

Carboxylation of Aromatic Compounds in a Supercritical Carbon Dioxide Medium

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Abstract—The reaction of direct carboxylation of benzene and its derivatives PhX (X = Me, Br, Ph, OPh, OMe), as well as mesitylene, durene, and ferrocene, in a supercritical CO₂ medium in the presence of various Lewis acids (AlCl₃, FeCl₃, ZrCl₄, and ZnCl₂) is studied. It is shown that, in all cases, secondary reactions proceed faster than the primary reaction of carboxylic acid formation. For the thoroughly studied AlCl₃–CO₂–toluene system, optimal conditions of the formation of *n*-toluic acid are determined. For the AlCl₃–CO₂–benzene system, as an example, quantum-chemical calculations of the characteristics of the allowed pathways of the carboxylation reaction are performed.

Keywords: supercritical carbon dioxide, carboxylation, aromatic compounds, Lewis acids

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INTRODUCTION

Since the emergence of supercritical (SC) fluid technology and during its subsequent development, carbon dioxide has attracted the attention of researchers not only as an extremely convenient medium for performing reactions, but also as one of the most eco-friendly and safe reagents [1–3]. In implementing these technologies, of primary practical interest are processes unfeasible under normal conditions, i.e., those in which an excess of CO₂ and its physical characteristics, as both an SC medium and a synthetic reagent, would play a crucial role.

In this paper, we present results of a systematic study of the direct carboxylation of simple aromatic substrates in the presence of Lewis acids, for the first time performed in the supercritical carbon dioxide (SC–CO₂) medium. Using SC–CO₂ as a reagent and solvent, we hoped for positive kinetic and thermodynamic effects. A positive thermodynamic effect may arise due to a natural shift of equilibrium under the action of an excess of CO₂ in the direction of formation of the target products [4], i.e., carboxylic acids. A kinetic effect in an SC medium may arise due to the low viscosity, high rate of heat and mass transfer, and excess of SC–CO₂ compared to the other reactants and, consequently, a high rate of the target process. At the same time, it was clear that, the process of carboxylation may involve a variety of secondary reactions. Thus, it was necessary to investigate the reaction system as a whole, not limiting ourselves to analyzing only the direct carboxylation products.

To date, the only commercial process of direct carboxylation of aromatic compounds is the Kolbe–Schmidt reaction. Studies of the carboxylation of phenol in the SC–CO₂ reaction via the Kolbe–Schmidt reaction [5], as well as in the presence of bases [6] and Lewis acids [7], similar to ours, were recently performed by T. Yamaguchi and coworkers. They determined optimal conditions for the selective high-yield production of salicylic acid and demonstrated benefits of carrying out the reaction in SC–CO₂ in comparison with conventional methods.

The carboxylation of other aromatic substrates with CO₂ using electrophilic catalysis by various Lewis acids, although such studies have been performed, repeatedly [3, 8–11], starting with the pioneering work of Friedel and Crafts [12], has not yet become a preparative process. Most thorough detailed in this regard are two recent works on the carboxylation of aromatic hydrocarbons to carboxylic acids by carbon dioxide in the presence of Lewis acids, those by G.A. Olah and coworkers [13] and by P. Munshi and coworkers [14], in which the carboxylation of toluene in the CO₂–toluene two-phase system was extensively studied. It was shown that substituted benzenes undergo carboxylation, but, with the exception of toluene [14], the results were unsatisfactory because of rapid secondary reactions. All numerous attempts to find conditions that would ensure a favorable ratio between carboxylic acids, as target products, and the others organic compounds formed in the process have failed. The relative failures of the previous studies suggest that the problem lies in the reaction itself, its mul-

tistage nature and, above all, in the absence of means of inhibition of its separate stages.

EXPERIMENTAL

The carboxylation reactions studied were performed using commercially available reagents: aromatic compound and Lewis acids; where necessary, the reagents were dried by known methods [15]. The reactions were conducted out at 50–100°C and 120–210 atm in a stainless steel reactor with an internal volume of 70 cm³, equipped with a magnetic stirrer, thermocouple, and pressure gauge. The temperature in the reactor was maintained using a water bath. The amount of CO₂ introduced into the reactor was calculated using the program [16]. Each synthesis was carried out from one to four times.

Method for the Extraction of the Organic Products of the Carboxylation Reaction

After cooling the reactor, CO₂ was released, slowly passing through diethyl ether (DEE). The resulting solution was then used for extraction in processing the contents of the reactor. The contents of the reactor were poured onto ice, and the remainder was washed with a water–ice–DEE mixture. The mixture was acidified with concentrated hydrochloric acid (conc. HCl) to dissolve metal hydroxides formed by the hydrolysis of the corresponding salts (Lewis acids), and then extracted DEE thrice.

