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Oxidation of Highly Chlorinated Benzenes and Biphenyls with Potassium Persulfate in the Presence of Perfluorinated Radicals

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Abstract—The interaction of 1,2,3,4-tetrachlorobenzene, 2,4,5-trichlorobiphenyl, 2,5,4'-trichlorobiphenyl, a mixture of 1,2,3- and 1,2,4-trichlorobenzene, and industrial mixtures of polychlorinated biphenyls with potassium persulfate in the presence of potassium perfluorobutyrate has been investigated. The oxidation of highly chlorinated benzenes and biphenyls proceeds with lower conversion than that of the low-chlorinated compounds. The oxidation of the highly chlorinated aromatic substrates is not selective; the reaction mixture contains products of several competitive reactions: addition and elimination of radical species, disproportionation, isomerization, etc. The structures of the products have been determined by means of gas chromatography with mass spectrometric detection.

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Inorganic persulfates are widely applied in contaminated soil and groundwater treatment due to their prominent oxidative properties and relatively simple activation [1]. Persulfates can be activated via radiolysis, photolysis, conventional heating, or treatment with transition metals salts [2–9]. The chemical processes involving persulfates in aqueous media at different pH are mainly induced by $SO_4^{\cdot -}$ ion-radical formed *in situ*. The pathways of the active particles formation from persulfates in alkaline medium are summarized by Eqs. (1)–(7) [3, 10, 11]:

$$S_2O_8^{2-} \rightarrow 2SO_4^{\cdot -}, \quad (1)$$

$$SO_4^{\cdot -} + HO^- \rightarrow HSO_4^- + HO^{\cdot}, \quad (2)$$

$$HO^{\cdot} + HO^{\cdot} \rightarrow H_2O + 1/2O_2, \quad (3)$$

$$S_2O_8^{2-} + HO^{\cdot} \rightarrow HSO_4^- + SO_4^{\cdot -} + 1/2O_2, \quad (4)$$

$$S_2O_8^{2-} + HO^{\cdot} \rightarrow S_2O_8^{\cdot -} + HO^-, \quad (5)$$

$$SO_4^{\cdot -} + HO^{\cdot} \rightarrow SO_4^{2-} + 1/2O_2, \quad (6)$$

$$SO_4^{\cdot -} + S_2O_8^{2-} \rightarrow SO_4^{2-} + S_2O_8^{\cdot -}. \quad (7)$$

In these processes, the active particles, capable of destroying persistent organic pollutants, are formed in the surficial layers of contaminated objects. Therefore, the inorganic persulfates are referred to as the reagents for *in situ* chemical oxidation.

Inorganic persulfates are known to initiate the oxidative decarboxylation of organic acids and their salts or esters [12–14]. For example, aliphatic perfluorocarboxylic acids salts decarboxylate within 50 minutes in the presence of $K_2S_2O_8$ in water at 95°C [15]. The products of the reaction are dimeric perfluoroalkanes [Eq. (8)]:

$$2R^FCOOK \rightarrow 2R^FCOO^{\cdot} \rightarrow 2CO_2 + 2R^{F\cdot} \rightarrow R^F\text{–}R^F,$$
$$R^F = \text{F-Alkyl}. \quad (8)$$

The radical $R^FCOO^{\bullet}$ formation is associated with the unpaired electron transfer from the *in situ* formed $SO_4^{\cdot -}$ particle to the carboxylate ion. Subsequent thermodynamically favorable release of carbon dioxide creates highly active radicals $R^{F\bullet}$ that further recombine.

To the very best of our knowledge, the examples of chlorine-containing aromatic compounds (persistent organic pollutants) oxidation by persulfate in the presence of perfluoroalkyl radicals formed *in situ*, are absent in the literature. We have been the first to study the interaction of low-chlorinated benzenes and biphenyls with $K_2S_2O_8$ in the presence perfluoropropyl radicals ($C_3F_7^{\cdot}$), generated from potassium perfluorobutyrate (C_3F_7COOK) [16]. We have found that the main products of the reaction of mono- and dichlorinated benzenes and biphenyls are compounds containing perfluoropropyl groups; these products result from hydrogen abstraction by $C_3F_7^{\bullet}$ radicals formed *in situ*. The monochlorinated compounds conversion in this reaction is full, whereas dichlorinated substrates reaction was not complete.

This study aimed to investigate the reactivity of highly chlorinated benzene and biphenyl derivatives, the persistent organic pollutants, towards interaction with $K_2S_2O_8$ in the presence of $C_3F_7^{\bullet}$. The model objects were: a mixture of 1,2,3- and 1,2,4-trichlorobenzene (constituent of "Sovtol-10", industrial mixture of polychlorinated biphenyls), 1,2,3,4-tetrachlorobenzene, 2,4,5-trichlorobiphenyl, 2,5,4'-trichlorobiphenyl, and the "Trichlorobiphenyl" and "Sovol" industrial mixtures of polychlorinated biphenyls.

