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Mechanism of the Catalytic Carbonylation of Aryl Halides with a Modified Cobalt Carbonyl

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Abstract—Investigation of the mechanism of the carbonylation of aryl halides in a catalytic system consisting of cobalt carbonyl, terminal olefin oxide, and base showed that this catalytic system activates aryl halides via a radical anion mechanism. The kinetic regularities of the process together with IR spectral data suggest reversible formation of the active catalytic complex under the reaction condition. The complex is a cyclic metal lactone, and it can form not only from olefin oxide but also from its methanolysis product, the corresponding glycol monomethyl ether.

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Carbonylation of aryl halides with a modified cobalt carbonyl catalyst has been known since mid-1980s [1, 2]. The catalytic system consisted of alkylcobalt carbonyl complexes $RCo(CO)_4$ synthesized prior to reaction or formed in situ from alkyl halide (activator) and $Co_2(CO)_8$, and bases (sodium or potassium alkoholates or hydroxides) in aliphatic alcohols at an atmospheric pressure of CO and temperatures of 50–60°C (Scheme 1).

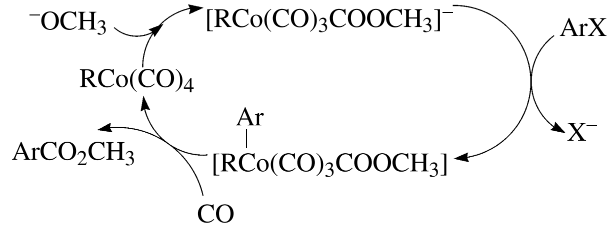
Scheme 1.

$$ArHlg + CO + CH_3O^- \xrightarrow{RCo(CO)_4} ArCOOCH_3 + Hlg^-,$$

$$Co(CO^-)_4 + RX \xrightarrow{\text{in situ}} RCo(CO)_4 + X^-.$$

We established that benzyl chloride is the best activator among the alkyl halides studied [3]. In the cited works, the formation of methyl arenecarboxylates was described by the mechanism shown in Scheme 2. It was also [3] shown that the stage of aryl halide activation is radical anion in nature.

Scheme 2.



The disadvantage of benzyl chloride as an activator is that in itself undergoes carbonylation to form phenylacetic acid as a by-product (Scheme 3).

Scheme 3.

$$PhCH_2Cl + CH_3O^- + CO \xrightarrow{Co(CO)_4^-} PhCH_2COOCH_3 + Cl^-.$$

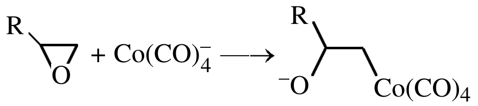
This fact prompted us to search for another activator which is not carbonylated under the reaction conditions. In 1994, a new catalytic system was found in which olefin oxides served as activators [4] (Scheme 4).

Scheme 4.

$$ArHal + CO + CH_3O^- \xrightarrow[\text{}]{Co(CO)_4^-} ArCOOCH_3 + Hal^-.$$

This system was shown to bypass the benzyl chloride catalytic system in efficiency. Cobalt carbonyl is activated here by ethylene oxide or olefin oxides with one alkyl substituent. The catalyst is evidently activated due to the formation of an alkylcobalt carbonyl complex described earlier in [5] (Scheme 5).

Scheme 5.



Propylene oxide was found to be the most accessible, cheap, and convenient in operation [6].

The new catalytic system was successfully used for preparing various aromatic mono- and dicarboxylic acid, such as 4-butylbenzoic, biphenyl- and oxybiphenyl-4,4'-dicarboxylic, and naphthalene-2,6-dicarboxylic acids. The reaction is extremely selective, and the yield of carboxylic acids achieves 95–99% (on the aryl halide conversion basis) [6]. This catalytic system was also employed for solving the ecological problem of dechlorination of polychlorobiphenyls (PCBs) which are wide-spread highly thermoresistant dielectrics presently related to dioxin-like persistent organic pollutants. Carbonylation of specially synthesized model PCBs with 3 or 4 chlorine atoms showed that they all are actively carbonylated under the considered conditions, forming various polychlorobiphenylcarboxylic acids. As a result of these investigations, a new technique for PCB utilization under mild conditions with accessible catalytic systems was suggested [7].

At the same time, despite the evident applied significance of this catalytic system, the mechanism of aryl halide activation and the nature of the catalytic complex still remain completely unexplored. The goal of the present work was to study the mechanism of the carbonylation of aryl halides in a catalytic system comprising cobalt carbonyl, a terminal olefin oxide, and a base, for its most effective application.

To solve this task, it was necessary to elucidate whether the regularities found earlier for the catalytic system on the basis of benzyl chloride are fulfilled with olefin oxides as activators or this system works in an absolutely different way.

First of all we checked the supposition that the radical anion mechanism of the aryl halide activation stage, operative in the catalytic system on the basis of benzyl chloride system, is preserved in the catalytic system on the basis of propylene oxide. To this end, the method described in [3] was used. We compared the activity of the catalytic system in hand on an example of the carbonylation of 1-bromonaphthalene both under standard conditions and in the presence of the one-electron acceptor nitrobenzene. In the first case, the conversion of the starting substrate in 2 h was 76%, while in the second case this reaction did not proceed at all. These findings provide evidence for a radical anion nature of the stage of aryl halide activation, which coincides with the mechanism described for the systems with alkyl halides as activators [3].

Further we studied the electronic effect of substituents in the aromatic ring of aryl halide on the carbonylation rate. We measured the relative carbonylation rate constants $k_{\mathrm{rel}} = k_X/k_H$ for various substituted bromobenzenes in the propylene oxide catalytic system. As substrates were used C_6H_5Br (σ 0), p-$CH_3C_6H_4Br$ (σ –0.17), p-$CH_3OC_6H_4Br$ (σ –0.27), p-ClC_6H_4Br (σ 0.227), p-$CH_3COC_6H_4Br$ (σ 0.502), m-$CF_3C_6H_4Br$ (σ 0.43), and p-CNC_6H_4Br (σ 0.66).

The effect of substitution in this case obeys the Hammett equation $\log k_{\mathrm{rel}} = \rho\sigma$. The reaction parameter ρ is 1.93 ± 0.17, and the correlation coefficient is 0.982.

Earlier for the catalytic system on the basis of benzyl chloride we found that the relative reactivity of *meta*- and *para*-substituted bromobenzenes nicely correlate with the σ constants of substituents in the aromatic ring [3]. Therewith, the reaction parameter ρ is equal to 1.8, i.e. electron-acceptor substituents accelerate the reaction.

Thus, for the catalytic system based on propylene oxide we observed certain regularities characteristic of the system with benzyl chloride as an acceptor, namely, the radical anion mechanism of the stage of aryl halide activation and acceleration of the reaction by electron-acceptor substituents in the benzene ring. These facts suggest similar mechanisms of the carbonylation of aryl halides in the considered systems.

At the same time, a comparative study of the two catalytic systems revealed significant differences. Thus, for example, the time dependence of aryl halide conversion in the propylene oxide system was studied. The substrate was 1-bromonaphthalene. The resulting data are shown in Fig. 1.

Since propylene oxide is not carbonylated under the reaction conditions, we expected that after the induction period the concentration of the catalytic complex would remain constant, and the reaction would be pseudo-first order in aryl halide. As shown in Fig. 1, the activity of the catalytic system strongly decreases with time, and a 100% conversion is not achieved. When the resulting data are represented as a plot of $\ln(C_0/C)$ vs. time (Fig. 2), it becomes obvious that the whole carbonylation process cannot be described by a single first-order kinetic equation.

The plot of $\ln(C_0/C)$ vs. time can be divided into three portions (Fig. 2). In portion I, the experimental

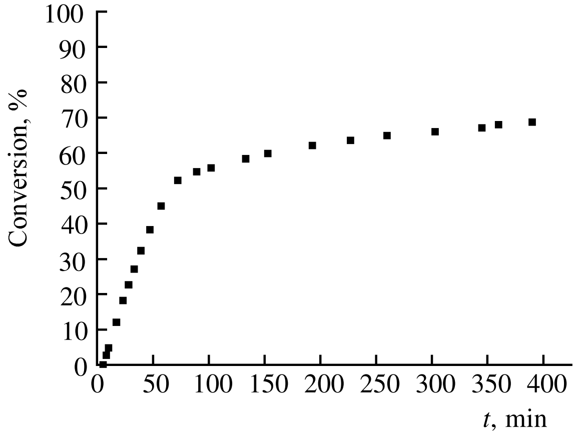


Fig. 1. Dependence of 1-bromonaphthalene conversion on time. *T* 62°C, p_{CO} 1 atm, C_0 [$Co(CO)_4^-$] 0.01 M, and 1-bromonaphthalene: $Co(CO)_4^-$: propylene oxide molar ratio 12 : 1 : 24.