After filtration, the organic phase was extracted with 10% aqueous KOH. The resulting aqueous phase was treated with conc. HCl to pH 1, DEE was extracted, the organic layer was separated, dried over CaCl₂, and filtered, the solvent was distilled off, and the product was weighed and analyzed by the ¹H and ¹³C NMR methods. The organic phase separated after extraction with aqueous KOH was dried over CaCl₂, DEE was distilled, and the residue was weighed. Its further treatment depended on the aromatic compound (substrate) used.

In the case of benzene or toluene, the remaining oily product was subjected to further distillation to remove part of the aromatic hydrocarbons. After distillation in a vacuum, the resulting products were analyzed by the GC–MS, ¹H NMR, and ¹³C methods. The yield of the identified products was determined by integrating the signals in the ¹H NMR spectra and by relating it to the initial composition of the mixture.

In the case of mesitylene, ferrocene, bromobenzene, durene, biphenyl, diphenyl ether and anisole, the substance remaining after distillation of DEE was immediately subjected to analysis by the GC–MS, ¹H NMR, and ¹³C NMR methods. The yield was determined by integrating the signals in the ¹H NMR spectra.

The ¹H and ¹³C NMR spectra were recorded on a Bruker Avance-400 spectrometer. Chromato-mass-spectrometric analysis was performed on a

HEWLETT PACKARD 5890 SERIES II instrument. The separation of the sample was performed by gas–liquid chromatography in the temperature-programmed mode, from 90 to 240°C at 2 K/min. The separation was carried out on a silica capillary column, 20 m in length and 0.25 mm in internal diameter, with a stationary liquid phase SE; the carrier gas was helium.

The quantum chemical calculations were performed within the framework of the density functional theory (DFT) using the ab initio generalized gradient approximation, the PBE functional [17, 18], and the TZ2P basis, as implemented in the PRIRODA program [19, 20]. For all stable compounds and transition states, geometry optimization was carried out. The nature of the found stationary points (minimum or saddle points) was determined by calculating the eigenvalues of the matrix of second derivatives of the energy with respect to the coordinates of the nuclei. Whether the transition state belongs to a given transformation was established by calculating the reaction coordinate. To refine the values of the relative energy, the zero-point energy amendments was included.

RESULTS AND DISCUSSION

The initial aromatic reagents for the carboxylation reactions were compounds of different activities in electrophilic substitution reactions: benzene, toluene, mesitylene, durene, bromobenzene, biphenyl, diphenyl ether, anisole, and ferrocene. The Lewis acids were anhydrous AlCl₃, FeCl₃, ZnCl₂, and ZrCl₄. The compositions of the reaction mixtures and the ratios of the reagents are presented in Tables 1 and 2.

To check the phase state of the reaction mixtures, we performed calculations for the CO₂–toluene binary system using the NIST Thermophysical Properties of Hydrocarbon Mixtures Database Software Package (Version 2.01), which makes it possible to calculate the phase states of CO₂–hydrocarbon mixtures at a given mixture composition, temperature, and pressure. The calculated characteristics of the states of these mixtures with component ratios of 7 : 1, 9.4 : 1, 16 : 1, and 28 : 1 show that, under the synthesis conditions, systems exists in the state of SC fluid (Fig. 1).

We performed qualitative experiments to determine the SC–CO₂ solubility of aluminum chloride, used as a catalyst. According to the data obtained, AlCl₃ is insoluble in SC–CO₂, while the substrate–AlCl₃ complex formed dissolves in it.

As a model system, we selected AlCl₃–CO₂–toluene, since toluene is the most accessible reagent and, in addition, due to the presence of the methyl group, more reactive in the reactions of aromatic electrophilic substitution than benzene; AlCl₃ is a catalyst often used in the Friedel–Crafts reactions. While studying this system, we varied the AlCl₃–to-toluene ratio, temperature, and reaction time. This reaction produces toluic acid (in all cases, ~90%, in the form of

Table 1. Conditions of the experiments on the carboxylation of aromatic hydrocarbons in a SC–CO₂ medium

Run no.	Amount of substrate, mol	CO ₂ : Lewis acid : substrate molar ratio	Pressure, atm	Temperature, °C
Toluene				
1.1	0.065	22.3/0.6/1	180	70
1.2	0.066	19.4/0.6/1	180	70
1.3	0.066	22.3/0.6/1	180	70
1.4	0.066	22.3/0.6/1	180	70
1.5	0.066	22.3/0.6/1	180	70
1.6	0.040	37.9/1/1	180	70
1.7	0.022	66.3/2/1	180	70
Benzene				
2.1	0.051	39.3/0.1/1	140	50
2.2	0.046	30.8/2/1	170	70
Mesitylene				
3.1	0.047	37.9/1.22/1	180	70
Durene				
4.1	0.033	59.9/2/1	155	60
4.2	0.017	117.7/2/1	160	60
4.3	0.041	47.8/2/1	210	60