Being a strong oxidizer, sulfate anion radical ($SO_4^{\bullet-}$) commonly interacts with organic molecules via the three pathways: single-electron transfer to an organic substrate, splitting off the hydrogen radical from an organic substance, and addition of the active particles to unsaturated fragments (alkene or arene) or their elimination. All these mechanisms were found operative in $K_2S_2O_8$ reaction with the studied model compounds, giving a variety of the products.

Similarly to the case of low-chlorinated benzenes and biphenyls [16], the interaction of higher chlorinated analogues with $K_2S_2O_8$ in the presence of C_3F_7COOK was not selective. Scheme 1 shows the products formed in $K_2S_2O_8$ reaction with a mixture of 1,2,3-trichlorobenzene and 1,2,4-trichlorobenzene in the presence of C_3F_7COOK, the products content is given in Table 1. The overall conversion of that mixture (79.8%) was lower than the conversion of *o*-dichlorobenzene, *p*-dichlorobenzene, or chlorobenzene under similar conditions [16].

The major products of the reaction were **Ia** and **Ib** (25.5%) resulting from abstraction of one or two hydrogen atoms, respectively, with $C_3F_7^{\bullet}$ radicals [16]. It was not possible to identify the location of perfluoroalkyl substituents in the benzene ring by GC–MS, however, formation of five isomers of **Ia** supported high reactivity of all unsubstituted carbon atoms of 1,2,3-trichlorobenzene and 1,2,4-trichlorobenzene.

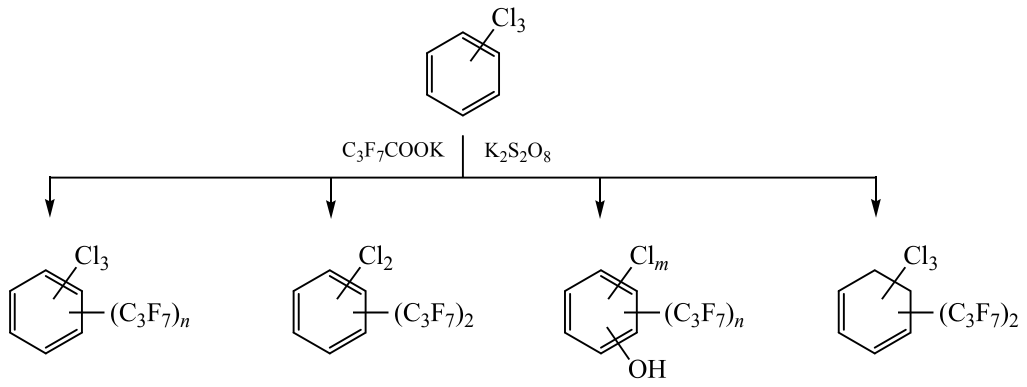
The product **II** contained less of chlorine atoms than did the starting substrates. It could not be formed via the C_{Ar}–Cl bond homolysis by $C_3F_7^{\bullet}$, followed by elimination of $Cl^{\bullet}$ and formation of the C_{Ar}–C_3F_7 bond: the homolysis of the C_{Ar}–Cl bond in polychlorinated benzenes is an energy-consuming process [17] that could not occur under the reaction conditions [18, 19]. The dichlorinated products **II** could rather result from several competing processes: addition and elimination of the radical species, disproportionation, isomerization, etc.

The compounds **IIIa–IIIe** were the minor products of the studied reaction (10.1%). Their formation could be understood as follows. Trifluoromethylbenzene is known to give hydroxytrifluoromethylbenzene under photolytic initiation of $SO_4^{\bullet-}$ [9]. Basing on the

Table 1. Identification of products of 1,2,3- and 1,2,4-trichlorobenzenes mixture reaction

Comp. no.	Formula	m/z (I_{rel}, %)	Base ion, m/z	Number of isomers	Product content, %
Ia	$C_6H_2Cl_3C_3F_7$	348 (23)	229	5	22.6
Ib	$C_6HCl_3(C_3F_7)_2$	516 (28)	397	1	2.9
II	$C_6H_2Cl_2(C_3F_7)_2$	482 (21)	363	3	12.5
IIIa	$C_6Cl_3(C_3F_7)_2OH$	532 (16)	413	1	2.9
IIIb	$C_6HCl_2(C_3F_7)_2OH$	498 (52)	212	1	0.6
IIIc	$C_6Cl_2(C_3F_7)_3OH$	666 (8)	547	3	3.9
IIId	$C_6H_2Cl(C_3F_7)_2OH$	464 (22)	345	1	0.6
IIIe	$C_6HCl(C_3F_7)_3OH$	632 (15)	513	3	2.1
IVa	$C_6H_3Cl_3(C_3F_7)_2$	518 (23)	349	2	16.0
IVb	$C_6H_2Cl_3(C_3F_7)_3$	686 (4)	169	3	7.0
The total content of the identified products					71.1

Scheme 1.



