
PEROXIDES-XI

Liquid-Phase Catalytic Oxidation of Methyl Derivatives of Biphenyl

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Abstract—Liquid-phase catalytic oxidation into acids by air was studied for the following hydrocarbons: isomers of cyclohexyltoluenes and cyclohexyl derivatives of *para*-xylene, mesitylene, pseudocumene, cyclopentyltoluene, cyclohexyladamantane, 4-methylbiphenyl, 2,4-, 2,5- and 3,4-dimethylbiphenyls, hydroxymethylbiphenyls, and hydroxymethylbenzenes. The oxidation of cyclohexyltoluenes involves a methyl group and proceeds without participation of the α -CH bond of the cyclohexyl fragment in the oxidative conversions. The reactivity of the hydrocarbons increases in the order *ortho* < *meta* < *para*. Consecutive conversions of the methyl groups to carboxyls occur during the oxidation of dimethylbiphenyls. In 3,4- and 2,5-dimethylbiphenyls, the methyl groups in the *para* and *ortho* positions, respectively, are first oxidized, whereas the reactivity of both of the methyl groups in 2,4-dimethylbiphenyl is virtually the same. The mechanism of the oxidation of hydroxymethylbiphenyls and hydroxymethylbenzenes involves the formation of an unstable cation radical, which is then stabilized by emitting a proton, giving hydroxybenzyl, a more stable radical.

Biphenylbenzoic and cyclohexylbenzoic acids are promising monomers for the production of composites, mesomorphic heat-resistant polymers, and substitutes of naphthenic acids [1]. Because of their outstanding strength and heat resistance, these materials are widely used in optoelectronics, instrument making, and the space industry. However, the above compounds are not commercialized in Russia or abroad. The known methods of their synthesis are multistep processes and suffer from low yields of desired products, high cost, and large auxiliary material consumption. The above disadvantages hinder, to a great extent, industrial implementation of these methods and, consequently, the production of materials that possess valuable properties and are necessary for the national economy.

This poses the challenging problem of developing efficient methods for producing various derivatives of cyclohexylbenzene and biphenyl containing alkyl, carboxyl, and hydroxyl groups.

The liquid-phase catalytic oxidation of cyclohexyl-substituted methylbenzenes (CHSMBs) is usable as an efficient method of synthesis of cyclohexylbenzoic acids (CHBAs). The substituted methylbenzenes can be obtained from readily available raw materials, namely, cyclohexanol and methylbenzenes. Note that the presence of two substituents (methyl and cyclohexyl groups) in the benzene ring of the CHSMB molecule makes it uncertain that the catalytic oxidation of CHSMB will selectively yield CHBA. Information on this route of CHBA synthesis was lacking in the literature when we began our research.

EXPERIMENTAL

Cyclohexyl-substituted methylbenzenes and phenols were synthesized by alkylation of methylbenzenes and phenols with cyclohexanol. The starting chemicals were toluene; *ortho*-, *para*-, and *meta*-xylenes; phenol; and *ortho*- and *para*-cresols (pure grade). The reactions were performed in a four-necked flask fitted with a stirrer, thermometer, reflux condenser, and an addition funnel. The starting hydrocarbon and sulfuric (or phosphoric) acid were charged into the flask, an appropriate amount of cyclohexanol was added over 1 h, and the mixture was left to stand at an appropriate temperature for 2–3 h. Next, the sulfuric acid layer was separated from the hydrocarbon layer in a separating funnel. The hydrocarbon layer was washed with distilled water until the washings were neutral and then was dried with calcium chloride. Finally, it was vacuum-distilled to obtain a product containing no less than 99.5% yield of the desired compound.

The synthesis of methylbenzenes, 2',5'-dimethyl-*para*-terphenyl, and methylbiphenylols was carried out by liquid-phase dehydrogenation of cyclohexyl-substituted methylbenzenes and phenols. The reaction was performed in a three-necked flask fitted with a refluxer and a thermometer. Appropriate amounts of a catalyst and a hydrocarbon were placed in a flask heated on a salt bath. The progress of the reaction was followed by measuring the hydrogen evolved. On completion of the process, the catalyst was filtered off and the reaction mixture was distilled in a vacuum. The resulting product contained no less than 99.5% desired compound.

