




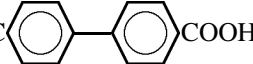
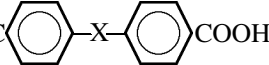
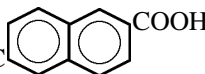
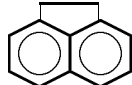
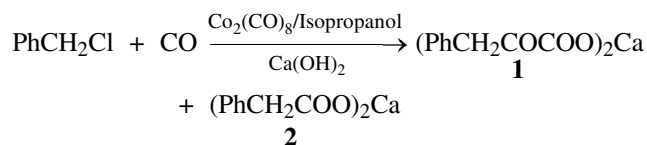


Table 1. Acids produced by the versatile process for carbonylation of organic halides

Product	Application
Fatty-aromatic and aliphatic acids	
X-C ₆ H ₄ CHR ₂ COOH X, R = Phenylacetic acid	Antibiotic precursor; used in production of dyes, optical brighteners, and fragrance compounds
X = <i>p</i> -OH, <i>o,p</i> ,-Cl; R=CH ₃	Production of pharmaceuticals
 α-Naphthylacetic acid	Heteroauxin plant growth stimulant; in pharmaceutical production
HOOCCH ₂  CH ₂ COOH <i>p</i> -Phenylenediacetic acid	Monomer in production of aviation oils and polymers
PhCH ₂ COCOOH Phenylpyruvic acid	In production of phenylalanine and synthetic sweetener, aspartame
CH ₂ (COOH) ₂ Malonic acid PhCH(COOH) ₂ Phenylmalonic acid	Intermediates in production of pharmaceuticals, vitamins, and dyes
Aromatic acids	
 <i>p</i> -Butylbenzoic acid (X = <i>p</i> -C ₄ H ₉) X = R, RO, RCO, R  , R 	} Liquid crystals and components of liquid-crystal systems
 4,4'-Diphenyldicarboxylic acid	
 X = O, SO ₂	} Monomers in production of highly heat-resistant liquid-crystal thermoplastics used in preparation of modern composites
 2,6-Naphthalenedicarboxylic acid	
 5,6-Acenaphthenedicarboxylic acid	Intermediate in synthesis of 1,4,5,8-naphthalenetetracarboxylic acid used in production of high-quality vat dyes (Vat Crimson 2Zh) and highly heat-resistant fibers

aliphatic (malonic) acids prepared by carbonylation of the corresponding halides by the above procedure are represented in Table 1.

Of particular interest is a modification of the method for carbonylation of benzyl chloride with calcium hydroxide in isopropanol serving as a base:



We found [2] that the product of double carbonylation of benzyl chloride (calcium phenylpyruvate) is formed in large amounts along with PAA under mild conditions (atmospheric CO pressure and 30–40°C) (Fig. 1). Phenylpyruvic acid can be used for preparing an important amino acid, phenylalanine, which is a precursor for production of a valuable sweetener, aspartame (Table 1).

Carbonylation of aromatic halides. It is known that, unlike fatty aromatic halides, nonactivated aryl halides do not enter into nucleophilic substitution. That is why, apparently, these compounds are not activated with the $\text{Co}(\text{CO})_4^-$ anion by the S_N2 mechanism under the conditions of benzyl chloride carbonylation.

First we activated more reactive aryl bromides and aryl iodides by oxidative addition of low-valent metal complexes [1]. We studied the preparation of acenaphthenedicarboxylic acid by carbonylation of 5,6-dibromoacenaphthene [3] under the conditions of phase-transfer catalysis by palladium halophosphine complexes. As determined by IR spectroscopy, the active catalytic species was the intermediate zero-valent palladium complex PdCOP_3 formed in the presence of carbon monoxide. The mechanism of this reaction was described in our previous paper [3]. It should be noted that palladium complexes have also been recently used to catalyze carbonylation of less active aryl chlorides with acceptor substituents. In this case, complex ligands (e.g., cyclohexyl-substituted ferrocenylphosphines) were developed to activate palladium [4]. However, these catalytic systems are difficultly available and expensive and can be used only for fine synthesis of small amounts of expensive compounds.