Ia, Ib **II** **IIIa–IIIe** **IVa, IVb**

$n = 1$ (**Ia**), 2 (**Ib, IVa**), 3 (**IVb**); $m = 3, n = 2$ (**IIIa**); $m = 2, n = 2$ (**IIIb**), $m = 2, n = 3$ (**IIIc**); $m = 1, n = 2$ (**IIId**); $m = 1, n = 3$ (**IIIe**).

Hammett constants, we concluded that the hydroxyl derivatives were formed via $SO_4^{\bullet-}$ addition to the aromatic substrate followed by the interaction with water and elimination of SO_4^{2-} and H^+. However, under non-photolytic conditions, the hydroxyl derivatives **IIIb–IIIe** were supposed to appear via interaction with $HO^{\bullet}$ radical formed *in situ* [see Eq. (2)] and further $H^{\bullet}$ elimination [20]. **IIIb–IIIe** contained less of chlorine atoms than did the initial substrates, and their formation mechanism was similar to that of **II**.

The non-aromatic nature of **IVa** and **IVb** was elucidated from GC–MS data. The mass of **IVa** and **IVb** molecular ions was two Da higher than those of the related aromatic substrates. The perfluorinated substituents fragmentation route was different as well. In the case of aromatic cycle, under electron ionization, the C_3F_7 primarily dissociated to form $[C_2F_5]^+$ with $m/z = 119$, and the peak of $[M - C_2F_5]^+$ was the base one in the mass spectra (compounds **I** and **II**). In the case of **IVa** and **IVb**, however, the $[C_3F_7]^+$ with $m/z = 169$ was formed, and the base peak was that of $[M - C_3F_7]^+$, whereas the $[M - C_2F_5]^+$ peak was of low intensity (1%). Basing on that, the cyclohexadienic structure of the cyclic fragment was suggested. The mass spectra of **Ib** and **IVa** are shown in Figs. 1 and 2, respectively.

Earlier, we suggested that the cyclohexadienyl derivatives were formed as a result of the attack of the second $C_3F_7^{\bullet}$ radical at the carbon atom located between those substituted with Cl, and C_3F_7 [16]. If so, the $H^{\bullet}$ elimination was impossible due to steric effect of bulky chlorine and perfluoropropyl substituents [21] , and the cyclohexadiene derivative would result from disproportionation. Therefore, in the case of 1,2,3- and 1,2,4-trichlorobenzenes mixture, the formation of **IVa** and **IVb** was only possible from 1,2,4-trichlorobenzene. Note also that the fragmentation of 1,3- and 1,4- cyclohexadienes during MS analysis was similar, thus the isomerization of **IVa** and **IVb** with the double bond shift from 1,3 to 1,4 position was possible as well.

Polychlorinated dibenzofuran and biphenyl derivatives were not identified in the products of 1,2,3-trichlorobenzene and 1,2,4-trichlorobenzene reaction with $K_2S_2O_8$ in the presence of C_3F_7COOK, in contrast with the case of similar reactions of *o*- and *p*-dichlorobenzenes [16].

The conversion of 1,2,3,4-tetrachlorobenzene in the reaction with $K_2S_2O_8$ in the presence of C_3F_7COOK was even lower (37.8%). In contrast with the case of 1,2,3- and 1,2,4-trichlorobenzenes, besides the mononuclear derivatives, the compounds of biphenyl type were formed, **IXa–IXe** (Scheme 2, Table 2). The products **Ib**, **IIIa–IIIc**, **IIIe**, **V**, **VI** and **VIII** formation mechanism has been described above.

The ester of trichlorophenol and perfluorobutyric acid (**VII**) likely resulted from the attack *in situ* formed [Eq. (8)] $C_3F_7COO^{\bullet}$ radicals at one of the carbon atoms of the aromatic ring. The alternative two-step route (formation of phenol via interaction with $HO^{\bullet}$ and hydrogen elimination followed by esterification with perfluorobutyric acid) seemed unlikely. Generation of the perfluorobutyric acid *in situ* was doubtful, due to highly alkaline reaction medium and the absence of esterification catalyst.