Cyclohexyltoluenes oxidation rate constants

Compound	$k_1 \times 10^4, \text{s}^{-1}$	$k_2 \times 10^4, \text{s}^{-1}$
<i>ortho</i> -CHT	0.45	2.66
<i>meta</i> -CHT	1.20	2.42
<i>para</i> -CHT	1.92	5.41

Note: $T = 90^\circ\text{C}$; $P_{\text{O}_2} = 760$ Torr; the concentrations of cobalt acetate and acetaldehyde are 0.13 and 0.10 mol/l, respectively.

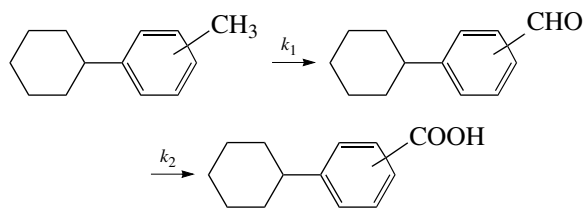
The oxidation of the cyclohexyl derivatives of toluene, methylbiphenyls, β -methylnaphthalene, and 2',5'-dimethyl-*para*-terphenyl was performed in a closed flow reactor. β -Methylnaphthalenes (pure grade) were used as starting compounds. Appropriate amounts of a hydrocarbon, catalyst components, and the solvent were placed into the reactor. The reaction mass was heated to a certain temperature, and oxygen was admitted into the reactor. The course of the reaction was followed by measuring the amount of oxygen consumed. The reaction time ranged from 1 to 3 h. On completion of the reaction, the mixture was cooled. The acid precipitate was filtered off, washed with water, and dried to constant weight.

The starting compounds and reaction products were analyzed by gas-liquid chromatography on an LKhM-72 chromatograph with a flame ionization detector and a 2-m-long column packed with Chromatone N loaded with 5% XE-60. The carrier-gas was nitrogen. Oven temperature was raised from 75 to 225°C at a rate of 13 K/min. Biphenylcarboxylic, *para*-terphenyl-2',5'-dicarboxylic, and 2-naphthalenecarboxylic acids were preliminarily esterified by diazomethane.

RESULTS AND DISCUSSION

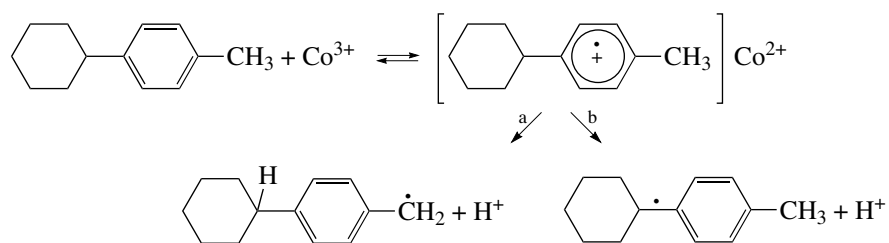
Ortho-, *meta*-, and *para*-CHBA were obtained in 93–98% yield by oxidation of cyclohexyltoluene (CHT) in acetic acid in the presence of a catalyst ($\text{Co}(\text{CH}_3\text{COO})_2 \cdot 4\text{H}_2\text{O}$, 0.13 mol/l) and an initiator (acetaldehyde, 0.1 mol/l) at a temperature of $85\text{--}95^\circ\text{C}$ [2].

The early stages of oxidation give an aldehyde, which is then converted to an acid. Based on experimental data, the process can be viewed as the following consecutive reactions:



The process can be described by a set of differential equations solvable for the rate constants (table). This calculation allows us to arrange the hydrocarbons examined in order of decreasing reactivity: *para*-CHT > *meta*-CHT > *ortho*-CHT.

