temperature (from 130 to 220^{0}C) on the course of the phenol carboxylation reaction with potassium ethyl carbonate at a CO_2 pressure of 25 atm was studied.

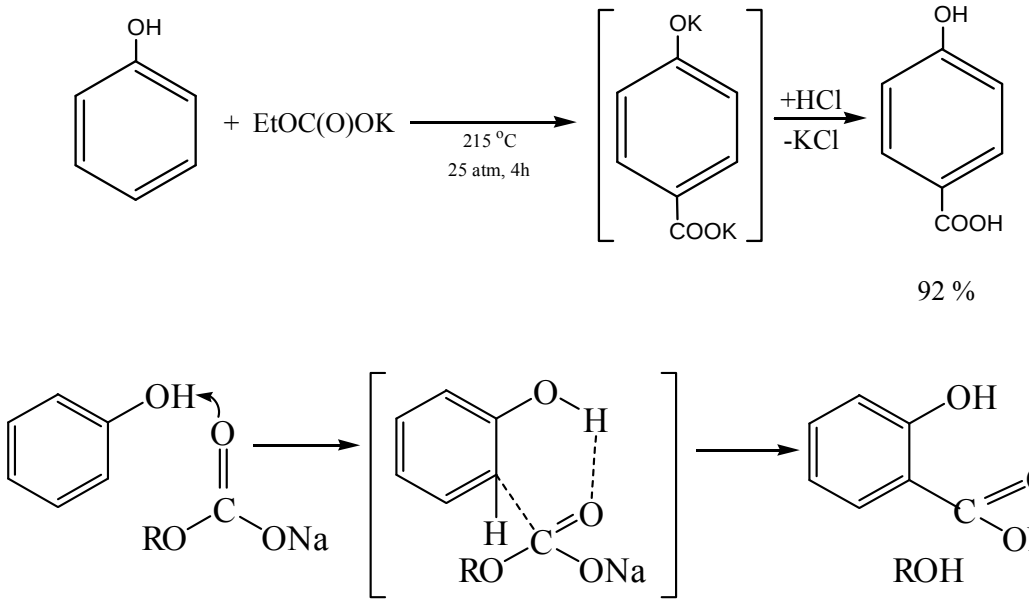
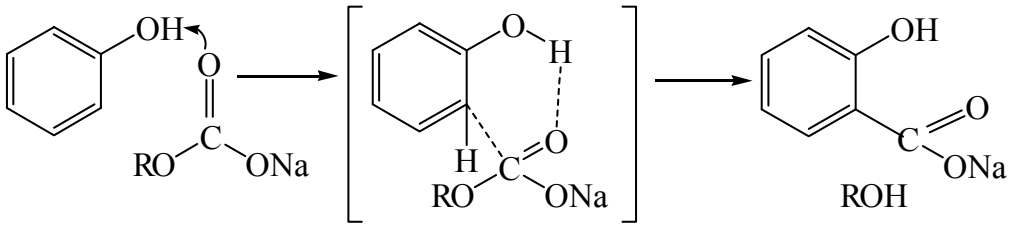


Figure 2 - The mechanism of the phenol carboxylation reaction with sodium and potassium ethylcarbonates

The following mechanism of the phenol carboxylation reaction with sodium and potassium ethyl carbonates can be suggested (Scheme 1). Apparently, the reaction proceeds through the initial association of metal alkyl carbonates through the oxygen of the carbonyl group with phenolic hydroxyl. Then, the metal-alkyl carbonate molecule activated in this way electrophilically attacks the o-position of the starting phenol with stabilization of the transition state by the formation of a six-membered ring. At lower temperatures (<200° C), carboxylation to the o-position takes place both in the case of sodium alkyl carbonate and potassium ethyl carbonate. At high temperatures (> 200° C) in the case of potassium ethyl carbonate, due to the larger volume of potassium ion, stabilization due to the formation of an intermediate six-membered state becomes impossible and carboxylation proceeds to a less spatially shielded p-position with the formation of p-hydroxybenzoic acid.



Scheme 1

Carboxylation at temperatures below 200^{0}C occurs with the formation of salicylic acid. The highest yield (78%) of salicylic acid is observed at 180^{0}C. With a further increase in temperature to 195^{0}C, the yield of salicylic acid decreases to 45%, while the yield of p-hydroxybenzoic acid gradually increases to 20%. A subsequent increase in temperature leads to the formation of only p-hydroxybenzoic acid, the maximum yield of which (92%) is observed at a temperature of 215^{0}C; a further increase in temperature decreases the yield of p-hydroxybenzoic acid, apparently due to a possible decarboxylation reaction.

Thus, a simple and convenient method for the synthesis of p-hydroxybenzoic acid by the reaction of phenol carboxylation with potassium ethyl carbonate has been developed, which allows one to obtain the target product without impurity of o-hydroxybenzoic acid. The optimal process conditions were found: