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Specific features of the resonant electron attachment to the chlorodibenzo-*p*-dioxin molecules*

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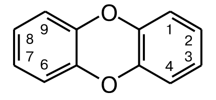
The processes of resonant dissociative electron attachment to the molecules of dibenzo-*p*-dioxin and its chlorinated derivatives containing one to four chlorine atoms (totally eight compounds) were investigated. It was established that 2,3,7-trichlorodibenzo-*p*-dioxin; 1,2,3,4-tetrachlorodibenzo-*p*-dioxin; 1,3,7,8-tetrachlorodibenzo-*p*-dioxin, and 2,3,7,8-tetrachlorodibenzo-*p*-dioxin molecules are chatacterized by positive electron affinities. At electron energies below 2 eV, the electron attachment is caused by the shape resonances. Based on the energy correlation between the negative ion resonance peaks at 3—4 eV and the UV band maxima, it was suggested that electron attachment in this energy region occurs by the mechanism of inter-shell resonance with the molecular singlet-excited states as parents. The possibility for the rearrangement processes resulting in oxy-anionic structures to occur is substantiated.

Key words: negative ion mass spectrometry, resonance dissociative electron attachment, dibenzo-*p*-dioxin, structural rearrangements, inter-shell resonances.

Chlorinated dibenzo-*p*-dioxins (CDD) are extraordinary toxic and very stable compounds. They are hazardous for living organisms and the environment. In this work we studied gas-phase processes of resonant dissociative electron attachment (DEA) to the molecules of unsubstituted dibenzo-*p*-dioxin ($C_{12}O_2H_8$, **1**) and its chloro derivatives, namely, 1-$ClC_{12}O_2H_7$ (**2**), 2-$ClC_{12}O_2H_7$ (**3**), 2,3-$Cl_2C_{12}O_2H_6$ (**4**), 2,3,7-$Cl_3C_{12}O_2H_5$ (**5**), 2,3,7,8-$Cl_4C_{12}O_2H_4$ (**6**), 1,3,7,8-$Cl_4C_{12}O_2H_4$ (**7**), and 1,2,3,4-$Cl_4C_{12}O_2H_4$ (**8**).



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Experimental

Mass spectra were recorded on an MI-1201B magnetic sector mass spectrometer modified for the generation and detection of negative ions (NI), the possibility of operating in the positive ion mode being retained. Experiments were carried out at an accelerating voltage of 2.5 kV and an ionization chamber temperature of 100 °C. The energy resolution of the electron beam (full width at half maximum of the SF_6^- peak) was 0.3 eV. The electron energy scale was calibrated against the maxima of the resonance peaks of the SF_6^-/SF_6 (~0 eV) and NH_2^-/NH_3 (5.65 eV) ions.

The samples of the dioxins under study were white crystalline powders or flakes. To detect the presence of impurities, the positive-ion mass spectra were obtained. Their comparison with the mass spectra retrieved from the database of pure samples* revealed no significant differences between both the peak intensities and the ion composition.

Because of high toxicity, small amounts of the compounds under study were used. A direct inlet system heated to the optimum sublimation temperature of the dioxins (30—80 °C) was used to introduce the samples into the ionization chamber. Earlier,[8] it was shown that some organic chlorine compounds (in particular, alkyl chlorides) can undergo decomposition followed by a release of HCl in the metallic ampoules of the direct inlet system, which causes the appearance of intense peaks of the Cl^- ions in the spectra. Therefore, to avoid undesired catalytic-thermal molecular decomposition upon contact with the metallic tube of the direct inlet system, the samples were placed in thin glassy capillaries that were introduced into the tube.

Results and Discussion

The negative ion DEA mass spectra of compound **1** and two CDD (derivatives of **1**) were studied earlier.[4] The mass spectrum of the most hazardous representative of the series (compound **6**) is shown in Fig. 1. The ion composition of the mass spectra of the other CDD is similar to that of **6**, though the relative peak intensities vary over a wide range. For compounds **1—8**, resonant electron attachment occurs in the energy range from 0 to 12 eV. Here, three regions of the most efficient ion

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* This paper is a continuation of the series of studies of the resonant electron attachment to chlorinated aromatic molecules.[1—7]

* The samples were kindly provided by the Bashkir Republic Ecology Center.