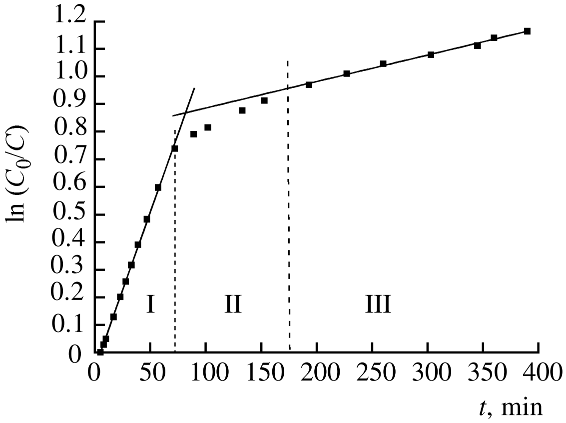


Fig. 2. Dependence of ln(C_0/C) for 1-bromonaphthalene on time. *T* 62°C, p_{CO} 1 atm, C_0 [$Co(CO)_4^-$] 0.01 M, and 1-bromonaphthalene: $Co(CO)_4^-$: propylene oxide molar ratio 12 : 1 : 24.

data are best approximated by a straight line described by the equation $\ln(C_0/C) = k_{obs}t + A$ [k_{obs} $(1.13 \pm 0.01) \times 10^{-2}$ min^{-1}, A $(-5.9 \pm 0.5) \times 10^{-2}$, R 0.9994]. Here the carbonylation reaction is described by the first-order kinetic equation. In portion II, the reaction rate decreases sharply until the curve achieves a plateau (portion III) where the reaction again obeys the first-order equation. In portion III, the experimental data are well approximated by a straight line described by the equation $\ln(C_0/C) = k'_{obs}t + A'$ [k'_{obs} $(9.6 \pm 0.3) \times 10^{-4}$ min^{-1}, A' 0.79 ± 0.01, R 0.9968].

Figures 1 and 2 show that the induction period which is necessary for the catalytic complex to form is really observed. Its duration can be found from Fig. 2: $t_{ind} = -A/k_{obs} = 5$ min. This time is not too long compared to the total reaction time.

The fact that the activity of the catalytic system decreases with time was also observed for the system on the basis of benzyl chloride [3]. In this system, the reaction stopped completely in 2–3 h because of the decomposition of the benzylcobalt carbonyl catalytic complex due to the side activator carbonylation reaction. However, this explanation is not good enough for the observed dependence of substrate conversion on time, because olefin oxides do not undergo carbonylation under the mentioned conditions. To explain the observed phenomenon, it was necessary to study reactions that occur in the catalytic system in the absence of aryl halides. Since propylene oxide is a volatile substance, for determination of the activator concentration in solution by GLC it was desirable to use higher boiling olefin oxides. We compared various olefin oxides as activators in the aryl halide carbonylation reaction. 1-Chloronaphthalene and 1,3,5-trichlorobenzene were used as model compounds.

Below are given data on the effect of the nature of olefin oxide on the conversion of 1-chloronaphthalene and 1,3,5-trichlorobenzene at 60°C, p_{CO} 1 atm, C_0 [$Co(CO)_4^-$] 3×10^{-2} M, 1-chloronaphthalene: $Co(CO)_4^-$: epoxide molar ratio 7.5 : 1 : 5, reaction time 1 h; 1,3,5-trichlorobenzene: $Co(CO)_4$-epoxide molar ratio 7.5 : 1 : 10, reaction time 2 h.

Olefin oxide	Conversion of 1-chloronaphthalene, %	Conversion of 1,3,5-trichlorobenzene, %
Propylene oxide	71	30
Hex-1-ene oxide	70	30
Oct-1-ene oxide	70.5	30.5

The presented data show that the length of the alkyl substituent in olefin oxide has no effect on the catalyst activity. In further investigations we used oct-1-ene oxide.

To check the contention of Heck [8] that olefin oxides are impossible to carbonylate under the above conditions, we studied the reaction of oct-1-ene oxide with methanol in the presence of cobalt carbonyl and potassium carbonate in a CO atmosphere (p_{CO} 1 atm). It was shown that the reaction produces a mixture of isomeric products of oct-1-ene oxide methanolysis, namely, 1-methoxyoctan-2-ol and 2-methoxyoctan-1-ol, in a 5 : 1 ratio (Scheme 6).

The rate constant of oct-1-ene oxide methanolys at 60° in the presence of potassium carbonate (0.3 M) as

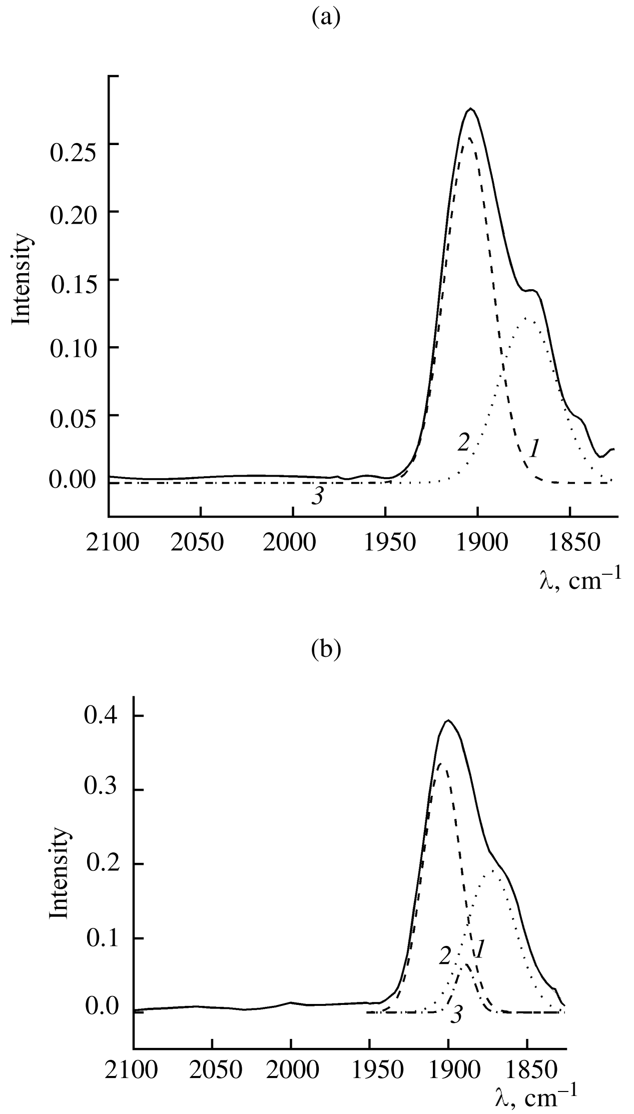
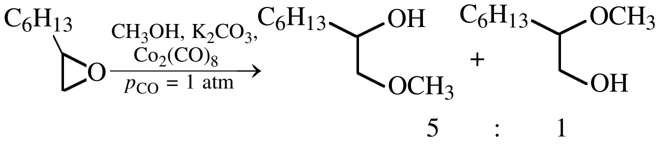


Fig. 3. IR spectra of the solution of potassium tetracarbonylcobaltate in isopropyl alcohol: (a) before addition of propylene oxide, C_0(Co) 0.018 M; (b) after addition of propylene oxide, C_0(Co) 0.018 M, propylene oxide : Co(CO)$_4^-$ 50 : 1. (*1* and *2*) Gaussian components of the C=O absorption band of tetracarbonylcobaltate anion in the absence of propylene oxide and (*3*) absorption band of the resulting alkylcarbonylcobalt complex.

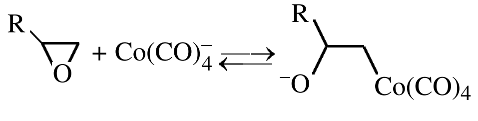
a base was found to equal 3×10^{-1} s^{-1}. Products of oct-1-ene oxide carbonylation were not found even in trace amounts. Thus, we obtained evidence against self-carbonylation of oct-1-ene oxide under the considered conditions. Therefore, we had to look for another reason for the decomposition of the catalytic complex.

Scheme 6.



We suggested that the reaction between olefin oxide and tetracarbonylcobaltate anion to form cobalt hydroxyalkyltetracarbonyl complex is reversible (Scheme 7).

Scheme 7.



This suggestion seems quite reasonable, because in protic solvents cobalt hydrotetracarbonyl HCo(CO)$_4$ is a strong acid, and, therefore, tetracarbonylcobaltate anion can act both as a nucleophile and as a leaving group.

Formation of the catalytic complex on the reaction of a preliminarily prepared potassium tetracarbonylcobaltate with propylene oxide was studied by means of IR spectroscopy. To exclude the possible nucleiophilic attack of the complex by methoxide anion, described in [9], isopropyl alcohol was used as a solvent instead of methanol. On addition of a 50-fold molar excess of propylene oxide to a solution of KCo(CO)$_4$ in a CO-purged isopropyl alcohol at 60°C (followed by cooling to room temperature under CO) the intensity of the carbonyl absorption band of tetracarbonylcobaltate anion at 1904 cm^{-1} (Fig. 3a) decreases. Therewith, a new C=O absorption band appears at 1889 cm^{-1} (Fig. 3b).

These facts show that the reaction of propylene oxide with tetracarbonylcobaltate anion aclually occurs under the mentioned conditions. However, as seen from the presented data, the carbonyl absorption band of tetracarbonylcobaltate anion does not disappear completely. After 1 h the reaction almost stops, and the intensity ratio of the tetracarbonylcobaltate and new bands remains constant for a long time. Futher addition of propylene oxide produces similar spectral changes: The intensity of the band at 1904 cm^{-1} initially decreases and then remains unchanged (Figs. 4a and 4b).

The carbonyl group absorption band of tetracarbonylcobaltate anion disappears only at [propylene oxide] : [Co(CO)$_4^-$] ratios higher than 1500 : 1 (Fig. 5).

