

## DESTRUCTION OF PCBS AND OTHER POLYHALOGENATED POLYAROMATIC COMPOUNDS VIA CARBONYLATION ON A MODIFIED COBALT CATALYST

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### Introduction

Destruction and transportation to the destruction site of PCB containing materials and toxic wastes of similar type is restricted in many countries and, therefore, it is very expensive. Our research is directed towards development of safe and flexible carbonylation technology, capable of destruction of polyhalogenaromatic compounds on site, with help of a mobile unit. Present report demonstrates the applicability of our method for destruction of PCBs, PCNs, PBDEs and PBDs.

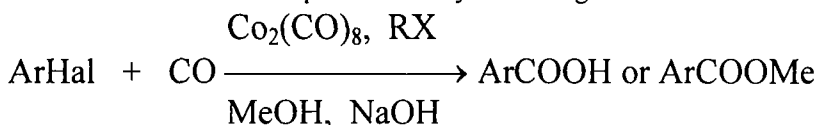
### Materials and methods

The key feature of the carbonylation is a catalyst, for our purposes it should be inexpensive and effective at atmospheric pressure. We developed a series of the new organocobalt catalysts. These compounds are the different alkyl cobalt carbonyls. They can be received *in situ* from dicobalt octacarbonyl or cobalttetracarbonyl anion in base-alcohol media (such as NaOH-methanol) by the reaction with certain Activators. Activators can be alkyl halides, haloethers or epoxides (Table 1).

**Table 1. Studied Organocobalt Complexes**

Activator	Organocobalt complex
CH <sub>3</sub> I	CH <sub>3</sub> Co(CO) <sub>4</sub> (1)
<i>p</i> -XC <sub>6</sub> H <sub>4</sub> CH <sub>2</sub> Cl X = Cl (a), H (b), CH <sub>3</sub> (c)	<i>p</i> -XC <sub>6</sub> H <sub>4</sub> CH <sub>2</sub> Co(CO) <sub>4</sub> (2a, b, c)
CH <sub>3</sub> O <sub>2</sub> CCH <sub>2</sub> Cl	CH <sub>3</sub> O <sub>2</sub> CCH <sub>2</sub> Co(CO) <sub>4</sub> (3)
HOCH <sub>2</sub> CH <sub>2</sub> Cl	HOCH <sub>2</sub> CH <sub>2</sub> Co(CO) <sub>4</sub> (4)
$\begin{array}{c} \text{O} \\ \diagup \quad \diagdown \\ \text{C H} \quad \text{C H}_2 \end{array}$	$\begin{array}{c} \text{C H}_3\text{C H C H}_2\text{C o(C O)}_4 \\   \\ \text{O H} \end{array}$
$\begin{array}{c} \text{O} \\ \diagup \quad \diagdown \\ \text{C H} \quad \text{C H}_2 \end{array}$	$\begin{array}{c} \text{O} \\ \diagup \quad \diagdown \\ \text{C H}_2\text{C H C H}_2\text{C o(C O)}_4 \end{array}$

Recently we used these complexes as catalysts for carbonylation of aryl halides into arylcarboxylic acids or their esters<sup>1,2,3</sup>. Examples of carbonylation are given in Table 2.



**Table 2. Carbonylation of two different aryl halides with different organocobalt complexes**  
( $t=60^{\circ}\text{C}$ ,  $P_{\text{CO}}=1\text{ atm}$ , solvent - methanol; NaOH, reaction time – 30 minutes)

Cobalt complex	2a	2b	3	4	5	6
Conversion of 1-chloronaphthalene, %	33	49	16	83	90	92
Conversion of bromobenzene, %		30	4	56	63	

The most active complexes are complexes with epoxides (complexes 5 and 6).

Thus we developed the new universal economic technology of organic acids production based on the carbonylation of halides with modified cobalt carbonyl as catalyst. The versatility and the economic feasibility of our technology are due to the possibility of carbonylation of different halides in the identical equipment under the same very mild condition with the same catalyst.

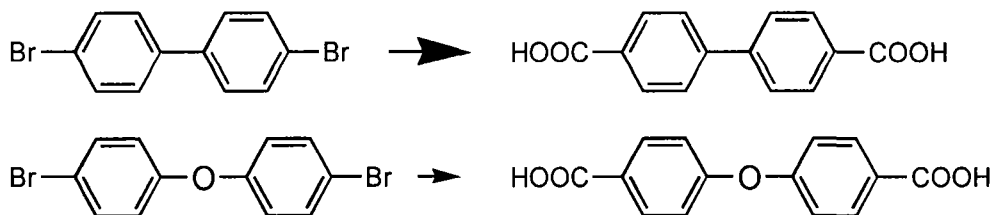
This flexible technology was tested on the pilot production unit in up to 50 kilo lots. The method is proven to be excellent for production of such acids as phenylacetic, acenaphtene dicarboxylic, phenylpyruvic and naphthylacetic. Developed technology, the catalytic system and synthesized products are covered by patents RU.

## Results and Discussion

**Application of carbonylation technology for destruction of environmentally relevant classes of polychloroaromatic compounds.**

### 1. PBDEs, PBBs and PCNs

We used 1-chloronaphthalene and 2,6-dichloronaphthalene as model compounds for Polychloronaphthalenes, 4,4'-dibromodiphenyl and 4,4'-dibromodiphenyl ether as model compounds for brominated flame retardants. All studied compounds react rapidly, yielding arylcarboxylic acids. 4,4'-DiBB and 4,4'-DiBDE both react very fast, giving nearly quantitative yields of corresponding dicarboxylic acids.



Relative reactivities for chlorinated compounds are given in Table 3.

**Table 3. Relative Reactivities Of Aryl Halides In Carbonylation**

Structure	$k$ (rel.)	Product
1-chloronaphthalene	1.0	1-naphthoic acid
2,6-dichloronaphthalene	1.8	2,6-naphthalenedicarboxylic acid
PCB (Sovol-30)	1.2	Mixture of mono- and dicarboxylic acids

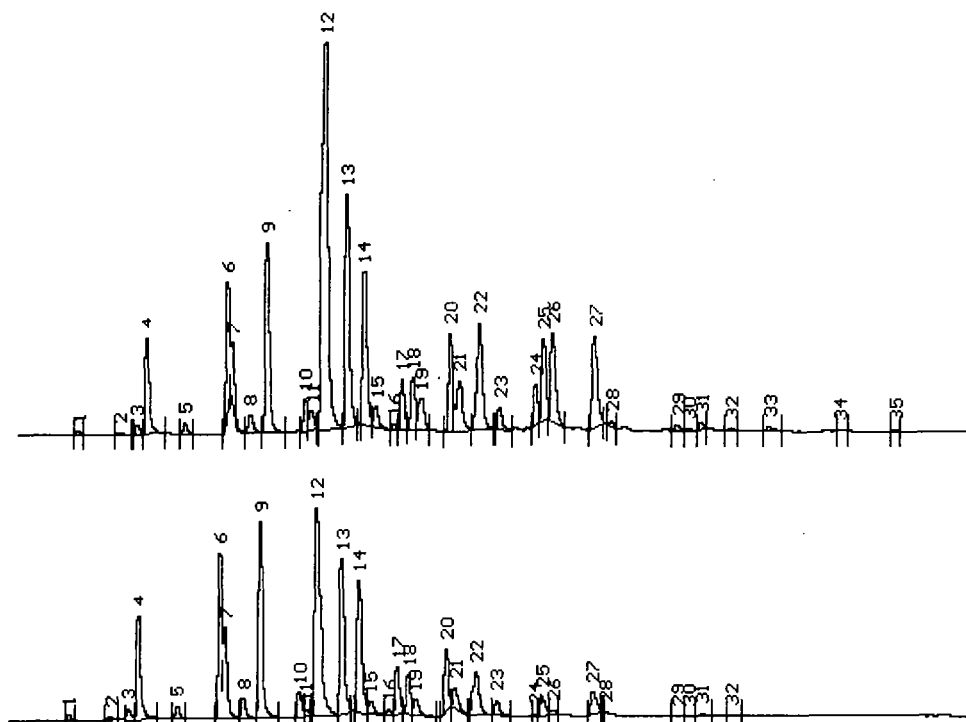
### 2. PCBs – Sovol-30

Also we began the research on PCB technical product - Sovol-30, commercially produced in the USSR for decades. Sovol-30 is a mixture of polychlorobiphenyls, containing 30% of chlorine by

weight. Isomeric distribution of PCBs in this mixture is similar to that in corresponding Arochlor. 500mg of Sovol-30, 50mg of Cobalt octacarbonyl in methanolic NaOH in presence of activator - propylene oxide reacted with CO at 60°C and atmospheric pressure. Reaction was stopped after 10 hours, when conversion reached 30% (measured by amount of mineralized Cl).