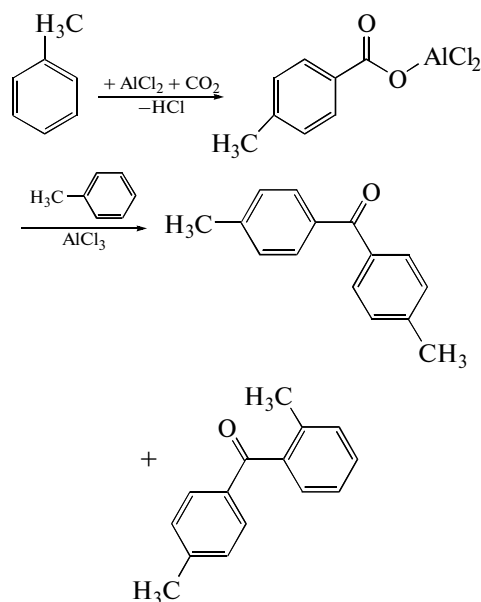
Table 2. Experimental conditions for the carboxylation of bromobenzene, biphenyl, diphenyl ether, anisole, and ferrocene in a SC–CO₂ medium

Run no.	Substrate and its amount, mol	CO ₂ : Lewis acid : substrate molar ratio	Pressure, atm	Temperature, °C
5	Bromobenzene 0.066	29.8/0.5/1	220	75
6	Biphenyl 0.010	201.8/1/1	170	60
7	Diethyl ether 0.020	99.7/2/1	210	70
8	Anisole 0.061	32.2/1/1	250	85
9.1	Ferrocene 0.0084	239.2/2/1	210	70
9.2	Ferrocene 0.0078	258.1/2.2/1	160	60

para-isomer) and the 2,4'-dimethylbenzophenone and 4,4'-dimethylbenzophenone isomers, as well as other minor products of their further acylation and condensation. The yield of the main product was found to be strongly dependent on the reaction conditions.

Table 3 presents the results of the experiments on toluene carboxylation, in which the greatest amount of acid was formed. Only the reaction time was varied, whereas the temperature, pressure, and the AlCl₃-to-toluene ratio remained constant. In all experiments (Tables 3–8), the product yield and degree of conversion were determined relative to the initial substrate.

In experiment 1.1 (Table 3), a variety of byproducts is formed, with 2,4'-dimethylbenzophenone and 4,4'-dimethylbenzophenone being predominant, according to ¹H and ¹³C NMR:



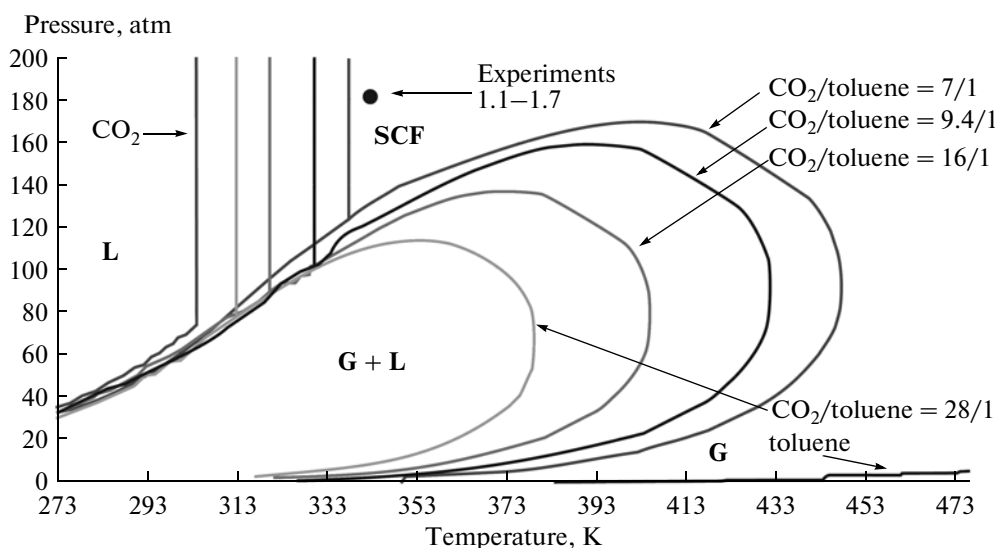


Fig. 1. Calculated phase diagram of the CO₂–toluene system at various CO₂–to–toluene ratios: 7 : 1, 9.4 : 1, 16 : 1, and 28 : 1; 273–473 K, 1–200 atm.