The fact provides evidence showing that the reaction between olefin oxide and tetracarbonylcobaltate anion, forming the catalytic complex is actually equilibrium, and the full conversion of the cobalt carbonyl

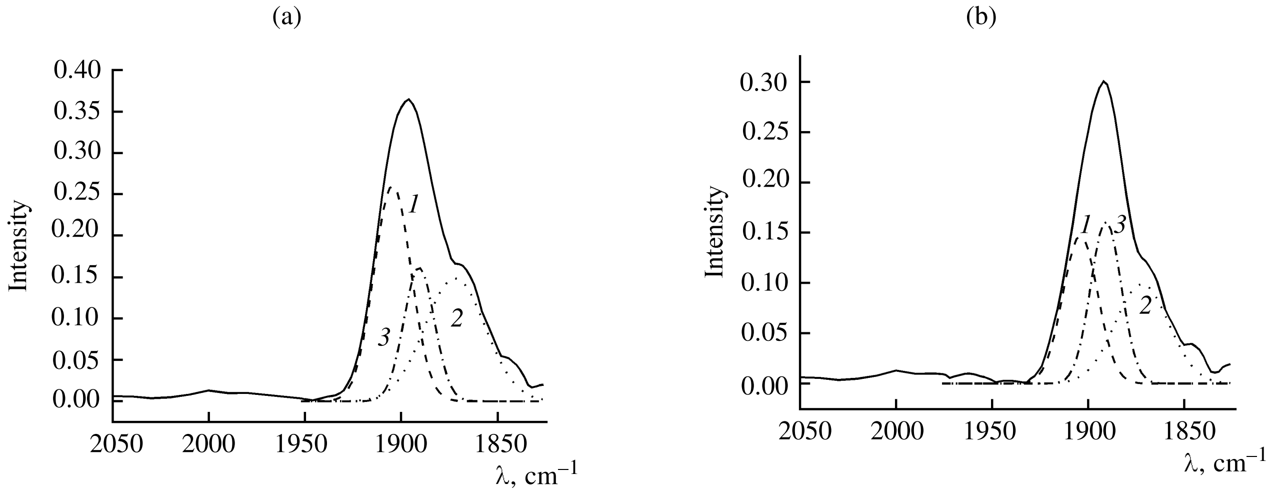
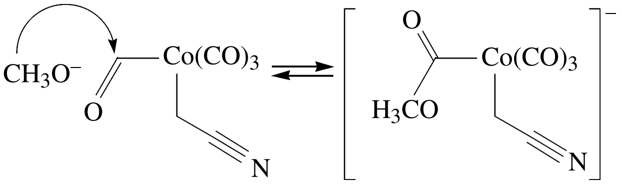


Fig. 4. IR spectra of the solution of potassium tetracarbonylcobaltate in isopropyl alcohol 1 h after addition of propylene oxide, C_0(Co) 0.009 M: (a) propylene oxide : $Co(CO)_4^-$ 140 : 1; (b) propylene oxide : $Co(CO)_4^-$ 460 : 1. (*1* and *2*) Gaussian components of the C=O absorption band of a tetracarbonylcobaltate anion in the absence of propylene oxide and (*3*) absorption band of the resulting alkylcarbonylcobalt complex.

complex into alkylcobaltcarbonyl complex is possible only at a large molar excess of propylene oxide.

Noieworthy is the fact that in the reaction of potassium tetracarbonylcobaltate with propylene oxide gives rise to a new complex with the absorption band at 1889 cm^{-1}. The C=O group of cobalt alkylcarbonyl complexes usually absorb at 2100–2000 cm^{-1} [9, 10]. Such a low-frequency shift of the band during reaction can be explained by the formation of a complex in which the negative charge resides on the metal atom and carbonyl ligands rather than on the oxygen atom. This assumption is quite reasonable, because it is known [1, 2, 9] that alkylcobaltcarbonyl complexes easily undergo nucleophilic attack by methoxide anion on the carbonyl ligand to form methoxycarbonyl anionic complexes (Scheme 8).

Scheme 8.



Therewith, the C=O absorption band actually shifts by about 100 cm^{-1} to lower frequencies (to 1934 cm^{-1} in the case of the cyanomethyl complex) [9].

In the case of the cyclization of the cobalt alkoholate complex into a five-membered metal lactone, the nucleophilic attack of the carbonyl ligand will occur intramolecularly rather than intermolecularly (as described in the literature), which is much more favorable both from the kinetic and thermodynamic viewpoints (Scheme 9).