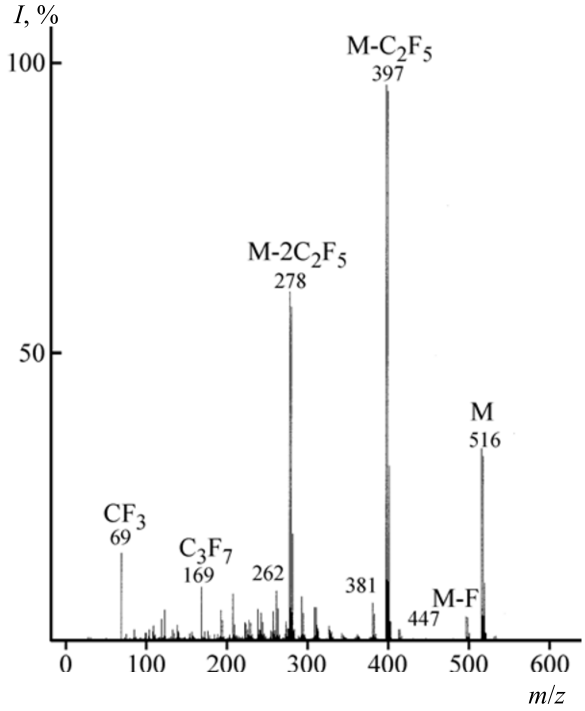


Fig. 1. The mass spectrum of trichlorobis(perfluoropropyl)benzene **Ib.**

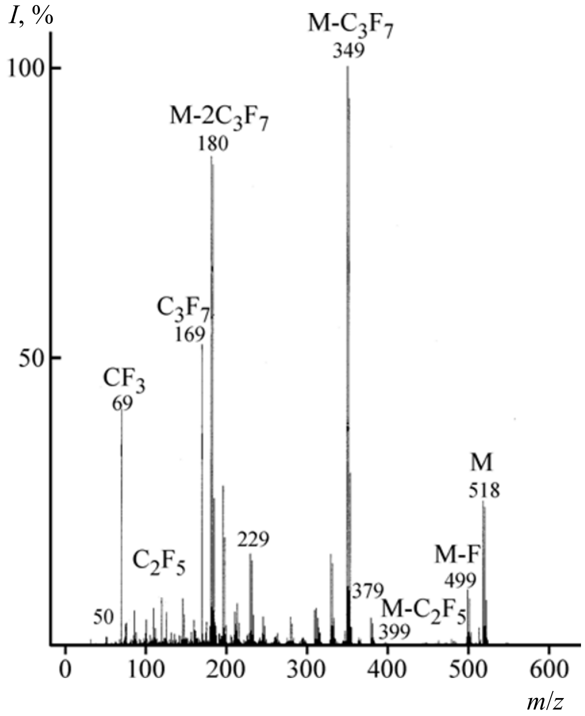
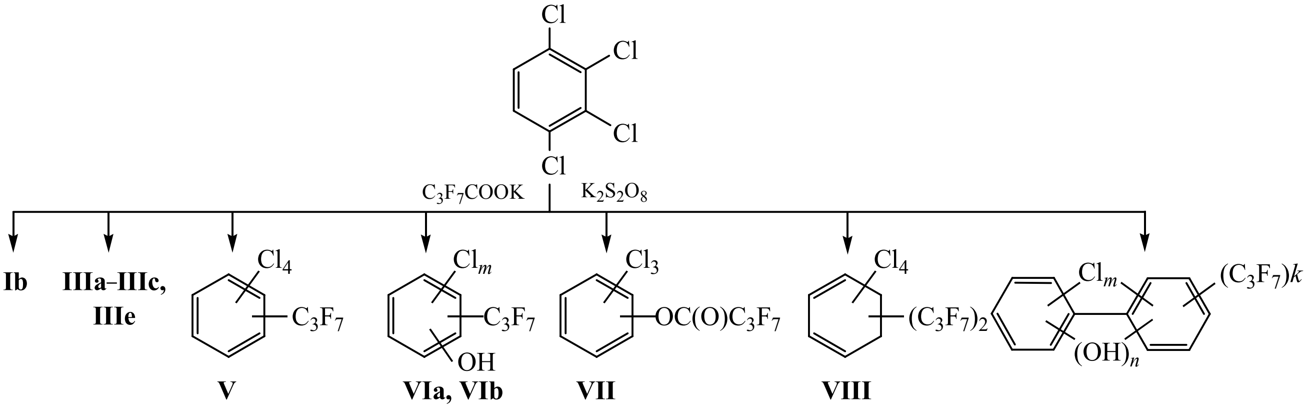


Fig. 2. The mass spectrum of trichlorobis(perfluoropropyl)cyclohexadiene **IVa.**

Hydroxycyclohexadienyl and aryl radicals are known to form substituted biphenyls via dimerization [9, 19]. This explained the presence of **IXa–IXe** in the reaction mixture. The **IXa–IXe** derivatives were products of 1,2,3,4-tetrachlorobenzene dimerization, however, none of them retained all the chlorine atoms of the initial substrate, thus indicating the complexity of the processes involved. Pentachlorobenzene (present in 1,2,3,4-tetrachlorobenzene as admixture) was not transformed. Quantitative composition of the identified products is given in Table 2.