It can be concluded that the dependence of the yield of the acid on the reaction time passes through a maximum. The conversion of toluene is less than 100%, but increases with the reaction time. The highest yield of acid is observed at a reaction time of 12 h. With increasing reaction time, the yield of the acid decreases because it undergoes further transformations. Note that a similar time dependence was observed by the authors of [13] for the reaction in an excess of toluene, which served as a solvent.

Table 4 compares the efficiencies of various Lewis acids in toluene carboxylation. As might be expected,

Table 3. Experimental results on the carboxylation of toluene at different reaction times (70°C, 180 atm, AlCl₃–to–toluene molar ratio 0.6 : 1)

No.	Reaction time, h	Products and their yields		Conversion, %
		acid*	ketone	
1.2	4.5	10**	5	20
1.5	12	15	9	35
1.1	22	11	—	70

Notes: * The *p*-toluic acid–to–*o*-toluic acid ratio was 99 : 1.

** Small amounts of cresols were detected by ¹H and ¹³C NMR spectroscopies.

AlCl₃ is a more effective catalyst compared to FeCl₃, the use of which gives no satisfactory results.

Data on the carboxylation of toluene at various AlCl₃–to–toluene ratios are presented in Table 5. The highest yield of the acid was observed when toluene was taken in excess with respect to AlCl₃. Increasing the amount of AlCl₃ leads to an increase in the degree of conversion of toluene, but, at the same time, the yield of the acid reduces greatly, while the yield of ketones falls to zero. This is apparently due to further transformations of the acid into other products in the presence of an excess of AlCl₃. Ketones also undergo further transformations to heavier products, while AlCl₃ is effectively consumed by being bound to the reaction products.

We also investigated mesitylene and durene, alkyl-substituted benzenes that are more active than toluene in reactions of aromatic electrophilic substitution. In the case of durene, the reaction is complicated by the side process of intra- and intermolecular migration of the methyl groups. In this case, according to NMR spectroscopy, the main product was 2,3,4,6-tetramethylbenzoic acid. Small amounts of 2,3,5,6-tetramethyl-, 2,3,4,5,6-pentamethyl-, and 2,4,6-trimethylbenzoic acid were also present. Table 6 contains the results on durene carboxylation in the presence of AlCl₃, ZrCl₄, and ZnCl₂, the latter of which was inactive.

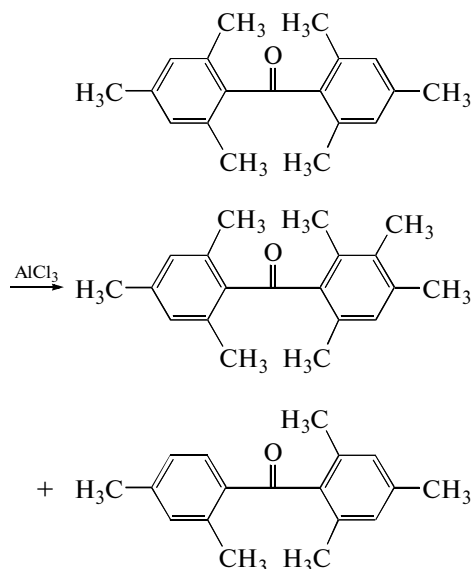
Table 4. Comparison of the effectiveness of AlCl₃ and FeCl₃ in toluene carboxylation (70°C, 180 atm)

No.	Lewis acid and the Lewis acid–to–toluene molar ratio	Reaction time, h	Products and their yields, %		Conversion, %
			acid	ketone	
1.5	AlCl ₃ 0.6/1	12	15	9	35
1.4	FeCl ₃ 0.6/1	11	0	Trace amounts	32

Table 5. Carboxylation of toluene at various AlCl_3 -to-toluene ratios (70°C, 180 atm)

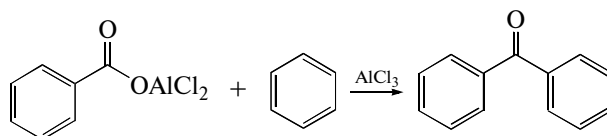
No.	Lewis acid-to-toluene molar ratio	Reaction time, h	Products and their yields, %		Conversion, %
			acid	ketone	
1.5	0.6/1	12	15	9	35
1.6	1/1	12	4	Trace amounts	40
1.7	2/1	12	1	Trace amounts	75

Table 7 compares the data on the carboxylation of toluene and mesitylene in the presence of AlCl_3 . The table shows that, the reaction with mesitylene is characterized by a higher degree of conversion in comparison with toluene. In addition, other reaction products are formed, including a significant amount of 2,2',4,4',6,6'-hexamethylbenzophenone, as demonstrated by ^{13}C NMR measurements. Analysis of organic products by GC–MS after separation of the acid showed that the mixture contains products of migration of methyl groups from one ketone molecule to another. One possible variant of this process can be described as