The fact that the oxidation of CHT involves the methyl group without attacking the α -CH bond of the cyclohexyl fragment is inconsistent with the classical theory of the reactivity of alkyl groups in free-radical oxidation. It is probable that electron transfer from the hydrocarbon to the metal ion with the formation and subsequent stabilization of a cation radical takes place:



The stabilization of the cation radical can proceed by two routes. The deprotonation of the methyl group results in cyclohexylbenzoic acid.

The MO LCAO SCF AM I calculation of the geometry of the ground state and the cation radical for the model systems (*para*-cymene and *para*-ethyltoluene) confirms that the deprotonation of the CHT cation radical mainly involves the CH bond of the methyl group. Proton emission from the cation radical is possible under certain geometrical constraints [3].

The data on oxidation of other cycloalkyltoluenes (cyclopentyltoluene, adamantyltoluene, ditolyladamantane) show that the one-electron oxidation mechanism is common for these hydrocarbons.

Methylbiphenyl oxidation in acetic acid in the presence of a bromide-activated cobalt catalyst [4] was used as a basis in developing a synthetic procedure for biphenylcarboxylic acids (BPCAs). To optimize oxidation conditions, we studied, for 4-methylbiphenyl oxidation, the influence of temperature and the concentrations of the hydrocarbon, catalyst, and its components on the yield of 4-BPCA. The oxidation of methylbiphenyls (MBPs) at 90°C and a hydrocarbon concentration of 0.1–0.45 mol/l in the presence of cobalt acetate (1.86×10^{-2} mol/l), manganese acetate (1.86×10^{-3} mol/l), and sodium bromide (1.86×10^{-2} mol/l) produced 2-, 3-, and 4-BPCAs in 92–97% yield. The apparent rate constants of oxidation of 2-, 3-, and 4-MBPs were cal-

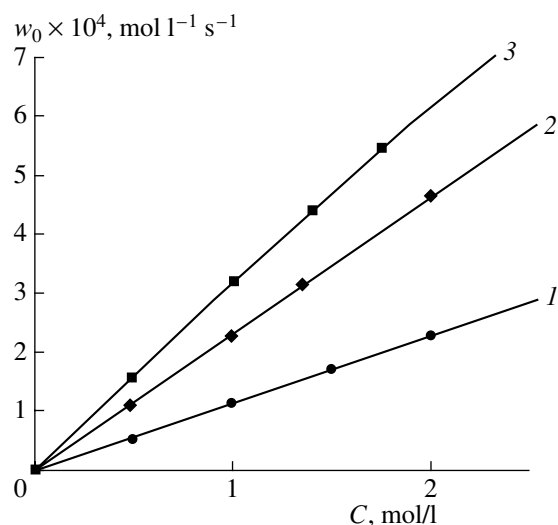


Fig. 1. Dependence of the initial oxidation rate of methylbiphenyls on their concentrations (C): (1) 2-MBP, (2) 3-MBP, (3) 4-MBP; $T = 90^\circ\text{C}$; [cobalt acetate] = 1.86×10^{-2} mol/l; [manganese acetate] = 1.86×10^{-3} mol/l; [sodium bromide] = 1.86×10^{-2} mol/l.

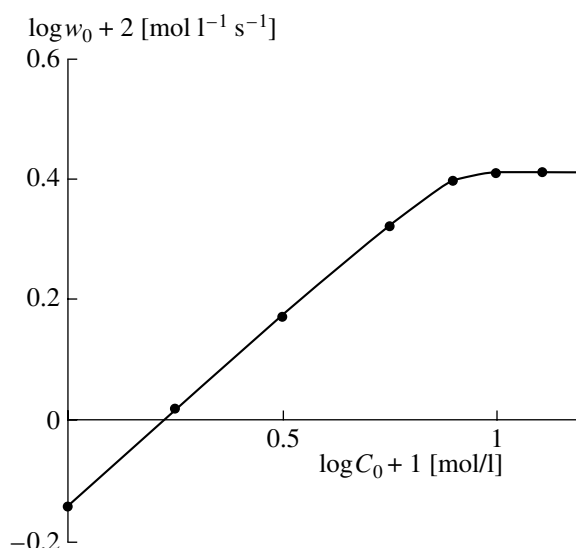
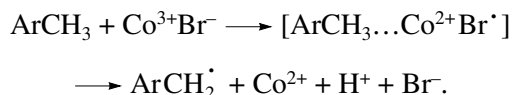


