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Д.В. Сокольский атындағы «Жанармай,  
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# Х А Б А Р Л А Р Ы

## ИЗВЕСТИЯ

НАЦИОНАЛЬНОЙ АКАДЕМИИ НАУК  
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## NEWS

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## CARBOXYLATION OF HYDROXYARENES WITH POTASSIUM ETHYL CARBONATE

**Abstract.** The influence of the conditions for carrying out the carboxylation reaction of phenol and its derivatives (petrochemical products) with alkaline salts of alkylcarbonic acids (potassium ethyl carbonate), easily synthesized from carbon dioxide, alcohols and alkaline metal hydroxides, was studied in order to develop new, effective methods for producing practically valuable p-hydroxybenzoic acid and other hydroxybenzoic acids (a class of compounds having a wide range of biologically active properties and other beneficial properties) is relevant and timely. A new 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. For the first time, optimal conditions were found for the regioselective p-carboxylation of phenol (pressure of carbon dioxide, temperature and duration of the process) under which the yield of p-hydroxybenzoic acid is 71,0%, and the effect of various substituents in the aromatic ring on the yield of the target products of the carboxylation of phenol derivatives is determined sodium and potassium carbonates. The influence of the nature of the alkyl groups of potassium alkyl carbonates on the carboxylation activity of the latter in the phenol carboxylation reaction was determined. We have studied that temperature has a strong influence on the direction of phenol carboxylation. When carrying out the reaction below 200°C, carboxylation proceeds to the o- and p-positions with the formation of o-hydroxybenzoic and p- hydroxybenzoic acids; the o-isomer predominates (44,9-66,7%). When carrying out the reaction above 200°C, only p-hydroxybenzoic acid is formed without an impurity of o-hydroxybenzoic acid.

**Key words:** carboxylation, hydroxyarenes, hydroxybenzoic acid, carbon dioxide, potassium ethyl carbonate, p-hydroxybenzoic acid.

**Introduction.** Carbon dioxide in the future may become one of the most important sources of carbon raw materials for chemical synthesis [1,3]. Oil and coal reserves are gradually being depleted. After oil and coal natural gas reserves will also run out. Carbon dioxide reserves are almost inexhaustible. The most promising sources of CO<sub>2</sub>, as carbon raw materials can be waste gases of chemical industry enterprises and power plants, as well as natural gas deposits, in some of the which the CO<sub>2</sub> content reaches 30%. Carbon dioxide recovery in chemical synthesis is also of great environmental significance, since it is one of the ways to reduce CO<sub>2</sub> emissions, the main component greenhouse gases into the atmosphere [2].

Use of carbon dioxide as a carbon source in organic synthesis is an urgent problem of modern organic chemistry. The huge interest in this problem is evidenced by the ever-accelerating growth of scientific publications on this subject. Analysis of the available data shows that carbon dioxide, contrary to popular beliefs, is able to enter into various reactions. At the same time, a small number of CO<sub>2</sub> based reactions have been implemented on an industrial scale, which is primarily due to the insufficient development of carbon dioxide chemistry at the moment [4-6].

In the Republic of Kazakhstan, the development of petrochemistry is very acute. All three oil refineries existing in the republic do not have the so-called petrochemical wing-petrochemical plants based on petroleum hydrocarbons and carbon oxides. The country also has an acute issue of developing

industrial fine organic synthesis to meet the needs of the population and the national economy in such useful organic products as medicines, food preservatives, detergents, etc.

Oxybenzoic acids are widely used o-hydroxybenzoic acid (salicylic acid) and its derivatives exhibit biological activity and are used as pharmaceuticals (aspirin, p-aminosalicylic acid, etc.) [8,9]. o-Oxybenzoic acid is used to obtain polymeric materials and liquid crystal polyesters with high heat resistance [10,11].

The most common industrial method for the synthesis of hydroxybenzoic acids is carboxylation of phenol with carbon dioxide under pressure (Kolbe – Schmidt reaction) [7,12,13]. One of the big disadvantages of this method is the need for preliminary synthesis of dry sodium (potassium) phenolates, which is associated with great experimental difficulties: distillation of water in a vacuum and the extreme hygroscopicity of dry alkali metal phenolates [14-16]. In connection with the foregoing, it is of interest to synthesize oxybenzoic acids that exclude the use of alkali metal phenolates. One of these methods is the carboxylation of phenol with alkaline salts of alkyl carbonic acids.