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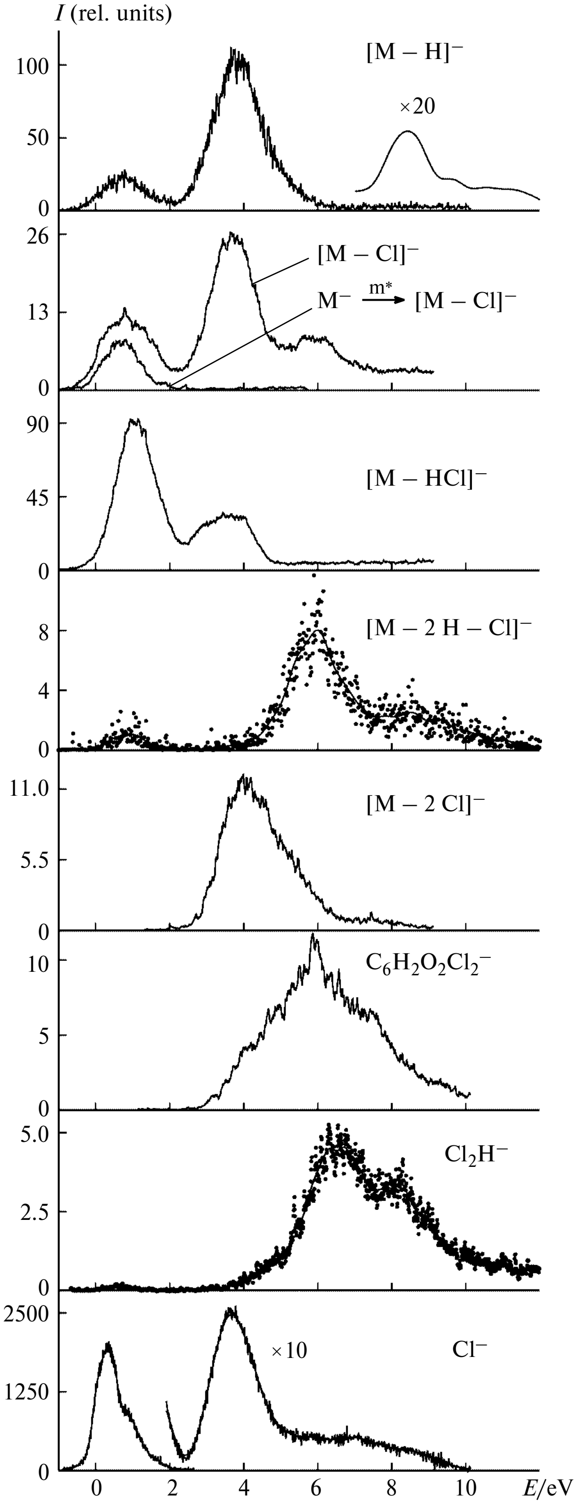

Fig. 1. Negative ion DEA mass spectrum of 2,3,7,8-tetrachlorodibenzo-*p*-dioxin (**6**).

formation are clearly seen. This is similar to the case of benzene derivatives studied earlier.[1,7]

The mass spectra of compounds **5—8** exhibit peaks of negative molecular ions at electron energies ~0 eV, which indicates positive electron affinities of the corresponding molecules. For dioxins **6** and **8**, this is consistent with the results of quantum-chemical calculations.[9]

The most intense peaks in the negative ion mass spectra of the CDD under study are the peaks of the Cl^- and $[M - H]^-$ ions and of the $[M - Cl]^-$ ions (for isomers **6—8**). Similarly to the case of chlorophenol isomers,[6] these peaks appear obeying general laws of the formation of negative ion DEA mass spectra.[10] In particular, the high peak intensity of the Cl^- ions from CDD is due to the high electron affinity of Cl atoms. The $[M - H]^-$ and $[M - Cl]^-$ ions that appear at energies of the order of 4 eV can also be generated by simply cleaving the C—H or C—Cl bonds, respectively, which should also be taken into account. The peaks of the other NI, which are formed *via* elimination of several Cl (and/or H) atoms and fragmentation of the dioxin skeleton involving the C—O bonds (see Fig. 1, $C_6H_2O_2Cl_2^-$ ions), are less intense, because this requires cleavage of several bonds and/or a rearrangement. However, it should be noted that in the mass spectra of compounds **6** and **7** the relative peak intensities of the $[M - HCl]^-$ ions approach those of the $[M - H]^-$ ions. No peak of the $[M - HCl]^-$ ions was detected for compound **8** due to the absence of neighboring H and Cl atoms in the molecular structure of this compound. From this it follows that in the other cases the $[M - HCl]^-$ ions are formed as a result of rearrangement involving elimination of the HCl fragments rather than by successive elimination of the H and Cl atoms. Yet another feature of the mass spectrum of compound **8** is the peak of the Cl_2^- rather than Cl_2H^- ions as is the case of the other polychlorinated compounds of the series under study, which is caused by the same reasons.