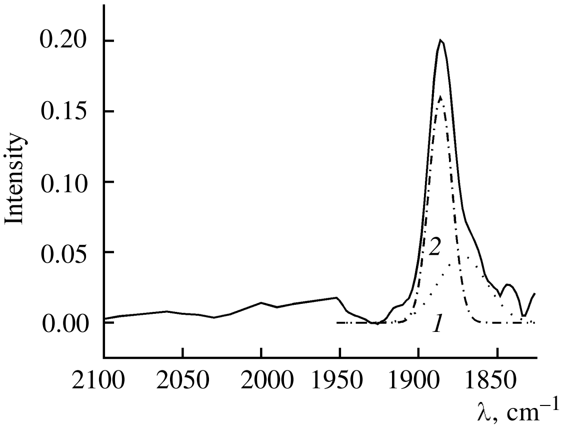
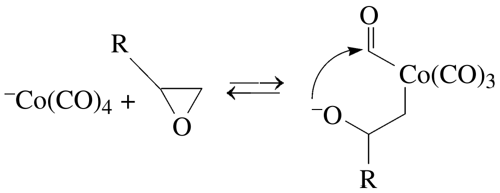
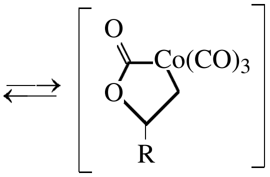


Fig. 5. IR spectrum of the solution of potassium tetracarbonylcobaltate in isopropyl alcohol 1 h after addition of propylene, C_0(Co) 0.009 M, propylene oxide : $Co(CO)_4^-$ 1560 : 1. (*1*) Gaussian component of the C=O absorption band of tetracarbonylcobaltate anion in the absence of propylene oxide and (*2*) absorption band of the resulting alkylcarbonylcobalt complex.

Scheme 9.

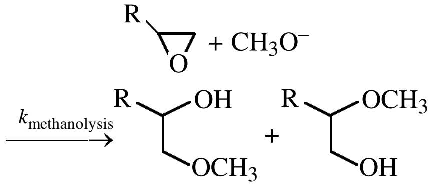




The reversible formation of the catalytic complex along with the methanolisys of olefin oxide partly explain the pattern of the plot of substrate conversion vs. time (Figs. 1 and 2). To explan these curve patterns, the following kinetic scheme was proposed.

(1)

$$\mathrm{ArHlg + CO + CH_3O^- + CC} \xrightarrow{k} \mathrm{ArCOOCH_3 + Hlg^- + CC}, \qquad (2)$$



(3)

Here CC stands for catalytic complex.

Since under the reaction conditions $C(\mathrm{CO})$ and $C(\mathrm{CH_3O^-})$ are constant, the rate of reaction (2) has the following equation.

$$-\frac{d[\mathrm{ArHlg}]}{dt} = k[\mathrm{ArHlg}][\mathrm{CC}]. \qquad (4)$$

Since the induction period is short compared to the total reaction time, we can suggest that equilibrium (1) is established faster than reactions (2) and (3) occur. Hence, the concentration of the catalytic complex [CC] can be expressed through the concentrations of olefin oxide [OO] and tetracarbonylcobaltate anion $C_0[\mathrm{Co(CO)_4^-}]$. Taking into account the material balance in cobalt [Eq. (5)] and the equation for the equilibrium constant of reaction (1), we obtain Eq. (6).

$$C_0[\mathrm{Co(CO)_4^-}] = [\mathrm{Co(CO)_4^-}] + [\mathrm{CC}], \qquad (5)$$

$$[\mathrm{CC}] = \frac{C_0[\mathrm{Co(CO)_4^-}]}{1 + \dfrac{1}{\mathrm{K[OO]}}}. \qquad (6)$$

In portion I (Fig. 2), when the system contains fairly much olefin oxide (until the condition $K[\mathrm{OO}] >> 1$ is fulfilled), the concentration of the catalytic complex remains constant and is equal to $C_0[\mathrm{Co(CO)_4^-}]$ [from Eq. (6)]. Therewith, the carbonylation reaction (2) is described by a pseudo-first-order reaction equation with the rate constant $k_{\mathrm{obs}} = k[\mathrm{CC}]$.

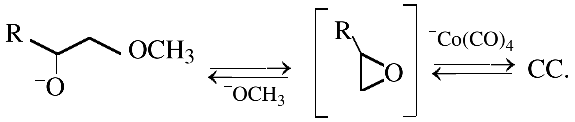
$$-\frac{d[\mathrm{ArHlg}]}{dt} = k_{\mathrm{obs}}[\mathrm{ArHlg}]. \qquad (7)$$

As olefin oxide is consumed in methanolysis, the equilibrium of the formation of the catalytic complex shifts to starting reagents, so that its concentration gradually decreases. Therefore, in portion II the carbonylation reaction is no longer described by the kinetic equation of a pseudo-first-order equation. The reaction rate decreases more rapidly than might be expected for a first-order reaction.

The fact that the carbonylation reaction still occurs 3 h after its initiation (portion III), when the system contains no more than 1% of oct-1-ene oxide of its initial quantity, is impossible to explain exclusively in terms of reversibility of the catalytic complex formation.