It is known that in the Kolbe – Schmidt reaction, the use of potassium phenolate promotes the formation of p-hydroxybenzoic acid [17-18]. In order to verify the effect of the nature of the alkaline metal in the starting salts of carbonic esters on the direction of carboxylation, the phenol carboxylation reaction with potassium ethyl carbonate was studied [19-20].

**Experimental part.** The reagents used were dry sodium and potassium carbonates, reactive phenol by Sigma Aldrich. The experiments were carried out without the use of solvents in gaseous carbon dioxide. The individuality of the synthesized products was determined by physicochemical constants (mp), the study of mixed samples (absence of melting temperature depression) with pure reactive samples of the reaction products, as well as according to IR and PMR spectroscopy. IR spectra were recorded on a Nicolet 5700 single-beam infrared spectrometer of Thermo Electron Corporation (USA) in the region of 400–4000  $\text{cm}^{-1}$ . NMR1H spectra were recorded on a Bruker DPX 400 instrument, operating frequency 300 MHz. Tetramethylsilane was used as the standard. The chemical used were dry potassium ethyl carbonate, synthesized by reacting carbon dioxide with potassium ethyl carbonate as described in [20], and phenol. The experiments were conducted in the solvent free mode in a medium of gaseous  $\text{CO}_2$ . The IR spectra were recorded on a Mattson SatelliteFTIR Fouriertransform IR spectrometer in the frequency range of 4000–400  $\text{cm}^{-1}$  and the NMR spectra were recorded on a Bruker DPX 400 instrument operating at a frequency of 300 MHz.

**Synthesis of salicylic acid.** A glass reactor placed into a steel autoclave and equipped with a stirrer, electric heating, and carbon dioxide gas inlet (outlet) fittings, was loaded with 2,3 g (0,025 mol) of phenol and 3,46 g (0,027 mol) of potassium ethyl carbonate (reactants ratios was [phenol] : [potassium ethyl carbonate] = 1 : 1,1); the autoclave was pressurized; purged twice with  $\text{CO}_2$  to remove air and filled with  $\text{CO}_2$  to a pressure of 10 atm; after which stirring and heating were switched on. The reaction mixture was heated to 215°C over 6 h (at a heating rate of 40°C/h) and held at this temperature and a  $\text{CO}_2$  pressure of 10 atm for 5 h. After that, stirring and heating were stopped and the autoclave was cooled down to room temperature. The reaction mixture was treated with water. The obtained aqueous solution was extracted with ether to separate unreacted phenol. Unreacted phenol was recovered from the ether phase. The product (p-hydroxybenzoic acid) was isolated by acidifying the aqueous phase with hydrochloric acid to afford 2,46 g (71,0%) of p-hydroxybenzoic acid; melting temperature 203-205°C ; after recrystallization (water) at melting point 214-216°C.

*Synthesis of salicylic acid 7.05 g (0.075 mol) of phenol and 2.8 g (0.025 mol) of sodium ethyl carbonate are charged into a glass liner placed in a steel autoclave equipped with a stirrer, electric heating and the inlet (outlet) of carbon dioxide gas. The autoclave is sealed, flushed twice with carbon dioxide to remove air, and then filled with carbon dioxide to a pressure of 10 atm, include stirring and heating. The temperature of the reaction mixture is raised to 160 ° C over 4 hours, and at this temperature and a carbon dioxide pressure of 10 atm, it is held for 1 hour. After this, stirring and heating are stopped, the autoclave is cooled to room temperature. The reaction mixture is treated with water. The aqueous phase is extracted with toluene to separate unreacted phenol. The reaction product (salicylic acid) is isolated by acidification of the aqueous phase with hydrochloric acid. 3 g (86.0%) of salicylic acid are obtained; so pl. 154-155°C.*

It should be noted that at present the properties of alkaline salts of alkyl carbonic acids have been studied very little. They are difficult to clean white crystalline substances, extremely poorly soluble in many organic solvents (ether, ethanol, acetone, benzene, etc.); they do not have a clear melting point: when heated to 380-400°C, they slowly decompose without melting with the release of gaseous products.