Although aryl halides are completely inactive in carbonylation catalyzed by cobalt carbonyl under ordinary conditions [in alcohols in the presence of bases (B)], the making possible use of cobalt carbonyl (the cheapest and the most available catalyst of oxo synthesis) in carbonylation of aryl halides is a very attractive practical and theoretical task.

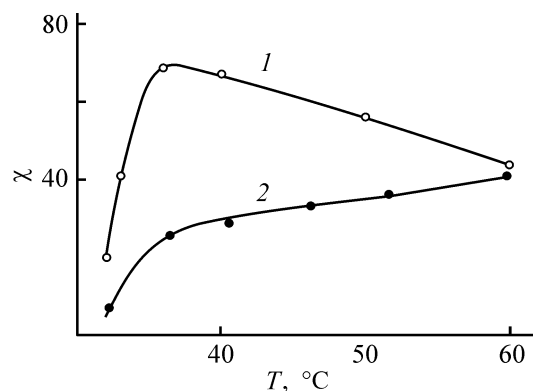
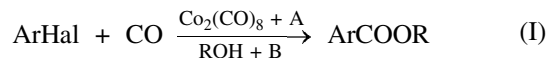


Fig. 1. Yield χ of (1) phenylpyruvic and (2) phenylacetic acids vs. temperature T ($P = 1$ atm).

Some alkylcobalt carbonyl complexes $\text{RCo}(\text{CO})_4$ formed in situ in the course of carbonylation of alkyl halides RX can catalyze carbonylation of low-active aryl halides [5]. In this case, alkyl halides are co-catalysts (A) (activators) of cobalt carbonyl in carbonylation of aryl halides. The reaction occurs under very mild conditions (CO pressure 1 atm, 60–65°C):



We have shown previously [2, 6] that the most reactive catalytic complex, $\text{PhCH}_2\text{Co}(\text{CO})_4$, is formed in the reaction with benzyl chloride as a cocatalyst [A, scheme (I)].

The results of a study of the catalytic effect of acceptor substituents on carbonylation of substituted bromobenzenes and of the inhibition of aryl halide carbonylation with one-electron acceptors (nitrobenzene, anthraquinone) [7] suggest the $S_{RN}1$ radical anion mechanism of aryl halide activation. The active catalytic species of carbonylation is the anionic complex $[\text{RCo}(\text{CO})_3\text{COOCH}_3]^-$ [5, 7] formed by nucleophilic attack of the methylate anion on the carbon atom of the carbonyl group of alkylcobalt carbonyl. The nucleophilic power of this complex is very high. Because benzyl chloride is also carbonylated under these conditions [scheme (I)], we determined the mode and rate of feeding the cocatalyst, benzyl chloride, to maintain the catalyst in the active form, thus providing an almost complete conversion [7]. The catalytic cycle of the reaction in the presence of benzyl chloride as a cocatalyst has been suggested and analyzed [7].

A series of practically significant aromatic acids was prepared for the first time by carbonylation in the presence of a new effective catalytic system, cobalt carbonyl–benzyl chloride–base, in methanol (Table 1). This catalytic system is the most suitable

Table 2. Main process parameters of carbonylation in the presence of benzyl chloride

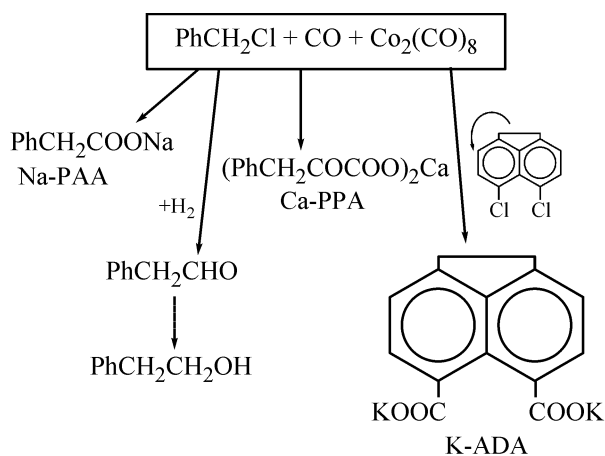
Product	Solvent	Base	CO pressure, atm	T, °C	Yield, %	By-product
Na-PAA	Methanol	NaOH	1–3	60–65	94–97	MBE*
Ca-PPA	Isopropanol	Ca(OH) ₂	1–5	35–40	75–85	PAA
K-ADA	Methanol	KOH	1–1.5	55–62	90–95	PAA