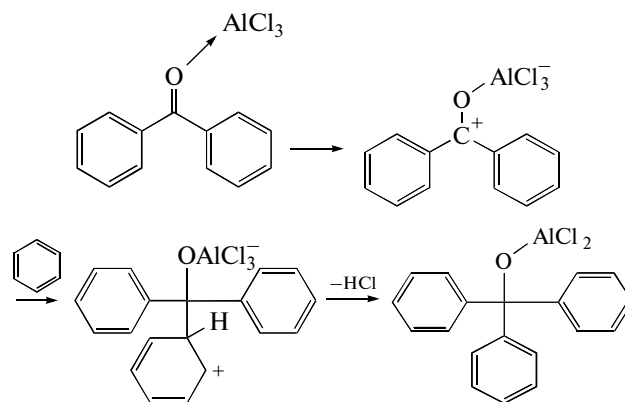


Two experiments were conducted on benzene carboxylation in the presence of AlCl_3 (AlCl_3 -to-benzene ratios of 0.1 and 2, 50–70°C, 140 and 170 atm); however, the yield of benzoic acid was close to zero at a degree of conversion of benzene of 20–57% (the acid

is detected only by mass spectrometry). The reaction products identified by GC–MS data were benzophenone, diphenylmethane, acetophenone, 9-H-fluoren-9-one, triphenylmethane, and triphenylcarbinol. Under these conditions, benzoic acid formed is almost completely consumed by the subsequent reaction with an excess of benzene to form benzophenone:



Benzophenone, acting as an arylating agent, reacts with benzene to form aluminum alkoxide, a predecessor of triphenylcarbinol:



Triphenylmethane is probably a product of the reduction of triphenylcarbinol. We can assume that diphenylmethane and 9-H-fluoren-9-one are products of benzophenone disproportionation. According to NMR data, the main reaction product is triphenylcarbinol, the yield of which is 41% with respect to the initial amount of benzene.

We also carried out experiments on the carboxylation of bromobenzene, biphenyl, diphenyl ether, anisole, and ferrocene—aromatic compounds with a lower activity in the reactions of aromatic electrophilic substitution than benzene (Table 8). It was shown that, under the specified conditions, bromobenzene and biphenyl do not react with CO_2 . In the case of biphenyl, no other substances except for the initial were found, but in the case of bromobenzene, ^1H and ^{13}C NMR measurements revealed small amounts of dibromobenzenes. Anisole, diphenyl ether, and ferrocene are electron-enriched aromatic systems, so the yield of

Table 6. Comparison of the effectiveness of various Lewis acids by the example of durene carboxylation (60°C, reaction time 10 h)

No.	Lewis acid and the Lewis acid to durene molar ratio	Pressure, atm	Acid yield, %	Conversion, %
4.1	AlCl_3 , 2/1	155	16	31
4.2	ZnCl_2 , 2/1	160	0	0
4.3	ZrCl_4 , 2/1	210	6	13

Table 7. Comparison of the carboxylation of toluene and mesitylene in the presence of AlCl_3 (AlCl_3 to substrate ratio 1 : 1, 70°C, 180 atm, reaction time 12 h)

No.	Substrate	Products and their yields, %		Conversion, %
		acid	ketone	
1.6	Toluene	4	0	40
3.1	Mesitylene	5	—	84

the acid is quite high for the last two. According to NMR spectra, in the case of anisole, the reaction mixture contains a significant amount of ring-methylated compounds. More specifically, under these conditions, the side reaction of O—Me bond cleavage occurs, leading to methylalumoxane-type compounds, known as active alkylating agents for aromatic systems.

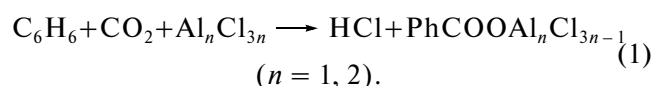
We also reproduced the reaction of carboxylation of phenol in the presence of K_2CO_3 in conditions close to those used in [6]. The degree of conversion of phenol (70%) determined by our method of extraction and analysis turned out to be comparable with that found in [6] using HPLC. However, in our case, the content of *p*-hydroxybenzoic acid in a mixture with salicylic acid was significantly higher (~40%).