The “Trichlorobiphenyl” industrial mixture is analogous to the industrial mixture “Delor 103” consisting of mono- (0.3%), di- (10.8%), tri- (52.3%), tetra- (35.5%), and pentachlorinated (1.1%) biphenyls [22].

Scheme 2.



$m = 3$ (**VIa**), 4 (**VIb**); $m = 6$, $n = 1$, $k = 1$ (**IXa**); $m = 7$, $n = 1$, $k = 1$ (**IXb**), $m = 6$, $n = 2$, $k = 1$ (**IXc**); $m = 7$, $n = 2$, $k = 1$ (**IXd**); $m = 6$, $n = 1$, $k = 2$ (**IXe**); $m = 6$, $n = 2$, $k = 2$ (**IXf**).

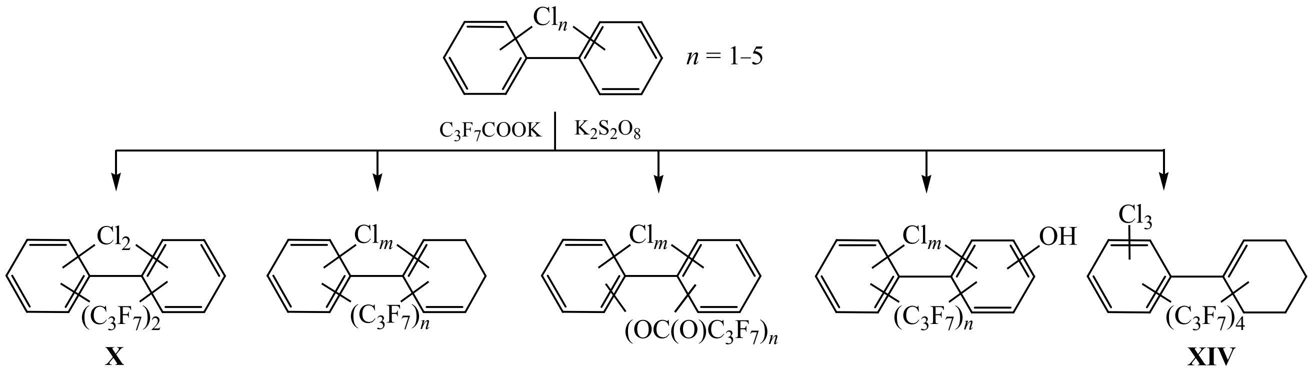
Table 2. Identification of products of 1,2,3,4-tetrachlorobenzene reaction

Comp. no.	Formula	*m*/*z* (*I*_{rel}, %)	Base ion, *m*/*z*	Number of isomers	Product content, %
Ib	$C_6HCl_3(C_3F_7)_2$	516 (28)	397	4	4.7
IIIa	$C_6Cl_3(C_3F_7)_2OH$	532 (16)	413	7	6.5
IIIb	$C_6HCl_2(C_3F_7)_2OH$	498 (52)	212	4	4.0
IIIc	$C_6Cl_2(C_3F_7)_3OH$	666 (8)	547	6	0.9
IIIe	$C_6HCl(C_3F_7)_3OH$	632 (15)	513	1	0.2
V	$C_6HCl_4C_3F_7$	382 (23)	263	1	5.6
VIa	$C_6HCl_3C_3F_7OH$	364 (23)	245	3	2.3
VIb	$C_6Cl_4C_3F_7OH$	398 (100)	398	2	1.7
VII	$C_6H_2Cl_3OCOC_3F_7$	392 (48)	169	1	0.4
VIII	$C_6H_2Cl_4(C_3F_7)_2$	552 (6)	214	1	2.9
IXa	$C_{12}H_2Cl_6C_3F_7OH$	542 (100)	542	3	0.4
IXb	$C_{12}HCl_7C_3F_7OH$	576 (100)	576	3	0.2
IXc	$C_{12}HCl_6C_3F_7(OH)_2$	558 (87)	69	1	0.1
IXd	$C_{12}Cl_7C_3F_7(OH)_2$	592 (13)	423	2	0.1
IXe	$C_{12}HCl_6(C_3F_7)_2OH$	710 (44)	591	3	0.1
IXf	$C_{12}Cl_6(C_3F_7)_2(OH)_2$	726 (71)	591	6	0.6
The total content of the identified products					30.7

The reactivity of “Trichlorobiphenyl” was expected to be similar to that of 1,2,3-trichlorobenzene, 1,2,4-trichlorobenzene, and 1,2,3,4-tetrachlorobenzene, other conditions being the same, as di-, tri-, and tetrachlorinated biphenyls were the major components of ”Trichlorobiphenyl”.

