Table 2. Carboxylation of potassium phenoxide with potassium alkyl carbonates in a carbon dioxide atmosphere at atmospheric pressure [25]

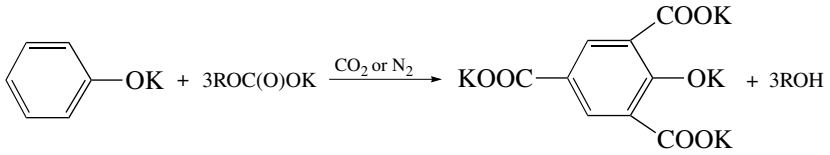
ROCOOK		T[b], °C	Total yield of hydroxyacids, %	Rate of carboxylation, %	Yields of individual hydroxyacids, wt %				
R	ratio[a]				I	II	III	IV	V
C_2H_5	2	240	96	151	6	45	28	10	7
n-C_5H_{11}	1	240	80	104	11	45	24	0	0
C_2H_5	2	240	82	135	8	34	27	13	0
n-C_5H_{11}	3	180	98	130	50	18	28	2	0
n-C_5H_{11}	3	200	86	146	18	22	30	14	2
n-C_5H_{11}	3	220	86	160	14	15	36	17	4
n-C_5H_{11}	3	240	85	174	5	19	33	28	0
n-C_5H_{11}	5	240	85	198	12	10	13	50	0

[a] ROCOOK/PhOK (mol/mol); [b] duration, 2 h.

1 h, 1 atm) and $PhNO_2$ (220°C, 2 h, 5 atm) media are 34 and 76%, respectively [24]. An increase in the temperature above 200°C increases the yield of hydroxyacids. It has been also shown that the total yield of hydroxyacids and the proportion of *p*-hydroxybenzoic acid in the reaction product fall with the growth in the length of the alkyl radical in alkyl carbonic acids (from 1 to 8 carbon atoms).

The influence of excess quantities of a reagent (potassium alkyl carbonates) in the carboxylation reaction was studied in [25]. It was shown that phenol polycarboxylic acids were formed with good yields in the reaction of potassium phenoxide with an excess of potassium salts of alkyl carbonic acids. The effect of the [PhOK] : [ROC(O)OK] ratio, temperature, composition of the atmosphere (CO_2, N_2), and pressure on the product yields was studied (Tables 2–4). Significant yields of 4-hydroxyisophthalic (III) and hydroxytrimesic (IV) acids under mild conditions are a distinctive feature of the reaction with a large excess of potassium alkyl carbonates (acid III is also formed in the interaction between equimolar quantities of the reagents, but it is always a minor product). 4-Hydroxyisophthalic acid is formed with a yield of 36% even at atmospheric pressure in the reaction of potassium phenoxide with potassium pentyl carbonate at a ratio of 1 : 3 (220°C, 2 h); 2-hydroxyisophthalic acid (V) is formed as well, although in smaller quantities.

The dependence of the total yield of phenol carboxylic acids on the temperature and the [ROC(O)OK] : [PhOK] molar ratio (the so-called carbonate ratio) is insignificant. However, the degree of carboxylation increases with an increase in both the temperature and the carbonate ratio. The degree of carboxylation is defined as the number of carboxyl groups introduced into the benzene ring, being taken as 100% per one group introduced. According to the following reaction equation for the formation of hydroxytrimesic acid (IV), the theoretical values for the carbonate ratio and the degree of carboxylation should be 3 and 300%, respectively. However, Table 2 shows that the maximum degree of carboxylation is 198% (66% of the theoretical value), even at a carbonate ratio of 5 : 1 and a temperature of 240°C. Therefore, it can be concluded that the degree of carboxylation (the number of carboxyl groups introduced into the benzene ring) is determined by not only the carbonate ratio ([ROC(O)OK] : [PhOK]), but also other factors, e.g., steric hindrances upon polycarboxylation and a decrease in the electrophilicity of the benzene ring with an increase in the number of electron-withdrawing carboxyl groups.



IV

The pressure of CO_2 substantially affects the yield of carboxylation products. As is seen from Table 3, the carboxylation of potassium phenoxide with a threefold excess of potassium pentyl carbonate at a CO_2 pressure of 5 atm proceeds to a degree of carboxylation of 284%. Hydroxytrimesic acid (IV) is practically the only prod-