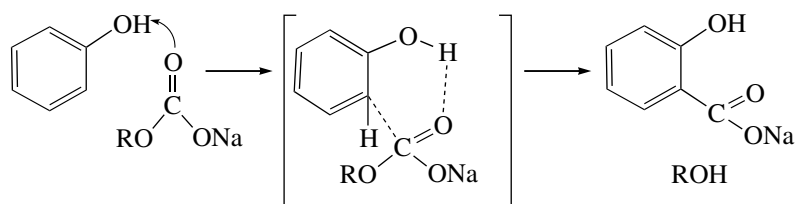


tion of phenol carboxylation with sodium ethyl carbonate (see Fig. 1). It has been supposed that such a strong difference cannot be caused only by the previously described [22, 33] thermal rearrangement of the initially formed alkali metal salt of salicylic acid into the salt of *p*-hydroxybenzoic acid at a high temperature. Supposedly, both the nature of the alkali metal (sodium, potassium) in the reactant ethyl carbonic acid salts and the reaction mechanism play a role in the difference.



Carboxylation at the ortho position occurs both in the case of sodium alkyl carbonate and potassium ethyl carbonate at temperatures below 200°C. In the case of potassium ethyl carbonate, the stabilization of the six-membered intermediate state at temperatures higher than 200°C seems to become less likely for yet unknown reasons, and the carboxylation is directed to the less sterically hindered para position with the formation of *p*-hydroxybenzoic acid.

CARBOXYLATION OF NAPHTHOLS WITH SODIUM ETHYL CARBONATE

The carboxylation of α - and β -naphthols with sodium ethyl carbonate was also studied in [31, 32]. It was found that the carboxylation of α -naphthol with sodium ethyl carbonate is regioselective, in the 2 or 4 position, depending on the reaction conditions (nature of gas medium, temperature). In an air medium ($p_{\text{air}} = 1.2\text{--}1.4$ atm), the reaction proceeds at the 2 position with the formation of 1-hydroxy-2-naphthoic acid only. The temperature dependence of the product yield is nonmonotonic in character, with a maximum yield at 160°C. The optimal time of the reaction is 5 h (4 h of the rise of temperature up to 160°C and holding at this temperature for 1 h). A further increase in the reaction time results in a sharp decrease in the yield of the product. Under optimal conditions of the process ($p_{\text{air}} = 1.2\text{--}1.4$ atm, $T = 160^\circ\text{C}$, $\tau = 5$ h), the yield of 1-hydroxy-2-naphthoic acid is 74.5% (93.1% on a converted α -naphthol basis).

An interesting dependence of the direction of carboxylation on the temperature has been revealed when the reaction of α -naphthol carboxylation with sodium ethyl carbonate was run in a carbon dioxide medium ($p_{\text{CO}_2} \sim 100$ atm, $\tau = 5$ h) (Fig. 3). At temperatures of 80–130°C (region 1), the formation of 1-hydroxy-4-naphthoic acid alone was observed; i.e., the carboxylation proceeded in the 4 position, the maximum product

Akhmetova et al. [34] suggested the following mechanism for the reactions of phenol carboxylation with sodium and potassium ethyl carbonates. Presumably, the reaction goes via an initial association of metal alkyl carbonates with phenolic hydroxyl through the carbonyl oxygen atom. Then, the molecule of metal alkyl carbonate activated in this way electrophilically attacks the ortho position of the reactant phenol with the stabilization of the transition state via the formation of a six-membered ring:

yield of 48.0% (94.3% on a converted α -naphthol basis) was at 115°C. At higher temperatures, from 140 to 190°C (region 2), carboxylation proceeded in the 2 position with the formation of 1-hydroxy-2-naphthoic acid only; the maximum yield of the product (66.0%, 93.4% on a converted α -naphthol basis) was observed at 160°C [32].

In contrast to α -naphthol, β -naphthol is carboxylated with sodium ethyl carbonate in a carbon dioxide, argon, or air medium at 110–230°C in the 3 position giving 2-hydroxy-3-naphthoic acid. The best gas medium for the reaction is carbon dioxide. The yield of 2-hydroxy-3-naphthoic acid is 38.3% (91.4% on a converted β -naphthol basis) under the optimal conditions found for the process ($p_{\text{CO}_2} = 10$ atm, $T = 190^\circ\text{C}$, $\tau = 5$ h). Carboxylation of α -naphthol with sodium methyl carbonate and sodium propyl carbonate in the optimal conditions of 1-hydroxy-2-naphthoic acid synthesis from

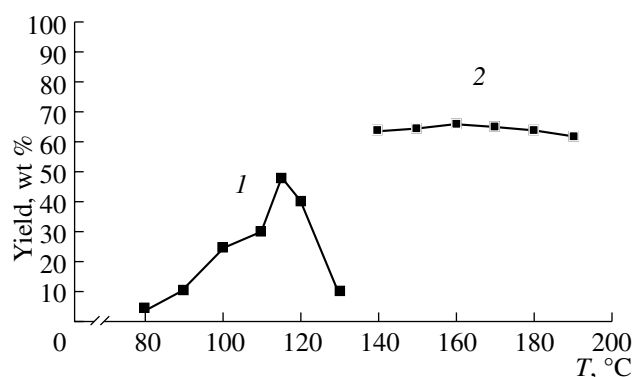


Fig. 3. The dependence of the yield of a product of the α -naphthol carboxylation reaction with sodium ethyl carbonate in a CO_2 medium ($p_{\text{CO}_2} = 10$ MPa; $\tau = 5$ h) on the temperature of the process. Region 1: 1-hydroxy-4-naphthoic acid; region 2: 1-hydroxy-2-naphthoic acid.