Comparing the results of three works, present, [13], and [14], we can claim that, given the differences in the general procedure of the experiment (subcritical 57 atm and SC conditions, two-phase system (80°C, 70 atm)) and in the ways of treatment of the reaction mixtures, these studies generally show a sufficiently close agreement between the investigated parameters of the process. The results presented in the above papers reveal a common key factor that determines the ratio and composition of the products. This factor is the ratio between the rates of the first (direct carboxylation with formation arylcarboxylic acids) and the subsequent (the formation of ketones and carbinols from these acids) reactions. In most cases, the subsequent reactions are much faster than the first. Thus, the occurrence of the subsequent reactions greatly complicates the process of carboxylation, making it impossible to stop the reaction after the first stage. Nevertheless, this fact, on the one hand, does not exclude the possibility of optimizing the conditions for increasing the yield of carboxylic acids for each aromatic substrate and, on the other, opens up the prospect for the

development of methods of production of perhaps even more valuable synthetic secondary products.

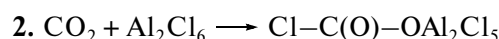
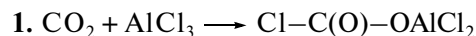
QUANTUM CHEMICAL CALCULATIONS OF THE REACTION OF BENZENE CARBOXYLATION

To interpret the results obtained, we performed quantum-chemical calculations (see Experimental) of the pathway of the reaction of benzene carboxylation using the PRIRODA software package:



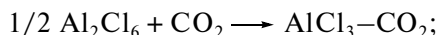
The choice of benzene as the simple model object for calculations was motivated by the fact that, despite the near-zero yields of benzoic acid during its carboxylation because of secondary processes, its formation in the first stage is obvious. The degree of conversion of benzene is only slightly lower than that of toluene (Tables 3 and 8). Therefore, we can hardly expect substantial differences in the calculation results for these two substrates.

It was found that the direct bonding of AlCl_3 to CO_2 and benzene is impossible. The reaction proceeds via the formation of a stable complex (semi-chloranhydride: a semi-salt of carbonic acid), which is then acylates benzene. Since aluminum chloride can exist in the reaction mixture as a monomer and as a dimer, we considered two pathways of conversion with their participation (Figs. 2 and 3, respectively):



Pathway **1** involves the AlCl_3 monomer (Fig. 2) and includes the following steps:

(1) the endothermic reaction of Al_2Cl_6 dissociation and the subsequent interaction with carbon dioxide, resulting in the formation of the $\text{AlCl}_3-\text{CO}_2$ complex (the activation energy of 52.0 kJ/mol corresponds to Al_2Cl_6 dissociation):

**Table 8.** Carboxylation of bromobenzene, biphenyl, diphenyl ether, anisole, and ferrocene

No.	Lewis acid, substrate, and molar ratio thereof	Temperature	Pressure, atm	Reaction time, h	Acid yield, %	Conversion, %
5	AlCl_3 , PhBr 0.5/1	75	220	9.5	0	51
6	AlCl_3 , Ph—Ph 1/1	60	170	10.5	0	10
7	AlCl_3 , Ph—O—Ph 2/1	70	210	9	20	48
8	AlCl_3 , PhOMe 1/1	85	250	8	5	51
9.1	AlCl_3 , $(\text{Cp})_2\text{Fe}$ 2/1	70	210	8.5	21	30
9.2	ZnCl_2 , $(\text{Cp})_2\text{Fe}$ 2.2/1	60	160	3.5	0	10