Analysis of the products of ”Trichlorobiphenyl” interaction with $K_2S_2O_8$ in the presence of C_3F_7COOK revealed the relatively low polychlorinated biphenyls conversion (10.9%), the major products being esters **XIIa–XIId** (4.1%) (Scheme 3). The content of exclusive perfluoroalkylation products (**X**) was rela-

Scheme 3.



m = 2, *n* = 3 (**XIa**); *m* = 3, *n* = 2 (**XIb**); *m* = 3, *n* = 3 (**XIc**); *m* = 0, *n* = 2 (**XIIa**); *m* = 1, *n* = 2 (**XIIb**); *m* = 2, *n* = 1 (**XIIc**); *m* = 3, *n* = 1 (**XIId**); *m* = 1, *n* = 3 (**XIIIa**); *m* = 2, *n* = 3 (**XIIIb**); *m* = 3, *n* = 3 (**XIIIc**); *m* = 3, *n* = 4 (**XIIId**).

Table 3. Identification of products of the industrial mixture “Trichlorobiphenyl” reaction

Comp. no.	Formula	m/z (I_{rel}, %)	Base ion, m/z	Number of isomers	Product content, %
X	$C_{12}H_6Cl_2(C_3F_7)_2$	558 (28)	439	3	0.4
XIa	$C_{12}H_7Cl_2(C_3F_7)_3$	728 (9)	69	1	0.1
XIb	$C_{12}H_7Cl_3(C_3F_7)_2$	594 (55)	371	1	0.7
XIc	$C_{12}H_6Cl_3(C_3F_7)_3$	762 (50)	69	2	0.4
XIIa	$C_{12}H_8(OCOC_3F_7)_2$	578 (89)	381	1	0.8
XIIb	$C_{12}H_7Cl(OCOC_3F_7)_2$	612 (100)	612	4	1.8
XIIc	$C_{12}H_7Cl_2OCOC_3F_7$	434 (62)	202	6	1.4
XIId	$C_{12}H_6Cl_3OCOC_3F_7$	468 (54)	236	1	0.1
XIIIa	$C_{12}H_5Cl(C_3F_7)_3OH$	708 (11)	372	2	0.2
XIIIb	$C_{12}H_4Cl_2(C_3F_7)_3OH$	742 (32)	623	5	0.9
XIIIc	$C_{12}H_3Cl_3(C_3F_7)_3OH$	776 (29)	69	4	0.3
XIIId	$C_{12}H_4Cl(C_3F_7)_4OH$	876 (7)	617	1	0.03
XIV	$C_{12}H_7Cl_3(C_3F_7)_4$	932 (17)	201	6	0.4
The total content of the identified products					7.5

tively low (0.4%). The resulting mixture contained cyclohexadienyl compounds **XIa–XIc**, hydroxyl derivatives **XIIIa–XIIId**, and cyclohexyl derivatives with four perfluoropropyl groups **XIV** as well (Table 3).

The low reactivity of polychlorinated biphenyls in the industrial “Trichlorobiphenyl” could only be explained by peculiarities of the structure of individual components of the mixture. Among the trichlorinated and tetrachlorinated biphenyls, there were no isomers with all the chlorine atoms attached to the same aromatic ring [22]. In [16], we showed that the reactivity of dichlorinated biphenyls containing both chlorine atoms in the same ring was higher than of those containing chlorine atoms in both rings. Therefore, the biphenyls containing all three or four chlorine atoms in the same ring should be more reactive.

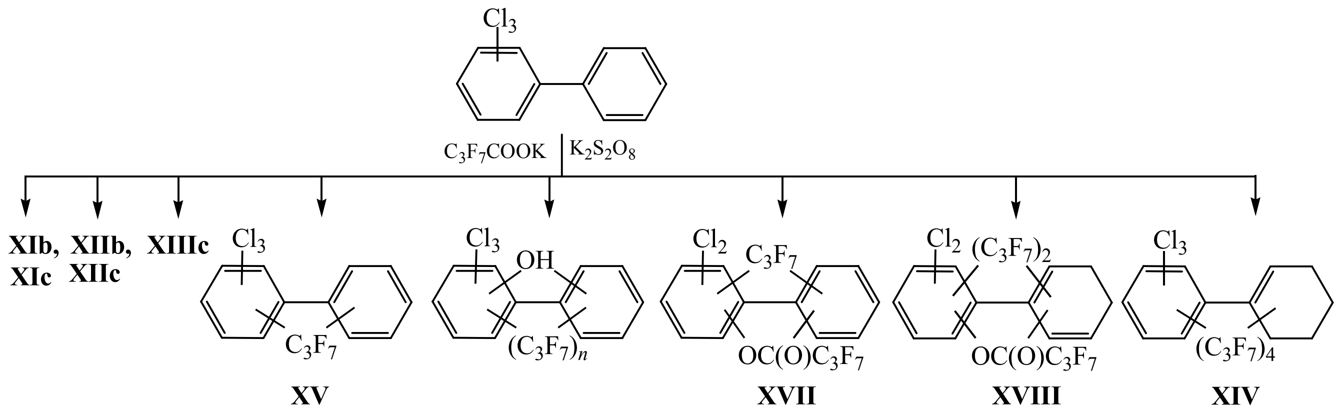
This was checked by studying the model individual trichlorinated biphenyls prepared as described in [23]. Namely, 2,5,4'-trichlorobiphenyl (PCB 31) with chlorine atoms in both aromatic rings was prepared via Gomberg–Bachmann–Hey reaction from 1,4-dichlorobenzene and 4-chloroaniline in the presence of isopentylnitrite. Similar reaction of benzene and 2,4,5-trihloroaniline gave 2,4,5-trichlorobiphenyl (PCB 29) with all three chlorine atoms located in the same ring.

