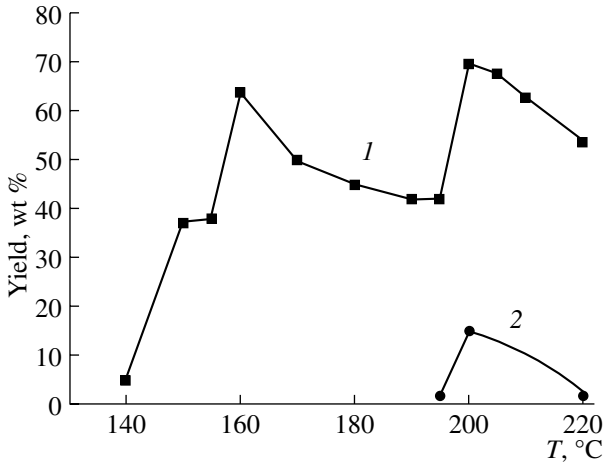


Fig. 1. Dependence of the product yields on the temperature of the process (sodium ethyl carbonate; heating rate, 35°C; time of holding at the final temperature, 1 h; p_{CO_2} = 1.0 MPa): (*1*) salicylic acid and (*2*) *p*-hydroxybenzoic acid.

perature of 200°C makes up 87% [30]. With a further increase in temperature, only the formation of salicylic acid was observed, the yield of which is gradually reduced to 56% at 220°C. Such a bimodal dependence was repeatedly reproduced, but it has not been explained yet.

In a study of the phenol carboxylation reaction with sodium ethyl carbonate in an argon atmosphere (p_{Ar} = 10 atm), it was found that the rate of temperature elevation to 160°C (in the range of 10 to 70°C/h) had an effect on the yield of salicylic acid, with the optimum rate of rise in the reactor temperature being 35–40°C/h [30].

The reactant ratio, [phenol] : [EtOC(O)ONa], substantially affects the yield of salicylic acid. It has been found that the optimum ratio is 3 : 1, which results in a product yield of 86% (T = 160°C; p_{CO_2} = 10 atm; τ = 5 h) [31].

The pressure of a gas medium (CO_2, argon) of the process in the range 1.2–10 atm (T = 160°C, τ = 5 h) slightly affects the yield of salicylic acid; a further increase in pressure to 15–20 atm sharply reduces its yield. The optimum CO_2 or Ar pressure is 10 atm [30].

The activities of sodium methyl carbonate, sodium ethyl carbonate, and sodium propyl carbonate in the phenol carboxylation reaction were compared. The reaction of phenol carboxylation with these sodium salts of alkyl carbonic acids was carried out under the *ortho*-carboxylation conditions ([phenol] : [EtOC(O)ONa] = 1 : 1.2; p_{CO_2} = 10 atm, T = 160°C, τ = 5 h). The yields of salicylic acid in the case of sodium salts of methyl and ethyl carbonic acids were almost identical at 63.8–65.7%; in the case of sodium propyl carbonate, the yield fell to 13%.

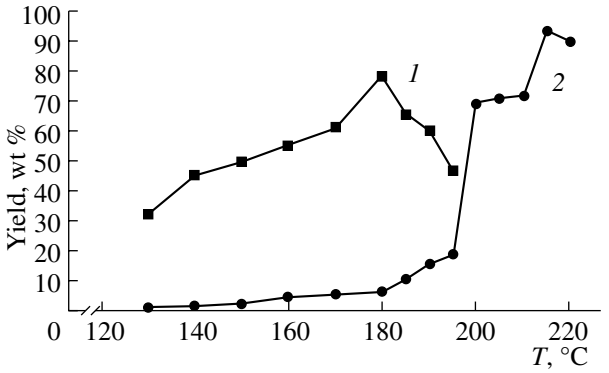
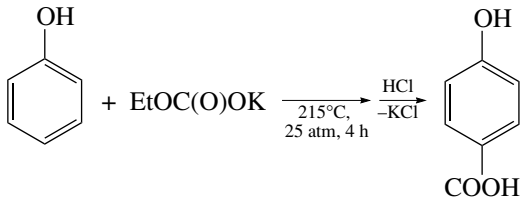


Fig. 2. The dependence of the product yields on the temperature of the process (potassium ethyl carbonate; p_{CO_2} = 2.5 MPa; τ = 7 h); (*1*) salicylic acid, (*2*) *p*-hydroxybenzoic acid.

The influence of the conditions of phenol carboxylation with potassium ethyl carbonate on the course of the reactions and the yield of products was also studied in [30]. The pressure of the gas medium (CO_2) substantially affects the yield of *p*-hydroxybenzoic acid when the reaction is conducted under the following conditions: τ = 7 h (6 h of the temperature rise to 215°C + 1 h of holding at this temperature); [phenol] : [potassium ethyl carbonate] = 1 : 1.1. The optimum pressure of the gas medium is 25 atm [30]:



92%

The influence of the temperature (from 130 to 220°C) on the course of the phenol carboxylation reaction with potassium ethyl carbonate at a pressure of 25 atm was studied under the same conditions (Fig. 2). Carboxylation at temperatures below CO_2 proceeds with the formation of salicylic acid. The highest yield of salicylic acid (78%) was observed at 180°C. As the temperature increases to 195°C, the yield of salicylic acid reduces to 45%, with the decline being accompanied by a gradual increase in the yield of *p*-hydroxybenzoic acid up to 20%. The subsequent increase in the temperature results in the formation of *p*-hydroxybenzoic acid alone, the maximum yield of which (92%) is attained at a temperature of 215°C; a further increase in the temperature reduces the yield of *p*-hydroxybenzoic acid, apparently because of the possible decarboxylation reaction.

Note that the temperature dependence of the yield of products of the phenol carboxylation reaction with potassium ethyl carbonate differs from that for the reac-