We also use potassium ethyl carbonate (as a carboxylating agent), synthesized by bubbling carbon dioxide through a solution of potassium hydroxide in ethanol, for the fixation and storage / disposal of carbon dioxide from industrial waste gases. The method for the synthesis of potassium alkyl carbonates from potassium metal is quite convenient for their synthesis in laboratory conditions, it is not suitable for industrial production due to the explosiveness of the mixture of hydrogen released at the stage of production of alcoholates with air. In [21], a method was described for producing potassium ethylate by the interaction of potassium hydroxide with ethanol in simple equipment that almost completely transfers potassium hydroxide to potassium ethylate when using quicklime as a water-removing agent. Based on the improvement of the method for producing potassium ethylate described in [21], we developed a simple and convenient method for the synthesis of potassium and sodium ethylates from ethanol and the corresponding sodium and potassium hydroxides (reaction 2) [22]. This reaction proceeds with the release of water; therefore, quicklime was used as a dewatering agent to shift the equilibrium to the right.



M = Na, K

Potassium ethylate is synthesized in two vessels interconnected with two tubes (flasks A and B), and potassium ethylate is obtained from caustic potassium and ethanol in vessel A, and alcohol with quicklime is drained in vessel B (Fig. 1). Both vessels are heated to a boil of ethanol. Vapors of alcohol and water liberated during the reaction (azeotropic mixture) from vessel A flows into the refrigerator, condensate from which flows through the alcohol gate to the second vessel B, where the wet alcohol is dried with quicklime, after which the alcohol vapor flows through the other tube into vessel A, continuously bubbling through an alcoholic solution of potassium hydroxide and potassium ethylate. The process is carried out for 3-7 hours at a ratio of reagents  $[\text{KOH}]: [\text{C}_2\text{H}_5\text{OH}] = 1: 8$ .

The developed simple, industrially applicable method for the production of potassium and sodium ethylates was used by us for the synthesis of potassium ethyl carbonate and sodium ethyl carbonate. The latter are used as carboxylating reagents of hydroxyarenes for the synthesis of hydroxyaromatic acids.

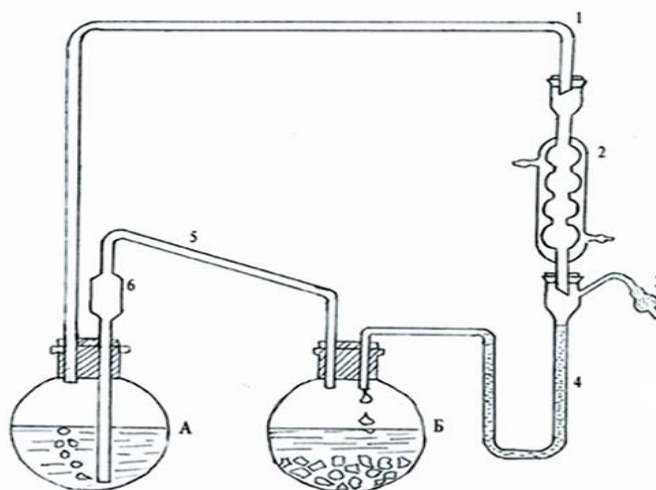


Figure 1 - Installation for the synthesis of sodium ethoxide

A and B - reaction vessels (flasks) 1 - tube for distillation of the azeotropic mixture, 2 - refrigerator, 3 - calcium chloride tube, 4 - alcohol shutter, 5 - tube for distillation of dried alcohol, 6 - anti-expansion

**Results and discussion.** The effect of phenol carboxylation with potassium ethyl carbonate on the course of the reaction and the yield of products was studied. The pressure of the gaseous medium (carbon dioxide) of the reaction ( $T = 215^{\circ}\text{C}$ ,  $\tau = 7$  h (6 h rise to  $215^{\circ}\text{C}$  + 1 h exposure at this temperature);  $[\text{phenol}]: [\text{potassium ethyl carbonate}] = 1: 1,1$ ) has a significant effect the output of p-hydroxybenzoic acid; the optimal pressure of the gaseous medium is 25 atm. Under the same conditions, the influence of



temperature (from 130 to 220°C) on the course of the phenol carboxylation reaction with potassium ethyl carbonate at a CO<sub>2</sub> pressure of 25 atm was studied.