The observed phenomenon can be explained assuming reaction between the product of olefin oxide methanolysis and tetracarbonylcobaltate anion (probably, through intermediate formation of an oxirane ring), forming the catalytic complex (Scheme 10).

Scheme 10.



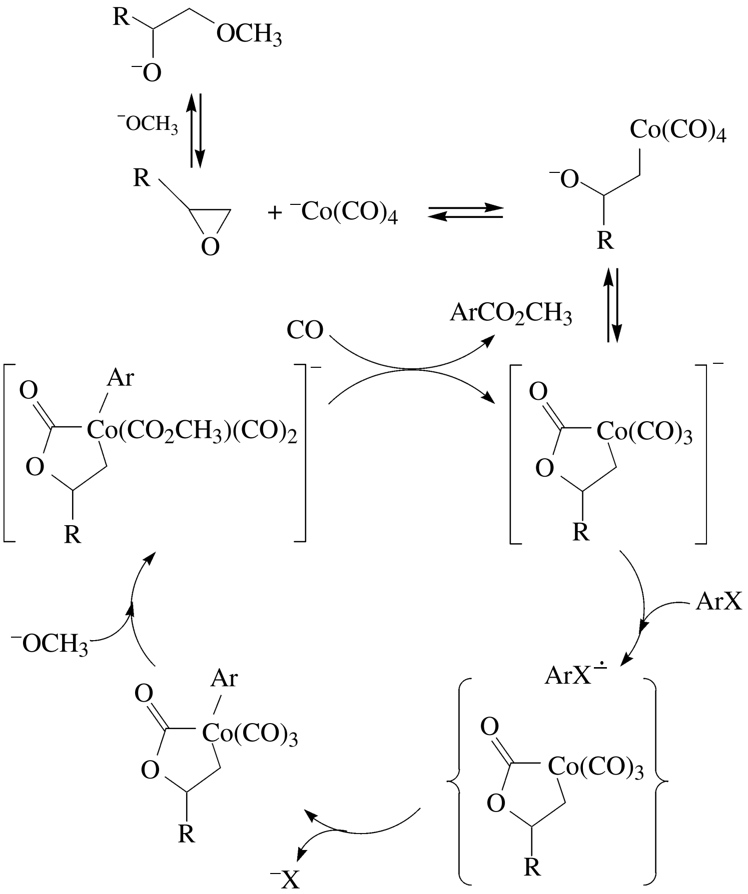
To confirm this assumption, we performed carbonylation of 1-bromonaphthalene with 1-methoxyoctan-2-ol as an activator under the same conditions as in the case of oct-1-ene oxide. Actually, some activation of the catalyst was observed. The substrate conversion achieved 7% in 5 h.

The resulting data allowed us to suggest the following mechanism of the carbonylation of aryl halides in the considered catalytic system (Scheme 11).

EXPERIMENTAL

Determination of the relative rate constants of carbonylation of substituted bromobenzenes by the competitive reactions technique. Reaction conditions: T 62°C and p_{CO} 1 atm. A flask equipped with a water-cooled jacket and a gas-outlet tube was charged with 0.5 g of potassium carbonate and 9 ml of a methanol solution containing a mixture of aryl halides and internal reference for GLC. The mixture was purged with CO with vigorous stirring at room temperature for 20 min. A methanol solution of potassium tetracarbonylcobaltate, 0.5 ml, was then added, and heat-

Scheme 11.



ing of the reaction mixture was initiated with a termostat. After the required temperature was achieved, 0.5 ml of a methanol solution of propylene oxide was added, purging with CO was discontinued, and a seconds counter was turned on. Substrate conversion was followed by the absorbed gas volume; the total conversion of aryl halides was within 20–70%. Every 10–15 min a sample of 0.2–0.3 ml was taken with a syringe from the system, hydrolyzed with 1 ml of water, and twice extracted with ether, and analyzed by GLC.

Procedure of GLC analysis. Gas chromatography was carried out on a Chrom-5 instrument, flame ionization detector, carrier gas argon, rate 20–30 ml min^{-1}. Glass columns 3 mm in diameter and 2500 mm in length were used, packed with 10% SE-30 on Chromaton N-Super (80–100 mesh). The relative carbonylation rate constants were calculated by the consumption of the starting substrates.

Carbonylation of aryl halides *(general procedure).* Reaction conditions: T 62°C and p_{CO} 1 atm. A flask equipped with a water-cooled jacket and a gas-outlet tube was charged with 0.5 g of potassium carbonate, 1–3 mmol of aryl halide, and 9 ml of methanol. The mixture was purged with CO with vigorous stirring at room temperature for 20 min. A methanol solution of potassium tetracarbonylcobaltate, 0.5 ml, was then added, and heating of the reaction mixture was initiated by a termostate. After the required temperature was achieved, 0.5 ml of a methanol solution of an activator was added, purging with CO was discontinued, and a seconds counter was turned on.