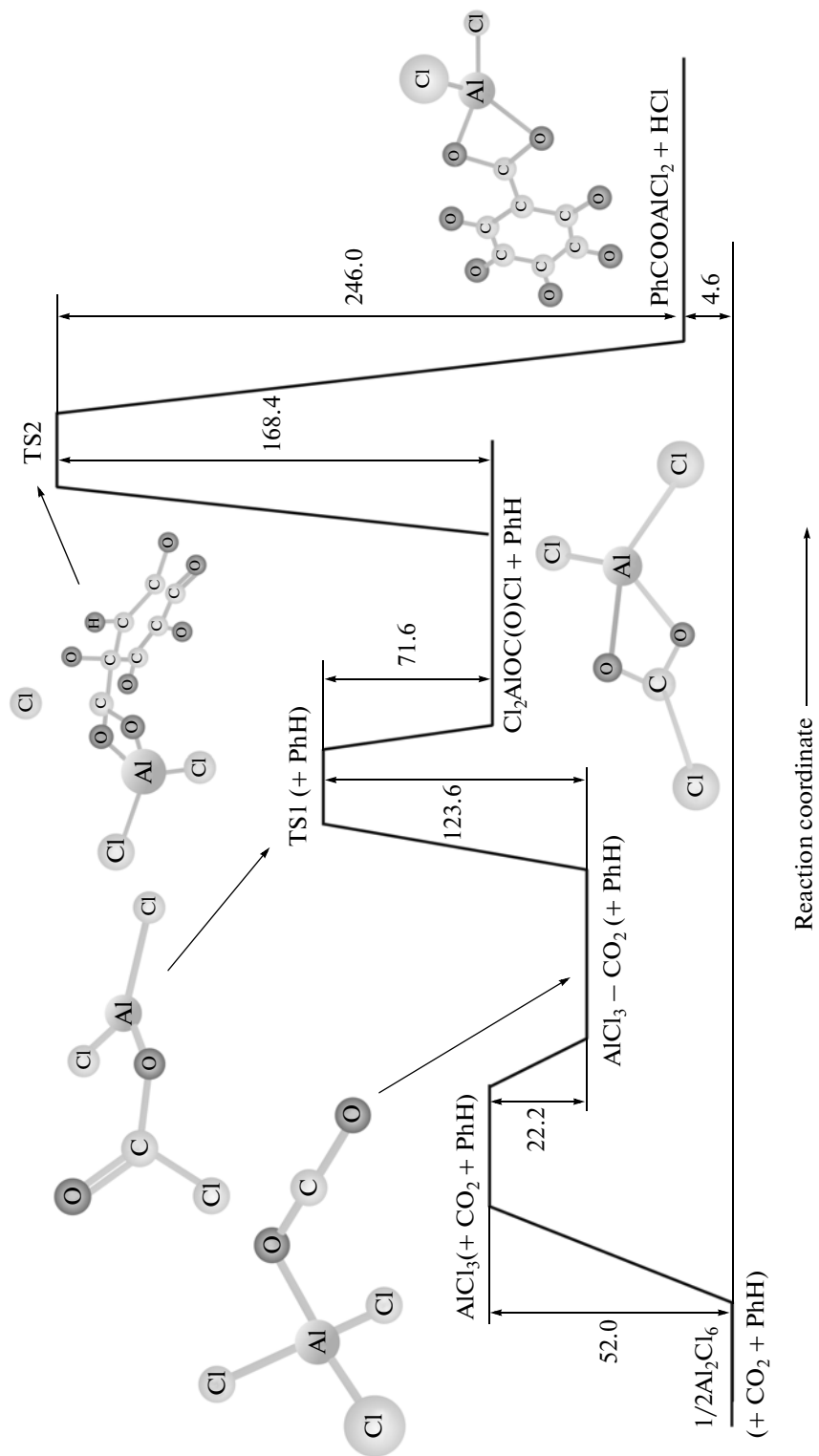


Fig. 2. Energy diagram of reaction (I) via pathway I; the activation energy, in kJ/mol.

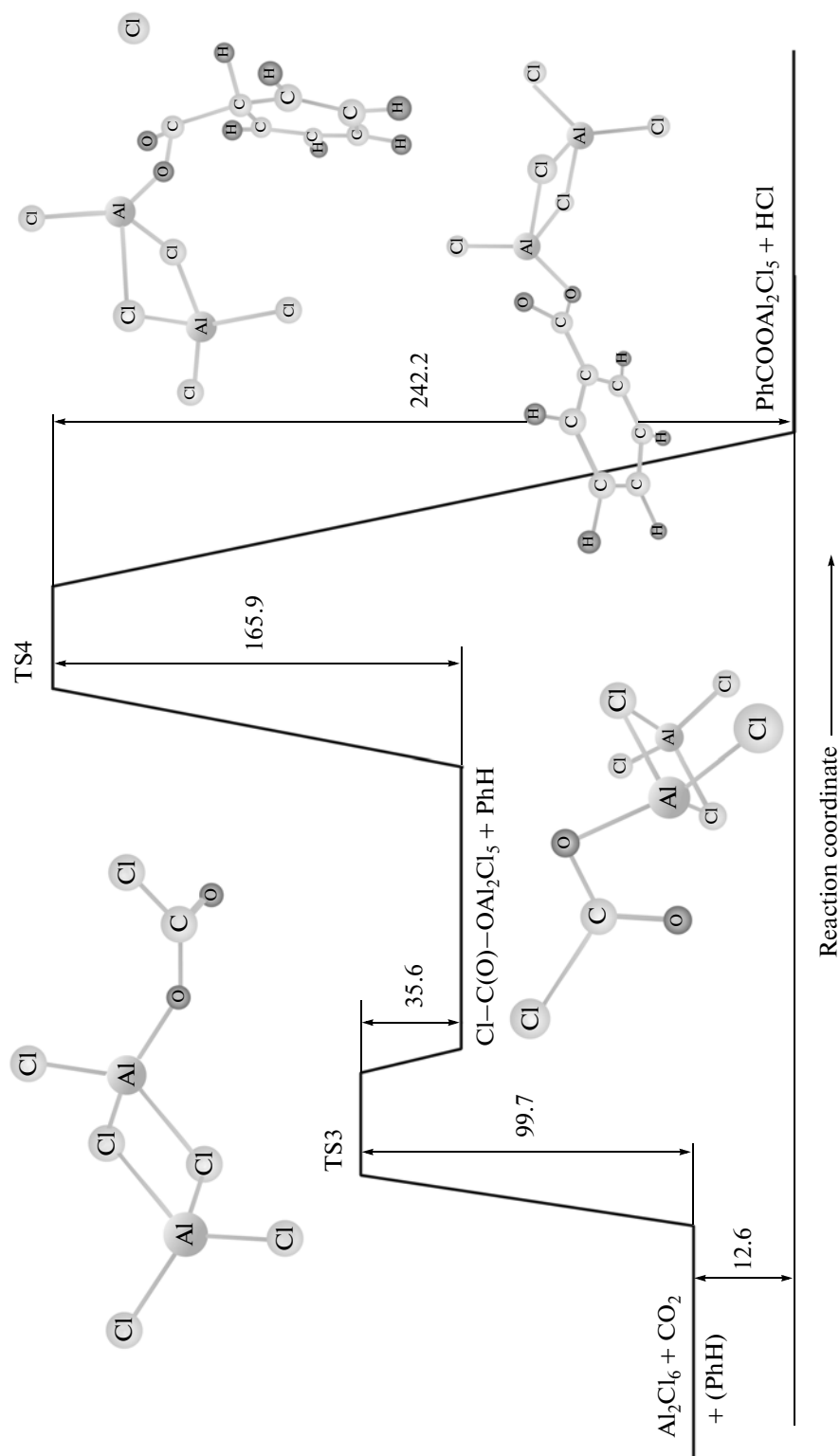
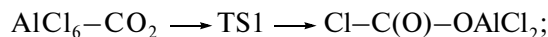
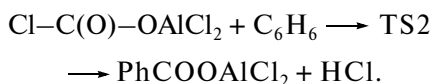