The conversion of 2,5,4'-trichlorobiphenyl in the reaction with $K_2S_2O_8$ in the presence of C_3F_7COOK was as low as 8.7%, the derivatives **XIIb** and **XIIc** were found in the products (4.5%). Under similar conditions, 2,5,4'-trichlorobiphenyl showed much higher conversion (43.5%). For both model compounds, the reaction products and the quantitative composition of their mixtures are given in Scheme 4 and Table 4, respectively.

Basing on data on 2,5,4'- and 2,4,5-trichlorobiphenyls reactivity, we concluded that the identified products of the industrial mixture “Trichlorobiphenyl” reaction with $K_2S_2O_8$ in the presence of C_3F_7COOK were majorly formed from dichlorinated biphenyls. Noteworthily, under the same conditions, none of the expected products were identified in the mixture after reaction with “Sovol” (a product similar to the “Aroclor 1254” mixture) consisting of tri- (1%), tetra- (20%), penta- (53%), hexa- (20%), and hepta-chlorinated (1%) biphenyls [24,25]; it seemed that no reaction occurred in that case.

In the mass spectra of all the identified products the corresponding molecular ions peaks were found, their relative intensity being of 10% to 100%. All the mass spectra contained the peaks of $[M - F]^+$, $[M - HF_2]^+$,

Scheme 4.



n = 1 (**XVIa**), 2 (**XVIb**).

and the peaks of ions characteristic of perfluoroalkyl group decay: $[C_3F_7]^+$, $[C_2F_5]^+$, and $[CF_3]^+$.

In the mass spectra of **Ia**, **Ib**, **II**, **V**, **X**, and **XV**, the base peak was that of $[MC_2F_5]^+$. Other peaks were weaker (10%). The main route of the molecular ions fragmentation was the perfluoroalkyl group elimination followed by that of chlorine atoms. For the compounds with several C_3F_7 groups, first, the perfluoroalkyl groups were successively split off, and then chlorine atom(s) were cleft upon fragmentation.

In the mass spectra of **IVa, IVb, VIII, XIa–XIc**, and **XIV**, the $[M - C_3F_7]^+$ peak was of high intensity or even the base one. The peak of $[M - C_2F_5]^+$ was much weaker or even absent. The peaks of $[C_3F_7]^+$, $[C_2F_5]^+$, $[CF_3]^+$ were strong, and in some cases the $[C_3F_7]^+$ or $[CF_3]^+$ peak was the base one. The main fragmentation route was a consecutive cleavage of perfluoroalkyl groups as well.

In the mass spectra of **IIIa–IIId, VIa, VIb, IXa–IXe, XIIIa–XIIId, XVIa,** and **XVIb**, the peak of

Table 4. Identification of products of 2,4,5- and 2,5,4'-trihlorbiphenyls (PCB 29 and PCB 31) reaction

Comp. no.	Formula	*m*/*z* (I_{rel}, %)	Base ion, *m*/*z*	Number of isomers		Product content, %	
				PCB-29	PCB-31	PCB-29	PCB-31
XIb	$C_{12}H_7Cl_3(C_3F_7)_2$	594 (55)	371	3	–	6.0	–
XIc	$C_{12}H_6Cl_3(C_3F_7)_3$	762 (50)	69	2	–	2.2	–
XIIb	$C_{12}H_7Cl(OCOC_3F_7)_2$	612 (100)	612	1	2	0.4	2.1
XIIc	$C_{12}H_7Cl_2OCOC_3F_7$	434 (62)	202	3	2	8.0	2.4
XIIIc	$C_{12}H_3Cl_3(C_3F_7)_3OH$	776 (29)	69	4	–	3.0	–
XIV	$C_{12}H_7Cl_3(C_3F_7)_4$	932 (17)	201	6	–	5.1	–
XVa	$C_{12}H_6Cl_3C_3F_7$	424 (48)	305	2	–	8.8	–
XVIa	$C_{12}H_5Cl_3C_3F_7OH$	440 (100)	440	1	–	0.4	–
XVIb	$C_{12}H_4Cl_3(C_3F_7)_2OH$	608 (100)	608	3	–	1.0	–
XVII	$C_{12}H_6Cl_2C_3F_7OCOC_3F_7$	602 (7)	483	5	–	3.0	–
XVIII	$C_{12}H_7Cl_2(C_3F_7)_2OCOC_3F_7$	772 (20)	169	3	–	2.0	–
The total content of the identified products						39.9	4.5