* MBE is methyl benzyl ether.

for synthesis of preparing acenaphthendicarboxylic acid (potassium salt K-ADA) by carbonylation of 5,6-dichloroacenaphthene. This acid is used for production of a valuable commercial product, 1,4,5,8-naphthalenetetracarboxylic acid (Table 1) [2, 8]. The technical documentation for this process was developed. A pilot batch of the product (50 kg) was produced for the first time by the carbonylation procedure and was tested in production of a valuable heat-resistant dye, Vat Crimson 2Zh.

Some implementations of the developed versatile process in carbonylation in the presence of benzyl chloride as both reagent and cocatalyst are shown in the scheme below. The process was tested in practice. The main process parameters are listed in Table 2.

The process for synthesis of a valuable aromatic compound, phenylethanol, an analog of rose oil, by carbonylation (hydroformylation) of benzyl chloride via intermediate formation of phenylacetaldehyde is also shown in the scheme.



To improve the efficiency of the catalytic system for carbonylation of aryl halides, we studied other cocatalysts of cobalt carbonyl. The main requirements to the cocatalyst are the low self-carbonylation rate and the absence of chlorine in their composition, to decrease the consumption of a base required for

halide binding. We developed new catalytic systems [7, 9, 10] containing ethylene chlorohydrin, olefin oxides, and epichlorohydrin as cocatalysts. The catalytic activity of these systems was higher by a factor of approximately 2 than that of the system containing benzyl chloride [7, 9]. These cocatalysts are not carbonylated under the reaction conditions but can undergo methanolysis, which, however, is insignificant in the presence of weak bases (B), alkali metal carbonates.

Epoxy cocatalysts are halogen-free compounds, and, hence, additional consumption of a base for halide binding is not required. The most available, low-cost, and convenient in use cocatalyst is propylene oxide. The mechanism of aryl halide carbonylation catalyzed by a cobalt carbonyl–epoxide system was analyzed in our previous paper [9].

Thus, cobalt carbonyl–epoxide–base system [9, 10] is a highly active and readily available catalytic system for selective carbonylation of aryl halides in a high (frequently quantitative) yield. This system, along with the catalytic system containing benzyl chloride as a cocatalyst, can be used as a highly efficient catalyst for both industrial production of many valuable products (Table 1) and fine laboratory synthesis [9]. This system is the most convenient for low-active substrates such as stable organic pollutants, polychlorobiphenyls [10].

A fundamentally new versatile process for synthesis of valuable industrial products by halide carbonylation was developed, based on the results of a study of new catalytic systems containing cobalt carbonyl. It should be noted that preparation of fatty-aromatic acids by carbonylation of the corresponding halides was described in [1], whereas the synthesis of aromatic acids is our original development.

A technological development of these processes showed that they can be performed using the same equipment. The preparation of the catalyst and carbonylation are performed with common units (Fig. 2). The units for feed preparation and isolation of the reaction products differ (depending on the properties