Fig. 3. Energy diagram of reaction (1) via pathway 2; the activation energy, in kJ/mol.

(2) the rearrangement of the $\text{AlCl}_3\text{--CO}_2$ complex into semi-chloranhydride of carbonic acid (a semi-salt) through transition state TS1 (with an activation energy of 123.6 kJ/mol):



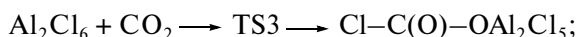
(3) the acylation of benzene by the semi-salt via transition state TS2 (with an activation energy of 168.4 kJ/mol) with the formation of HCl and a salt of benzoic acid in which the carboxylate anion plays the role of a chelating ligand:



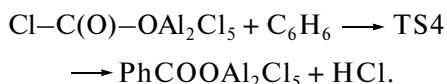
The overall result of the process is an endothermic (by 4.6 kJ/mol) transformation, with the limiting stage being benzene acylation (with an activation energy of 168.4 kJ/mol).

Pathway 2 involves the Al_2Cl_6 dimer (Fig. 3) comprises the following steps:

(1) the interaction of Al_2Cl_6 with CO_2 to form semi-chloranhydride (a semi-salt) via transition state TS3 (with an activation energy of 99.7 kJ/mol):



(2) the acylation of benzene with the semi-salt through transition state TS4 (activation energy 99.7 kJ/mol) with the formation of HCl and a benzoic acid salt:



The overall result of the process is an exothermic transformation (−12.6 kJ/mol), with the limiting stage being benzene acylation (activation energy 165.9 kJ/mol).

As is seen from the calculations, pathway 2 is characterized by energy release ($\Delta H = -12.6$ kJ/mol), whereas pathway 1, by energy consumption ($\Delta H = 4.6$ kJ/mol). This difference is due to a mismatch between the final states of the system accepted in the present calculation, i.e., due to the form (monomer or dimer) in which aluminum enters into the salt of benzoic acid. In both cases, these values are insignificant in comparison with the energy barriers.

CONCLUSIONS

A first systematic study of the reaction of simple aromatic compounds with SC- CO_2 , which simultaneously plays the role of a reaction medium and a reactant in the presence of various Lewis acids, is performed. The reaction occurs according to a complicated scheme, leading to a mixture of products, the composition and fractions of which depend on the initial substrate and process conditions, such as temperature, reagent ratio, and duration. The degree of conversion of aromatic compounds reaches 40–80%. The first stage of the reaction, producing an arylcarboxylic acid, is slow, with a little thermodynamic gain and a

large (up to ~160 kJ/mol, for example, for benzene) energy barriers. The acid, as a new electrophilic reagent, participates in further reactions, sequentially yielding ketones and carbinol. In the presence of alkyl substituents in the initial aromatic substrates, the parallel process of peralkylation takes place, which leads to the formation of homologues of the respective products and their regioisomers.

ACKNOWLEDGMENTS

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