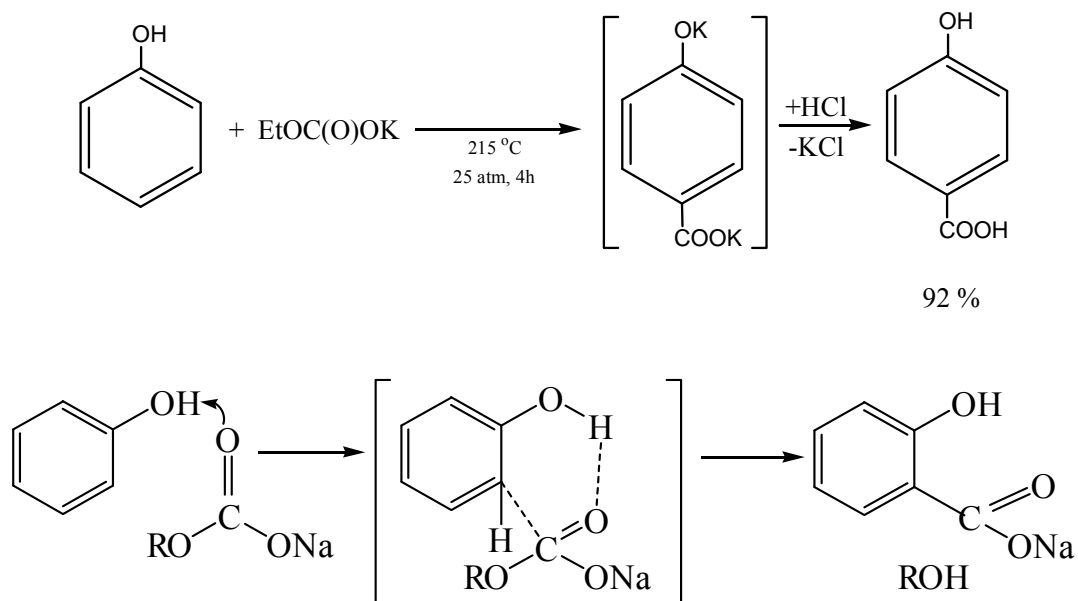
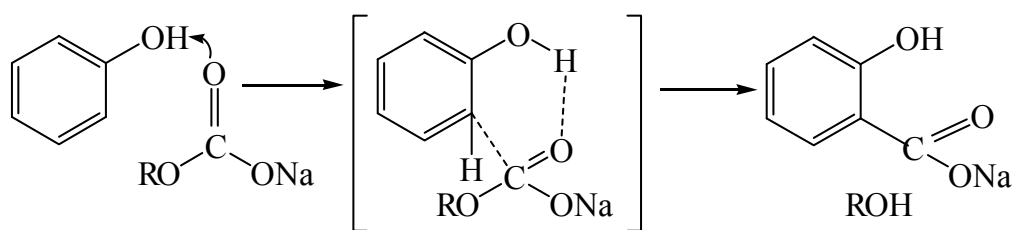


Figure 2 - The mechanism of the phenol carboxylation reaction with sodium and potassium ethylcarbonates

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°C occurs with the formation of salicylic acid. The highest yield (78%) of salicylic acid is observed at 180°C. With a further increase in temperature to 195°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°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:

$P_{CO_2} = 2.5 \text{ MPa}$ ,  $T = 210^\circ\text{C}$ ,  $\tau = 7 \text{ hours}$ , at which the yield of p-hydroxybenzoic acid is 71.0%. It should be noted that all previously known methods for the synthesis of p-hydroxybenzoic acid are based on the reaction of carboxylation of potassium phenolate with carbon dioxide (Kolbe-Schmidt synthesis), in which a mixture of o- and p-isomers is always formed; in this case, as a rule, the main reaction product is o-hydroxybenzoic acid.

The possibility of using alkaline salts of alkyl carbonic acids as a carboxylating reagent in the carboxylation of hydroxyarenes became known after the appearance of I. Jones in 1958 about the carboxylation of sodium phenol and potassium ethyl carbonate [26]. After that, starting in 1969, a number of works by Japanese researchers [23–25] appeared on the use of alkaline salts of alkyl carbon acids for the carboxylation of phenol and its derivatives.

The observed temperature dependence of the yield of phenol carboxylation reaction products with potassium ethyl carbonate differs from that of phenol carboxylation reaction with sodium ethyl carbonate. We believe that such a strong difference can be caused not only by the previously described [27, 28] thermal rearrangement of the initially formed alkaline salt of salicylic acid to the salt of p-hydroxybenzoic acid at high temperature. Apparently, here a certain role is played by both the nature of the alkali metal (Na, K) in the initial salts of ethyl carbonic acid, and the mechanism of this reaction.