$[MC_2F_5]^+$ was the base one in most cases. Fragmentation of the molecular ion occurred majorly by successive splitting off perfluoroalkyl group, HCO group, and chlorine atom(s). In the cases of derivatives containing two or more C_3F_7 groups, the characteristic peak was that of $[M - 119–166]^+$, possibly corresponding to $[M - 2C_2F_5–F–CO]^+$.

The mass spectra of **VII, XIIa–XIId, XVII,** and **XVIII** contained peaks of $[M–COC_3F_7]^+$, in some cases, those peaks were the base ones. In the mass spectra of the derivatives containing both C_3F_7 and $OCOC_3F_7$ groups, the first fragment to be cleft was C_2F_5 group (**VII** and **XVII)** or C_3F_7 (**XVIII)**, further, $OCOC_3F_7$ group was split off.

To conclude, this work in combination with data from [16] demonstrated that with increasing number of chlorine atoms in chlorinated benzenes and biphenyls, the conversion of the compounds in reaction with $K_2S_2O_8$ in the presence of C_3F_7COOK decreased. In all the studied cases of polychlorinated aromatic compounds, the process was non-selective. In the cases of mono- and dichlorinated benzenes and biphenyls, the major products corresponded to perfluoroalkylation reaction; in the cases of highly chlorinated compounds, a complex mixture of products was formed via several competitive mechanisms. In no experiment involving reaction of polychlorinated compounds did we observe formation of polychlorinated dibenzofurans, which were found in the cases of *o*- and *p*-dichlorobenzenes substrates [16]. Chemical processing of the chlorinated aromatic pollutants with $K_2S_2O_8$ and C_3F_7COOK was only efficient in the cases of the low-chlorinated substrates.

EXPERIMENTAL

The reaction products were identified using Agilent GC 7890A MSD 5975C Inert XL EI/CI gas chromatograph–mass spectrometer with HP-5MS quartz capillary column (30 m×25 mm), the stationary phase film thickness of 0.25 mm (polydimethylsiloxane, 5% of grafted phenyl groups), and quadrupole mass spectrometry detector (GC-MS). The scanning was performed across the full ion current in the mass range of 20–1000 Da in the electron ionization mode (70 eV). The carrier gas was helium, at flow partition of 1:50. Initial column temperature was of 40°C (3 min isotherm), followed by programmed raise at 10°C min^{-1} to 290°C (40 min isotherm), the evaporator temperature was of 250°C, the transition chamber temperature was of 280°C, the MS source temperature was of 230°C, the quadrupole detector temperature was of 250°C. Quantitative measurements were performed by the internal normalization of the chromatographic peaks areas recorded in the GC-MS mode while scanning over the total ion current.

The structures of compounds with the content in the products mixture above 0.1% were presented and discussed in this paper.

Potassium perfluorobutyrate. In all the cases, C_3F_7COOK was prepared by mixing of potassium hydroxide (40% solution in distilled water) and perfluorobutyric acid in the equimolar ratio; then the reaction mixture pH was adjusted to ≈ 10–11 with potassium hydroxide. In the subsequent reactions, the molar excess of C_3F_7COOK with respect to the chlorinated organic substrate corresponded to the number of aromatic carbon atoms not substituted with chlorine.

Typical procedure of chlorinated aromatic compounds reaction with C_3F_7COOK in the presence of $K_2S_2O_8$. A mixture of 1,2,3-trichlorobenzene and 1,2,4-trichlorobenzene (9.1 g, 0.05 mol) was added under vigorous stirring to aqueous solution of 0.15 mol of C_3F_7COOK prepared *in situ*. The reaction mixture was heated up to 50°C, and 9.0 g (0.03 mol) of $K_2S_2O_8$ was added. The mixture was heated up to 95°C, then it was cooled down to 40–50°C, and another portion of $K_2S_2O_8$ (9.0 g, 0.03 mol) was added. In total, 27.0 g (0.1 mol) $K_2S_2O_8$ was added to the mixture. Then the reaction mixture was stirred for 2 h at 95°C, cooled to 40–50°C, and 100 ml of water was added to dissolve the inorganic salts. If necessary, more of water could be added. After dissolution of all inorganic products, the reaction mixture was cooled to room temperature and extracted with $CHCl_3$ (2×30 ml).

The individual 2,4,5'-trichlorobiphenyl (PCB 29) and 2,5,4'-trichlorobiphenyl (PCB 31) were prepared as described in [23].

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