ON THE MECHANISM OF FORMATION OF PCDD/PCDFs IN THERMAL SOURCES. THE ROLE OF ELECTRONIC FACTORS

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The mechanism of chlorination aromatic compounds has been well-studied over many years [1]. It has been established that the rate and the direction of the reaction of the compound, containing an oxygen atom connected to an aromatic ring, is determined by electronic factors. This leads to the composition of the resulting mixture of chlorinated products being almost entirely made of *ortho-para* subsitute compounds. If the chlorination of 2,3,7,8-TCDD/Fs takes place according to this mechanism, then the composition of the mixture of resulting congeners also should be determined by the *ortho-para*-oriented influence of the oxygen atoms in molecules of dibenzodioxins and dibenzofurans.

Studying the composition of the mixture of congeners in various samples, we confirmed this hypothesis. This indicates also that in the overwhelming majority of cases the chlorination in thermal sources of dioxins (in various incinerators, stoves, etc.) takes place according to a single mechanism, including the chlorination of previously formed 2,3,7,8-TCDD/F.

Here a new approach to the elucidation of some details in the mechanism of dioxin formation is suggested. The chlorination path depends on the *ortho-para*-directing effects of oxygen and chlorine in the molecule. The *quasi*-steady-state concentrations of products (congeners) in the mixture formed depends on only the activity of a particular site in the reacting dioxin molecule and the rate of 'discharge' (consumption) of the congener formed.

On Fig. 1 shown distribution of congeners in different samples, analysed in different laboratories. See also Table.

To explain the results obtained, we used a model of consecutive chlorination of aromatic rings in TCDD and TCDF, the ancestors of toxic PCDD and PCDF groups, and compared these qualitative data to the experimental data published in terms of "***more-less***". We considered the slopes between two neighbouring points in graphs of the kind shown in Fig. 1. The expression of analytical data in terms of molar concentrations did not affect the results obtained.

In the model, TCDD **1** and TCDF **8** (see Table for the compound numbers) are the starting substances. In the consideration of the sequence (probability) of replacement by chlorine in aromatic rings, only a single assumption will be used: the reaction proceeds as usual electrophilic substitution in the aromatic compounds; therefore, *ortho*-substitution with respect to the oxygen atom is predominant. Correspondingly, isomers that are formed by *ortho*-substitution will exhibit higher concentrations in the mixture. The consumption of a formed isomer at the following step of chlorination will be considered as a correction factor. The resulting mixture of congeners is considered to be standard (independent of the sources of contamination) and *quasi*-stable. As an example, we consider the chlorination of TCDF (Scheme).

At the <u>first step</u> of the reaction, two pentachloro isomers **9** and **10** can be formed. Using the accepted model, it is easy to predict that the amount of isomer **10** formed at the first step will