Fig. 2. Dependence of the oxidation rate of 3,4-dimethylbiphenyl on its initial concentration. $T = 95^\circ\text{C}$; [cobalt acetate] = 0.07 mol/l; [sodium acetate] = 0.01 mol/l.

culated from the concentration dependence of the initial rates of hydrocarbon oxidation. The reactivity of MBPs increases in the order *ortho* < *meta* < *para* [5].

Addition of the manganese salt to the cobalt–bromide catalyst causes a nonadditive increase in the overall rate of the oxidation; i.e., synergism shows itself. The effective activation energy of the reaction examined is 72.0 ± 3.0 kJ/mol. The observed first order reaction with respect to the cobalt salt, bromide ion, and the hydrocarbon testify that the initial step in the series of oxidative conversions, of the hydrocarbon is of catalytic nature:

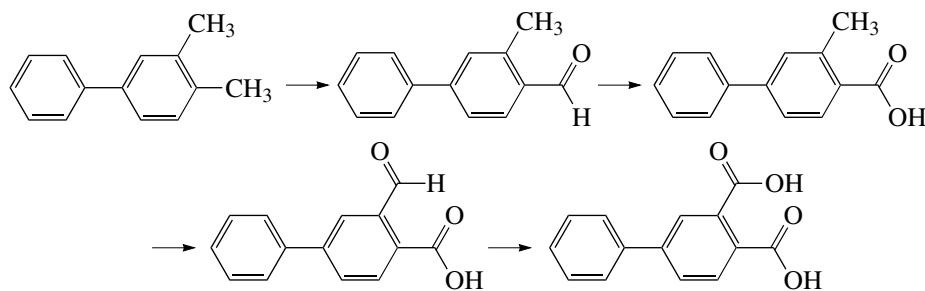


The change in the order of the reaction with respect to the bromide ion from 1 to 0 appears to be due to the

formation of the cobalt–bromide complex ($\text{Co}^{3+}\text{Br}^- \rightleftharpoons \text{Co}^{2+}\text{Br}^\cdot$). Introducing an excess of sodium bromide at a low cobalt concentration shifts this equilibrium to the right, and the oxidation rate becomes of the bromide concentration.

To optimize 3,4-dimethylbiphenyl (3,4-DMBP) oxidation conditions, we studied how the process depends on temperature and the initial concentrations of the hydrocarbon, catalyst, and its components. The oxidation of 3,4-DMBP at 95°C , an initial 3,4-DMBP concentration of 0.5–0.7 mol/l, and hydrocarbon : catalyst = (3–5) : 1 and cobalt acetate : sodium bromide = (5–7) : 1 molar ratios produced the corresponding dicarboxylic acid in >97% yield.

It was shown [6] that 3,4-DMBP oxidation proceeds by the consecutive oxidation of the methyl groups, giving aldehydes as intermediates, according to the scheme



The effective activation energy of the process is 71.0 ± 1.0 kJ/mol.

We determined the orders of the above reaction with respect to the hydrocarbon, cobalt salt, and bromide