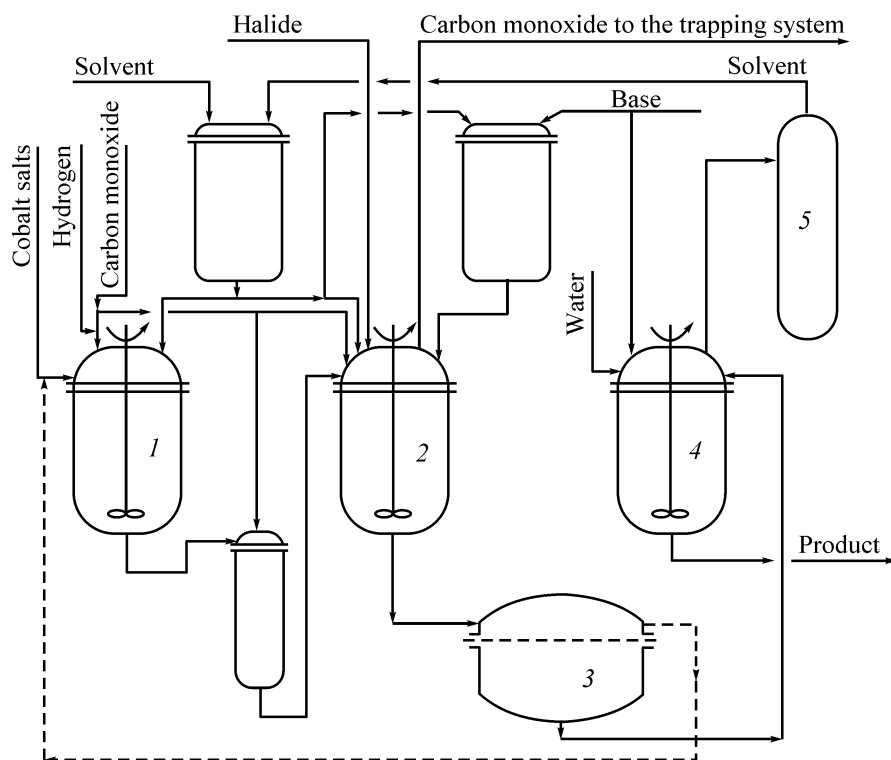


Fig. 2. Schematic of the installation for carbonylation of halides.

and aggregative state). The carbonylation is performed under mild conditions, which can be varied in a narrow range [CO pressure 1–5 atm, 35–70°C, alkali or alkaline-earth metal hydroxides and carbonates as bases, alcohols as solvents (we used methanol as the solvent in all processes except double carbonylation)]. To devise a process for synthesis of key products (fatty-aromatic and aromatic acids, namely, phenylacetic, penylpyruvic, and 5,6-acenaphthendicarboxylic acids) and thus the main units for the versatile process, we developed and fabricated an original pilot installation for carbonylation of halides [2] (Fig. 2). The installation consists of a reactor for preparing catalyst 1 (alcoholic solution of cobalt carbonyl), reactor for carbonylation 2, pressure filter 3 (product isolation step), reactor for hydrolysis 4, and collector of the solvent to be recycled 5. A pilot batch of the product in an amount of 10 to 50 kg was produced on this installation. The reactor volume is 100 l. The design productivity of the unit is 10 tons year⁻¹.

The aim of further studies is to broaden the range of compounds involved in the carbonylation, including, in particular, heteroaromatic compounds [pyridines, furans, thiophenes, polychlorobiphenyls (PCB)] and to develop processes for synthesis of new prod-

ucts and utilization of stable organic pollutants (PCB) [10] as highly heat-resistant industrial insulators and polybromodiphenyl ethers as fire-retardants.

EXPERIMENTAL

All laboratory carbonylation experiments were performed under atmospheric pressure of CO in temperature-controlled glass reactors under vigorous stirring in a CO flow. The experimental procedure was described in detail in [7]. The reaction products were analyzed by GLC, chromatography-mass spectrometry, and NMR spectroscopy, including 2D COSY spectroscopy, for identification of complex products.

The industrial process was developed using a 1-1 pressure vessel and the pilot unit described above (Fig. 2).

CONCLUSIONS

(1) Fatty-aromatic and aromatic carboxylic acids were prepared by carbonylation of the corresponding halides in alcohols in the presence of cobalt carbonyl as the catalyst and of bases under very mild conditions (CO pressure, up to 3 atm; temperature, up to 65°C).

(2) It was shown that the reaction is highly selective and occurs with a high yield. To carbonylate chemically stable aryl halides, benzyl chloride and epoxides were added as cocatalysts (promoters).

(3) A novel versatile and economically efficient process for producing a wide range of organic acids (mainly aromatic and fatty-aromatic carboxylic acids) and their derivatives by carbonylation of the corresponding organic halides was developed.

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