be significantly greater than that of isomer **9**. To determine the excess of isomer **10** over isomer **9**, the rates of consumption of these isomers at the following step of chlorination should be considered. Furan **9** has two *ortho*-positions accessible to chlorination, whereas furan **10** has only one position of this kind. Hence it follows that **9** will be consumed at the second step of the reaction more rapidly than **10**. Thus, furan **9** will be formed more slowly and consumed more rapidly than furan **10**. As a consequence, the concentration of furan **9** in the formed mixture of congeners will be lower than that of furan **10**. This conclusion ([**10**]>[**9**]) is supported by data obtained by different authors.
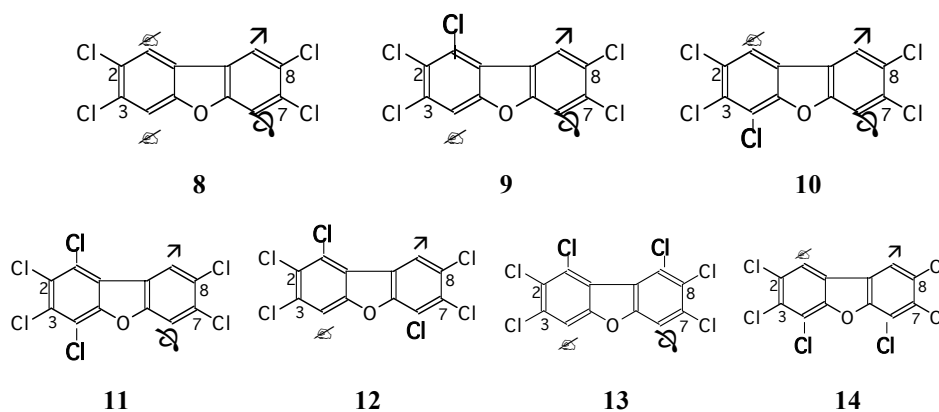
At the second step of chlorination, four hexachloro-derivatives of furan **11**, **12**, **13** and **14** are formed. Among these compounds, furan **13** can be mentioned. To form **13**, the substitution in the *ortho*-position with respect to chlorine in **9** is required. At the same time, the consumption of **13** is maximally facilitated by two active sites in the 4- and 6-positions. Consequently, among the hexachloro isomers, the rates of formation and consumption of isomer **13** are lowest and highest, respectively, and isomer **13** will exhibit the lowest concentration among all hexachloro isomers. This fact is in complete agreement with analytical data. The formation of isomer **11** also requires unfavourable replacement in the 1(*ortho*)-position of isomer **10**. However, isomer **11** will be formed at a higher rate than **13** because, in this case, **11** can also be formed from isomer **9**.

Absolutely such approach to formation rest congeners allows to draw a conclusion that the concentration distribution in the mixture of hexachloro isomers will be as follows: [**11**]≥[**12**]>[**14**]>>[**13**].

At the third step of the reaction, isomer **15** can be produced from three hexachloro isomers **11**, **12** and **14**, and isomer **16**, from isomers **11**, **12** and **13** (in the mixture is always small). The comparison between the rates of discharge of these isomers shows that isomer **16** will be consumed more rapidly than **15**, which has no free *ortho* 6-position favourable for chlorination. Hence it follows that isomer **15** will be formed more rapidly and consumed more slowly than **16**. Therefore, the concentration of isomer **15** will be higher than that of **16**, which is the case. As for the concentration of **17**, it will not be used for evaluating the reliability of the model suggested, as is the case with octachloro dioxin **7**. The reason is that

concentrations of these compounds, as well as concentrations of tetrachloro isomers, can vary significantly for unknown reasons.

The same model can be applied to the chlorination of TCDD.

Thus, the following concentration ratio in the standard *quasi*-stable mixture of toxic PCDD and PCDF congeners was found:

Dioxins
[1]/[2] and [6]/[7] (unknown)
[3]≥[5] (have to define more exactly)
[4]>>[3], [5]

Furans
[8]/([9]+[10]) (unknown)
[10]>>[9]
[11]≥[12]>[14]>>[13]
[15]>[16]
([15]+[16])/[17] (unknown)

For statistical checking, published data on the PCDD/PCDFs contamination of various matrices of both biological (blood, milk and foods) and anthropogenic origin (sludge, slimes, bottom sediments, soils, wastewater were considered [2-8]. The total number of analyses was 70; the total number of points was 1190; 910 points were used for comparison with the predicted composition of the mixture. The slopes for the first and last members of the series were not compared because of the absence of data on the initial concentrations. Deviations were observed for 40 points (4.3%).

For confirmation of the proposed scheme of the formation of a mixture of congeners during the operation of thermal sources of dioxins, we analyzed the data produced in the work [9]. In this work was reviewed 8 major thermal sources of dioxins. Although the resulting data is in percents by congener groups and are presented only in bars, it turned out that in the terms "***more-less***" a perfect match is observed for all sources (Fig. 2). In Fig. 2 we present the data received for 5 sources. For 3 sources, not included in the Figure — *lead smelter, zinc calciner, copper-anod furnance* — we observed three exceptions (one exception for each source). All together 80 datapoints were taken and 3 were exceptions, less than 4%.

Role of electronic effects reveals itself, naturally, and in all other events, available for our analysis. So in work [10] was found that in samples of smoke and soot, selected at fires, from the found chlorophenols (CP) are formed mainly *ortho*- and *para*-substituted CP and di-*orto*- and *orto-para*-dichloro substituted CP.