**Conclusion.** In summary, it has been shown that potassium ethyl carbonate can be used as a carboxylating agent in the carboxylation reaction of phenol. It has been found that the carboxylation of proceeds regioselectively with the formation of acid p-hydroxybenzoic acid. Optimum conditions for conducting this reaction have been found. The developed simple and convenient methods for the synthesis of p-hydroxybenzoic acids can be used for their industrial manufacturing. Carboxylation of hydroxyarenes (phenols and its derivatives) with alkali salts of alkyl carbon acids (metal alkyl carbonates) is a convenient method for the synthesis of hydroxy aromatic acids. Since the appearance of the first report in this field in 1957 (I. Jones) to date, there have been relatively few publications on the carboxylation of organic compounds with metal alkyl carbonates. The analysis of the known published data on the use of alkali salts of alkylcarboxylic acids for carboxylation of hydroxyarenes shows the undoubted promise of the method for the synthesis of hydroxyaromatic acids, which are widely used, by the carboxylation of hydroxyarenes with metal alkyl carbonates.

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#### КАЛИЙ ЭТИЛКАРБОНАТЫМЕН ГИДРОКСИАРЕНДЕРДІ КАРБОКСИЛДЕУ

**Аннотация.** Көмірқышқыл газынан, спирттен және сілтілік металл гидроксидтерінен оңай синтезделген алкилкарбон қышқылының сілтілі тұзымен (калий этил карбонаты) фенол мен туындыларының карбоксилдену реакциясын жүргізу жағдайының әсері зерттелді. П-гидроксibenзой қышқылын және басқа да гидроксibenзой қышқылдарын (биологиялық белсенді қасиеті мен басқа да пайдалы қасиетінің кең спектріне ие қосылыс класы) өндірудің тиімді әдістері өзекті және маңызды болып саналады. Гидроксibenзой қышқылын синтездеудің жетілдірілген әдісі көптеген параметрлерді (қысым, температура, реакция уақыты, реактивті заттар компоненттерінің қатынасы) оңтайландыруға мүмкіндік береді, тезірек, жеңіл және арзан және өнім шығымын көбейтеді. Фенолды калий этил карбонатымен карбоксилдеу реакциясымен п-гидроксibenзой қышқылын синтездеудің жаңа қарапайым және ыңғайлы әдісі жасалды, ол мақсатты өнімді о-гидроксibenзой қышқылын қоспасыз алуға мүмкіндік береді. Мақсатқа жету үшін және алға қойған міндеттерді шешу үшін келесі тапсырмалар орындалды: гидроксiарен мен оның туындыларын металл алкилді карбонаттармен карбоксилдену реакциясының оңтайлы параметрлерін табу; түрлі қысымда, температурада, реакция ұзақтығында және реактивтердің түрлі арақатынасында гидроксiарендердің сілтілі алкилді қышқыл тұзымен карбоксилдену реакциясының параметрлерін зерттеу. Технологиялық үдерістің оңтайлы параметрлеріне қол жеткізгенде мақсатты өнім, гидроксiароматикалық қышқылдардың шығымы артады деп болжанды.

Алғаш рет фенолдың региоселективті п-карбоксилденуінің оңтайлы жағдайы анықталды (көмірқышқыл газының қысымы, температура және үдерістің ұзақтығы), бұл кезде п-гидроксibenзой қышқылының шығымы 71,0% құрайды, сонымен қатар фенолды туындылардың карбоксилдену мақсатты өнімдері шығымында хошиісті сақинадағы түрлі алмастырғыш әсері натрий және калий карбонаттары

негізінде анықталады. Фенол карбоксилдеу реакциясындағы калий алкилді карбонаттарының алкил топтары соңғысының карбоксилдену белсенділігіне әсері анықталды. Біз температура фенолдың карбоксилдену бағытына қатты әсер ететіндігін зерттедік. Реакцияны 200 °С-тан төмен жүргізгенде карбоксилдену о- және п-позицияларда о-гидроксибензой және п-гидроксибензой қышқылдарының түзілуі негізінде жүреді; о-изомер басым (44,9-66,7%). Реакцияны 200 °С-тан жоғары температурада жүргізгенде тек п-гидроксибензой қышқылы о-гидроксибензой қышқылын қоспасыз түзеді.

Калийэтилкарбонат және натрийэтилкарбонат гидроксиарендердің (фенолдар мен оның туындылары) тиімді карбоксилдеуші реагенттері екендігі анықталды. Гидроксибензой және гидроксинафтой қышқылдарын синтездеудің негізгі өнеркәсіптік тәсілі бірқатар кемшілігі бар көміртегі диоксиді қысымымен (Кольбе-Шмидт реакциясы) сілтілі металдардың тиісті феноляттары мен нафтоляттарын карбоксилдеу болып саналады.