Investigation of the dependence of aryl halide conversion on time. 1-Bromonaphthalene was used as aryl halide, and propylene oxide as an activator. Substrate conversion was followed by the absorbed gas volume.

Effect of activator nature on aryl halide conversion. 1,3,5-Trichlorobenzene, 1-chloronaphthalene, and 1-bromonaphthalene were used as starting substrates. Preliminarily an internal reference for GLC (acenaphthene or biphenyl) was added to the system. Samples of 0.2–0.3 ml were taken at certain intervals and were diluted by half with benzene and analyzed by GLC.

Effect of nitrobenzene addition on aryl halide conversion. 1-Bromonaphthalene was used as aryl halide and propylene oxide as activator. Nitrobenzene, 0.15 g, was added to the reaction mixture. After the reaction was complete, the methanol was distilled off, and the reaction mixture was diluted with aqueous HCl and extracted with three portions of ether. The ethereal extracts were combined, the ether was distilled off, and the residue was analyzed by ^{1}H NMR spectroscopy on a Bruker instrument (300 MHz).

Investigation of the catalytic system in the absence of substrate. Oct-1-ene oxide was applied as activator, and no substrate was added to the reaction mixture. After the reaction was complete, the methanol was distilled off, and the reaction mixture was diluted with aqueous HCl and extracted with three portions of ether. The ethereal extracts were combined, the ether was removed, and the residue was analyzed by ^{1}H NMR spectroscopy.

Determination of the rate constant of oct-1-ene oxide methanolysis. A flask was charged with a solvent, a weighed sample of base, and internal reference. The mixture was stirred for 1 h at 60°C, after which oct-1-ene oxide was added, and a sample for GLC analysis was taken. Sampling was further performed every 15 min. The experiment was repeated three times.

Investigation of the reaction of propylene oxide with cobalt tetracarbonyl by IR spectroscopy. A flask equipped with water jacket and a gas-outlet tube was charged with 0.5 g of potassium carbonate and 9 ml of isopropyl alcohol. The mixture was purged with CO with vigorous stirring at room temperature for 20 min, after which 0.5 ml of an isopropanol solution of potassium tetracarbonycobaltate, $C_0[CO(CO)_4^-]$ 0.36 M, was added, and heating of the reaction mixture was initiated with a termostat. After the required temperature was achieved, 0.5 ml of an isopropanol solution of propylene oxide was added. The resulting solution was stirred for a preset time, cooled to room temperature, and a part of the solution was transferred under carbon oxide into a 0.072-μm CO-purged IR cell. The IR spectra of the solutions were taken at 20°C on a Specord IR-75 spectrophotometer, slit width 2 cm^{-1}, scan rate 20 cm^{-1} min^{-1}. The contour of the absorption band near 2000– 1800 cm^{-1} in the IR spectra of solutions of the starting potassium tetracarbonylcobaltate anion was deconvoluted into two Gaussian components. The position and half-widths of these components were taken the same on the deconvolution of the same band contour into three Gaussian components in the spectra of solutions containing propylene oxide.

REFERENCES

1. Francalanci, F., Foa, M., Gardano, A., and Bencini, E., *J. Organomet. Chem.,* 1985, vol. 285, nos. 1–3, p. 293.
2. Zhesko, T.E., Boyarskii, V.P., and Beletskaya, I.P., *Metaloorg. Khim.,* 1989, vol. 2, no. 2, p. 385.
3. Zhesko, T.E., Boyarskii, V.P., and Nikitina, A.G., *Zh. Obshch. Khim.,* 1998, vol. 68, no. 1, p. 85.
4. Zhesko, T.E. and Boyarskii, V.P., *Kinet. Katal.,* 1994, vol. 35, no. 2, p. 320.
5. Heck, R.F., in *Organic Syntheses via Metal Carbonyls,* New York: Interscience, 1968. Translated under the title *Organicheskie sintezy cherez karbonily metallov,* Moscow: Mir, 1970, p. 297.
6. Boyarskii, V.P., Zhesko, T.E., and Lanina, S.A., *Zh. Prikl. Khim.,* 2005, vol. 78, no. 11, p. 1875.
7. Zhesko, T.E., Boyarskii, V.P., Lanina, S.A. and Nikoforov, V.A., RU Patent 2215729, *Byull. Izobret.,* 2003, no. 31.
8. Heck, R.F., *J. Am. Chem. Soc.,* 1963, vol. 85, p. 1460.
9. Francalanci, F., Gardano, A., Abis, L., and Foa, M., *J. Organomet. Chem.,* 1983, vol. 251, p. C5.
10. Galamb, V., Palyi, G., Ungvary, F., Marko, L., Boese, R., and Schmid G., *J. Am. Chem. Soc.,* 1986, vol. 108, no. 12, p. 3344.