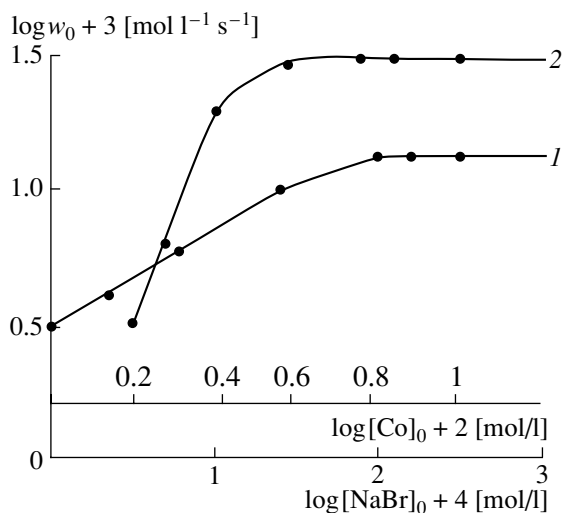


Fig. 3. Dependences of the oxidation rate of 3,4-dimethylbiphenyl on the initial concentrations of (1) cobalt acetate and (2) sodium bromide. $T = 95^\circ\text{C}$; [3,4-dimethylbiphenyl] = 0.07 mol/l; (1) [sodium bromide] = 0.01 mol/l; (2) [cobalt acetate] = 0.05 mol/l.

from experimental data (Figs. 2 and 3) and derived an expression for the oxidation rate:

$$w = k[\text{RH}]^{1\ldots 0}[\text{Co}^{2+}]^{1\ldots 0}[\text{Br}^-]^{1\ldots 0},$$

which agrees well with the oxidation rate equation for alkylaromatic hydrocarbons [7].

The conditions recommended for efficient 3,4-DMBP oxidation turned out to be unsuitable for the oxidation of 2,5- and 2,4-DMBPs. Therefore, we studied the oxidation of these compounds and found a catalytic system that allowed us to oxidize them by air in an acetic acid medium to obtain BPDCA.

The oxidation of 2,5- and 2,4-DMBPs also proceeds via the consecutive conversion of the methyl groups and aldehyde formation [8]. Note that, in the case of 2,5-DMBP, the methyl group in the *ortho* position relative to the benzene ring is initially oxidized and the *meta*-methyl group is subsequently involved in the reaction. In the 2,4-DMBP molecule, the reactivity of the methyl groups in the *ortho* and *meta* positions are similar. The fact that 2,5- and 2,4-DMBPs differ markedly in reactivity from 3,4-DMBP is explained in terms of electronic structure on the basis of NMR, IR, and UV spectroscopic data. The difference in reactivity between the methyl groups is consistent with the mechanism of free-radical oxidation, taking into account the effect of electron-donor substituents.

We found that the oxidation of 2,5- and 2,4-DMBPs at 95°C , an initial hydrocarbon concentration of 0.5–0.75 mol/l, and hydrocarbon : catalyst = (3–4) : 1, cobalt acetate : sodium bromide = (1–2) : 1, and cobalt acetate : manganese acetate = 1 : (90–100) ensured complete hydrocarbon conversion and 2,5- and 2,4-DMBP yields of 80–85%. Trimethylbiphenyl

and tetramethylbiphenyl were oxidized under similar conditions into the corresponding biphenyl polycarboxylic acids.

Based on our experimental data, we derived the following expression for the oxidation rate of 2,4- and 2,5-DMBPs

$$w = k[\text{DMBP}]^{1\ldots 0}[\text{Co}^{2+}]^{1\ldots 0}[\text{Br}^-]^{1\ldots 0}[\text{Mn}^{2+}]^{-0.4\ldots 0}.$$

The method of 5-methyl-2-biphenylol preparation from *para*-cresol and cyclohexanol (developed by us previously [9]) is a real prerequisite to the production of hydroxybiphenylcarboxylic acid (HBPCA), which contains hydroxyl and carboxyl groups in a benzene ring. To obtain derivatives of biphenyl with hydroxyl and carboxyl groups in different phenyl rings, we proposed using 3,4'-dimethyl-4-biphenylol and 4'-methyl-4-biphenylol [10].

Our HBPCA synthesis method is based on the oxidation of methylbiphenylols in acetic acid in the presence of the cobalt catalyst activated by manganese, zirconium, and bromine compounds. To optimize oxidation conditions, we studied how the acid yield depends on temperature and the concentrations of biphenylol, the catalyst, and its individual components.