Гидроксиарендердің карбоксилдеу реакциясымен гидроксиароматикалық қышқылдарды және оның туындыларының алкил көмір қышқылының сілтілік тұзы арқылы алудың зертханалық регламенті әзірленді, ол «Мұнайхимиялық синтездер» курсы аясында зертханалық және тәжірибелік жұмыстарды жүзеге асыруда, сондай-ақ әл-Фараби атындағы ҚазҰУ химия факультетінің «Органикалық заттардың химиялық технологиясы» және «Мұнайхимия» мамандығы бойынша дипломдық және магистрлік жобаларды орындау кезінде оқу бағдарламасында қолдануға болады.

**Түйін сөздер:** карбоксилдеу, гидроксиарендер, гидроксибензой қышқылы, көмірқышқыл газы, калий этил карбонаты, п-гидроксибензой қышқылы.

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## КАРБОКСИЛИРОВАНИЕ ГИДРОКСИАРЕНОВ ЭТИЛКАРБОНАТОМ КАЛИЯ

**Аннотация.** Изучено влияние условий проведения реакции карбоксилирования фенола и его производных (продуктов нефтехимии) щелочными солями алкилкарбоновых кислот (калий этилкарбонат), легко синтезируемых из диоксида углерода, спиртов и гидроксидов щелочных металлов. Эффективные способы получения практически ценной п-гидроксибензойной кислоты и других гидроксибензойных кислот (класс соединений, обладающих широким спектром биологически активных свойств и других полезных свойств) актуальны. Разработанный способ синтеза гидроксибензойных кислот позволяет значительно быстрее, проще и дешевле оптимизировать большинство параметров (давление, температура, продолжительность реакции, соотношение компонентов реагирующих веществ) и максимально увеличить выход продуктов. Разработан новый простой и удобный метод синтеза п-гидроксибензойной кислоты по реакции карбоксилирования фенола с этилкарбонатом калия, который позволяет получить целевой продукт без примеси о-гидроксибензойной кислоты. Для максимального достижения цели и раскрытия проблем были выполнены следующие задачи: нахождение оптимальных параметров проведения реакции карбоксилирования гидроксиаренов и их производных металлалкилкарбонатами. Исследование параметров проведения реакции карбоксилирования гидроксиаренов щелочными солями алкилугольных кислот при различных давлениях, температурых, продолжительности реакции и при разных соотношениях реагентов. При достижении оптимальных параметров процесса ожидается повышение выхода целевых продуктов – гидроксиароматических кислот.

Впервые были найдены оптимальные условия для региоселективного п-карбоксилирования фенола (давление диоксида углерода, температура и продолжительность процесса), при котором выход п-гидроксибензойной кислоты составляет 71,0%, а также влияние различных заместителей в ароматическом кольце по выходу целевых продуктов карбоксилирования фенольных производных определяется карбонаты натрия и калия. Установлено влияние природы алкильных групп алкилкарбонатов калия на карбоксилирующую активность последних в реакции карбоксилирования фенола. Мы изучили, что температура сильно влияет на направление карбоксилирования фенола. При проведении реакции ниже 200 °С карбоксилирование протекает в о- и р-положениях с образованием о-гидроксибензойной и п-гидроксибензойной кислот; преобладает о-изомер (44,9-66,7%). При проведении реакции при температуре выше 200 °С образуется только п-гидроксибензойная кислота без примеси о-гидроксибензойной кислоты.

Установлено, что калийэтилкарбонат и натрийэтилкарбонат являются эффективными карбоксилирующими реагентами гидроксиаренов (фенолов и их производных). Основным промышленным способом синтеза гидроксибензойных и гидроксинафтойных кислот является карбоксилирование соответствующих фенолятов и нафтолятов щелочных металлов под давлением диоксида углерода (реакция Кольбе-Шмидта), имеющий ряд серьезных недостатков.

Разработали лабораторный регламент получения гидроксикарбоновых кислот реакцией карбоксилирования гидроксикарбоновых и их производных щелочными солями алкилкарбоновых кислот, который может использоваться в учебной программе при реализации лабораторных и практических работ в рамках курса «Нефтехимические синтезы», а также при выполнении дипломных и магистерских проектов по специальности «Химическая технология органических веществ» и «Нефтехимия» химического факультета КазНУ им. аль-Фараби.

**Ключевые слова:** карбоксилирование, гидроксикарбоны, гидроксикарбоновая кислота, диоксид углерода, этилкарбонат калия, п-гидроксикарбоновая кислота.

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