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Table: Dioxin concentrations in human milk* (pg/g of fat) and bottom sediments from the river Severnaya Dvina** (pg/kg)

Dioxin/ Furan	Codes	Congeners	Salavat	Volgo- grad	Severn. Dvina
1	D_4	2,3,7,8-TCDD	5.3	2.73	22
2	D_5	1,2,3,7,8-PeCDD	3.9	1.47	20
3	$D_6(1)$	1,2,3,4,7,8-HxCDD	1.0	1.14	39
4	$D_6(2)$	1,2,3,6,7,8-HxCDD	2.7	3.26	48
5	$D_6(3)$	1,2,3,7,8,9-HxCDD	0.7	n.d	40
6	D_7	1,2,3,4,6,7,8-HpCDD	3.4	3.98	4420
7	D_8	OCDD	16.4	18.32	3900
8	F_4	2,3,7,8-TCDF	0.8	1.44	54
9	$F_5(1)$	1,2,3,7,8-PeCDF	0.4	0.62	20
10	$F_5(2)$	2,3,4,7,8-PeCDF	6.9	8.37	17
11	$F_6(1)$	1,2,3,4,7,8-HxCDF	3.7	4.64	48
12	$F_6(2)$	1,2,3,6,7,8-HxCDF	2.0	2.32	28
13	$F_6(3)$	1,2,3,7,8,9-HxCDF	0.7	n.d	7
14	$F_6(4)$	2,3,4,6,7,8-HxCDF	0.1	0.82	68
15	$F_7(1)$	1,2,3,4,6,7,8-HpCDF	1.5	1.34	370
16	$F_7(2)$	1,2,3,4,7,8,9-HpCDF	0.1	n.d	41
17	F_8	OCDF	0.3	n.d	1100

*) The data for Salavat received in lab. A.K.D. Liem (RIVM, the Netherlands), for Volgograd in lab. W.A. Traag (RIKILT-DLO, the Netherlands).

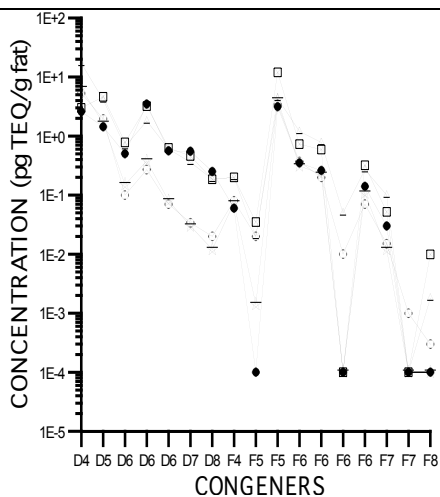**) The data (averaging for 8 samples) received in lab. N.A. Klyuev (IPEE RAS, Russia)

Fig. 1 Contamination of breast milk **[2-6]**

● Honolulu, USA ⊠ Suzdal, Russia
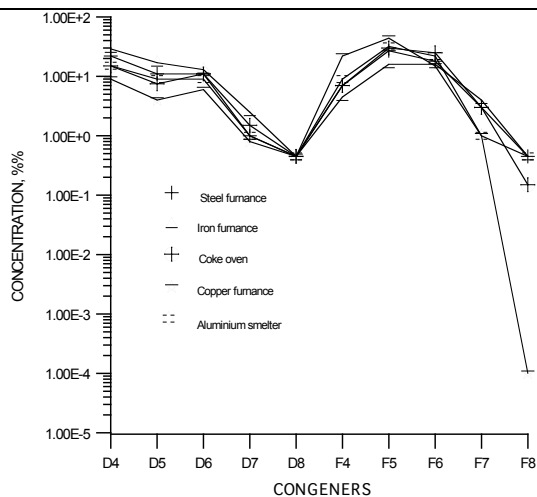⊟ South Vietnam
☐ West Germany ⊙ Salavat, Russia

Fig. 2. Composition of dioxin emission
in Thermal industrial processes [9]