1$(*n*-$C_5H_{11}OCOOM_2$)			*T*,[b] °C	Total yield of hydroxyacids, %	Yield of carboxylation, %	Yields of hydroxyacids, wt %				
M_1	M_2	ratio[a]				I	II	III	I V	V
K	K	2	220	82	178	9	17	12	40	4
Na	K	2	220	84	189	10	1	35	32	6
K	Na	2	220	76	140	24	4	20	16	12
Na	K	2	220	81	122	49	0	11	9	12
K	K	3	240	88	262	1	0	0	87	0
Na	K	3	240	75	219	3	0	0	72	0
K	Na	3	240	71	186	6	0	15	50	0
Na	Na	3	240	71	152	17	0	17	27	10

[a] *n*-$C_5H_{11}OCOOM_2$/$PhOM_1$ (mol/mol), where M_1 and M_2 are Na and K, respectively; [b] duration, 2 h; the initial CO_2 pressure, 0.5 MPa.