Typical chromatograms of starting material – Sovol-30 (upper chromatogram) and reaction product - extract of unreacted PCBs (lower chromatogram) are given on Figure 1.

**Figure 1. Sovol-30 before and after carbonylation**



The chromatographic data and calculated conversions for peaks 10 – 35 are summarized in Table 4.

The following conclusions regarding relative reactivity of different PCB congeners can be made

- Dichlorobiphenyls are stable under the used conditions, as can be seen from unchanged left part of a chromatogram 2 (peaks 1 – 9).
- Reactivity of different isomers of trichlorobiphenyls varies significantly. While PCB-31 (2,4'5-Trichlorobiphenyl) is stable under reaction conditions, PCB-28 (2,4,4'-Trichlorobiphenyl) is degraded by 70% (Peak 12).
- Conversion of other trichlorobiphenyls is in the range of 0 – 70% (peaks 10 – 23).
- Conversion of a majority of tetrachlorobiphenyls and higher chlorinated congeners is very high and in the range 70 – 100% (peaks 24 – 35).

**Table 4. Conversion of different PCB congeners in carbonylation**

SOVOL-30 before carbonylation				SOVOL-30 after carbonylation				
Peak No.	RT	Peak height	Peak area	Peak No.	RT	Peak height	Peak area	% Conversion
10	10:14.1	2.727	8.093	10	10:14.7	2.121	7.321	10
11	10:19.3	1.737	6.220	11	10:20.4	0.544	1.884	70
12	10:32.0	33.235	170.841	12	10:30.0	17.619	80.770	50
13	10:50.3	20.088	64.726	13	10:51.6	13.251	44.047	30
14	11:05.5	13.249	45.568	14	11:06.5	11.142	39.051	10
15	11:15.5	1.762	6.106	15	11:16.7	1.005	4.011	30
16	11:30.9	0.496	1.502	16	11:32.0	0.465	1.393	10
17	11:38.2	4.289	12.497	17	11:39.5	4.142	11.741	0
18	11:47.6	4.500	14.042	18	11:49.0	3.467	10.522	30
19	11:55.0	2.699	12.840	19	11:55.1	1.327	5.975	50
20	12:20.4	8.440	23.897	20	12:21.7	5.323	15.085	30
21	12:28.1	4.323	23.287	21	12:29.2	1.663	5.887	70
22	12:45.6	9.233	39.498	22	12:47.4	3.620	18.581	50
23	13:03.0	1.885	7.070	23	13:04.8	1.200	4.704	30
24	13:34.6	3.664	10.281	24	13:39.1	0.062	0.165	100
25	13:41.7	7.166	21.786	25	13:44.4	1.639	6.799	70
26	13:49.5	7.732	27.240	26	13:53.6	0.416	1.981	90
27	14:26.1	7.835	32.219	27	14:28.7	1.927	8.949	70
28	14:40.7	0.377	1.147	28	14:38.4	0.034	0.044	90
29	15:37.9	0.457	2.141	29	15:41.7	0.078	0.361	80
30	15:48.0	0.255	1.194	30	15:51.2	0.041	0.184	80
31	15:58.9	0.613	2.098	31	16:02.9	0.124	0.613	70
32	16:24.4	0.205	0.963	32	16:28.6	0.030	0.146	80
33	16:58.0	0.381	2.153		Not detected			100
34	17:58.7	0.020	0.068		Not detected			100
35	18:46.7	0.056	0.202		Not detected			100

**Conclusions**

Flexible technology allows producing caboxylic acids from environmentally dangerous halogenated POPs. The acids, provided they are non-toxic can find their use as raw materials for dyes industry or liquid crystals production. The main advantage of our catalytic system is its applicability for utilization of PCBs, PBDEs and PCNs on-site and under mild and safe conditions.

**References**

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