The oxidation of methylbiphenylols at $105\text{--}110^\circ\text{C}$ and a hydrocarbon concentration of 0.1–0.5 mol/l in the presence of cobalt acetate (0.05–0.1 mol/l), manganese acetate (0.003–0.01 mol/l), and sodium bromide (0.1 mol/l) gave HBPCA in a yield ranging from 80 to 90% upon complete methylbiphenylol conversion.

The following is common for methylbiphenylol oxidation: the necessity for shielding of the hydroxyl group by acylation with acetic anhydride and the conversion of the methyl group to carboxyl via intermediate formation of an aldehyde.

The fact that the reaction is first-order with respect to the cobalt salt, bromide, and biphenylol testifies that the initial stage of oxidation is dominated by the catalytic route involving the substrate in oxidative conversions by one-electron transfer. The rate-limiting step in the process is electron transfer from the oxidized substrate to the ion of the metal in the highest oxidation state with the formation of an unstable cation radical, which is stabilized through proton emission, resulting in hydroxybiphenylmethyl, a more stable radical. The latter reacts with oxygen to form an aldehyde, which finally converts to an acid.

We showed that, in the liquid-phase catalytic oxidation of methylbiphenylols and *ortho*- and *para*-cresols under the above conditions, the CH_3 group in the *ortho*-position with respect to the hydroxyl group was not oxidized. This phenomenon appears to be due to the different stabilities of the resulting cation radicals (methylbiphenylol and *ortho*-cresol cations, respectively) [11].

The features of the oxidation of methylcyclohexylbenzenes, methylbiphenyls, and dimethylbiphenyls were taken into account in studies of the oxidation of

β -methylnaphthalene (MN) and 2',5'-dimethyl-*para*-terphenyl (2',5'-DM-*p*-TP) to the corresponding carboxylic acids.

To optimize MN oxidation conditions, we studied the effect of various factors (temperature, initial hydrocarbon concentrations, and components of the cobalt-bromide catalyst) on the yield of 2-naphthalenecarboxylic acid. The optimum conditions ensuring complete hydrocarbon conversion and a 2-naphthalenecarboxylic acid yield as high as 90–95% are the following: $T = 105^\circ\text{C}$, $[\text{MN}]_0 = 0.6 \text{ mol/l}$, $[\text{cobalt acetate}] = 0.15 \text{ mol/l}$, $[\text{manganese acetate}] = 0.001 \text{ mol/l}$, and $[\text{sodium bromide}] = 0.01 \text{ mol/l}$.

The orders of the reaction with respect to MN, cobalt and manganese salts, and bromide were derived from the kinetic data obtained. The oxidation rate equation can be written as follows:

$$w = k[\text{MN}]^{1...0}[\text{Co}^{2+}]^{1...0}[\text{Br}^-]^{1...0}[\text{Mn}^{2+}]^{-0.4...0}.$$

In deciding on the regime of 2',5'-DM-*p*-TP oxidation, the conditions of the efficient oxidation of 2,5-DMBP [12] were taken into account.

It was found that the oxidation of 2',5'-DM-*p*-TP at 95°C , the initial hydrocarbon concentration 0.25 mol/l , and the molar ratios hydrocarbon : catalyst = (3–5) : 1, cobalt + manganese acetates : sodium bromide = 1 : 1 produced *para*-terphenyl-2',5'-dicarboxylic acid in 75–80% yield upon the complete conversion of the original hydrocarbon.

The oxidation of 2',5'-DM-*p*-TP proceeds via the consecutive oxidation of the methyl groups and the formation of aldehydes as intermediate products.

The orders of the reaction with respect to the hydrocarbon, cobalt and manganese salts, and bromide were determined from experimental data. The rate of 2',5'-DM-*p*-TP oxidation is described by the equation

$$w = k[2',5'\text{-DM-}n\text{-TP}]^{1...0}[\text{Co}^{2+}]^{1...0}[\text{Br}^-]^{1...0}[\text{Mn}^{2+}]^{-0.4...0}.$$

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