No peaks were detected in the low-energy region (0—2 eV) of the negative ion mass spectra of compound **1**.[4] However, this should not be interpreted as the absence of resonant processes, because the electron energy can be insufficiently high for the dissociation to occur. As is known,[11] the appearance energy (AE) of the ions A^- from the molecules AB obeys the energy balance equation, $AE(A^-/AB) = D(A—B) - EA(A^\bullet)$, where $D(A—B)$ is the homolytic bond dissociation energy and $EA(A^\bullet)$ is the electron affinity energy. In accord with this equation, as the Cl atoms possessing high electron affinity (EA(Cl) = 3.6 eV) appear in the structure, a dissociative channel of the formation of Cl^- ions is opened in the low-energy region (see Fig. 1).

In the case of tetra-substituted compounds **6—8**, the formation of the $[M - H]^-$ ions in the low-energy region cannot be explained by an increase in the electron affinity energy of the $[M - H]^\bullet$ fragment caused by the appearance of Cl atoms, because it can hardly reach a value that approaches the C—H bond dissociation energy (the $D(C—H)$ values for dioxins are unavailable; however, we can take the data[12] for chlorobenzene as an estimate, namely, $D(C_6H_4Cl{-}H) \approx 4.8$ eV). Therefore, the formation of the $[M - H]^-$ and $[M - Cl]^-$ ions from molecules **6—8** in the region 0—2 eV can be due to skeletal rearrangement processes that are responsible for transformation of these ions into oxy-anionic structures. The latter, as we showed earlier,[3—6] possess higher electron affinities and are more thermodynamically stable compared to carbanions.

However, in this case it still remains unclear why the negative ion mass spectra of compound **1** and the monochloro-substituted isomers do not exhibit peaks of the $[M - H]^-$ and $[M - Cl]^-$ or other ions (see Ref. 4), which could be formed in a similar way in the energy region under study. We can assume that molecular ions of these compounds, which are formed following the shape resonance mechanism (see below), have short lifetimes that are insufficient for the rearrangement processes to occur. In the case of tetra-substituted isomers **6—8**, the lifetimes of the negative molecular ions M^- are sufficiently long and such rearrangements become possible. This is indirectly indicated by a metastable peak with $m/z \approx 253.66$, which is observed in the mass spectrum of compound **6** and corresponds to "slow" decomposition $M^- \xrightarrow{m^*} [M - Cl]^-$ (see Fig. 1).

Initially, interpretation of both the spectroscopic states of the resonances and the mechanisms of their formation in dioxins was a too complicated problem because of the lack of data obtained using complementary methods electron transmission spectroscopy (ETS) and electron energy loss spectroscopy (EELS). Therefore, to perform a comparative analysis, we had to study a number of simpler compounds, namely, chlorinated benzene derivatives (building blocks for dioxins).[13]

Our recent DEA study[7] of chlorobenzene and chlorophenol isomers revealed that the effective yield curves of the Cl^- ions in the region 0—2 eV have complex contours (Fig. 2, *a*). Based on the ETS and EELS data, it was established that these ions are formed due to two $^2[\pi^*]$-shape resonances between the ground states of the molecules. Therefore, the electrons captured can be attached to two lowest unoccupied π^*-MOs (LUMOs). The effective yield curves of the Cl^- ions from CDD in the same energy region have a similar (see Fig. 2, *b*) and even more complex (for compounds **6—8**) shape (see Fig. 2, *c*). As the number of Cl atoms increases, maxima of the resonance peaks are shifted toward the low-energy region.

If the dioxin molecules are treated as combinations of two phenol fragments, we can suggest that their electronic structure must to some resemble those of chlorobenzene and chlorophenol. Two LUMOs of each phenol fragment form a system of four π^*-MOs of the dioxins and, probably, the more complex shape of the effective yield curves of the Cl^- ions from molecule **7** (see Fig. 2, *c*) is due to electron attachment to these MOs by the shape resonance mechanism ($^2\pi^*$-resonances). In this case, the shift of the peak maxima with an increase in the number of Cl atoms is a consequence of stabilization of the LUMO energies due to the inductive effect (substituent effect). An additional evidence is provided by the presence of the peaks of negative molecular ions in the mass spectra of compounds **5—8**. Apparently, the LUMOs of the corresponding molecules are so stable that they are in the region of negative energies (*i.e.*, the extra electron can be in the bound state).

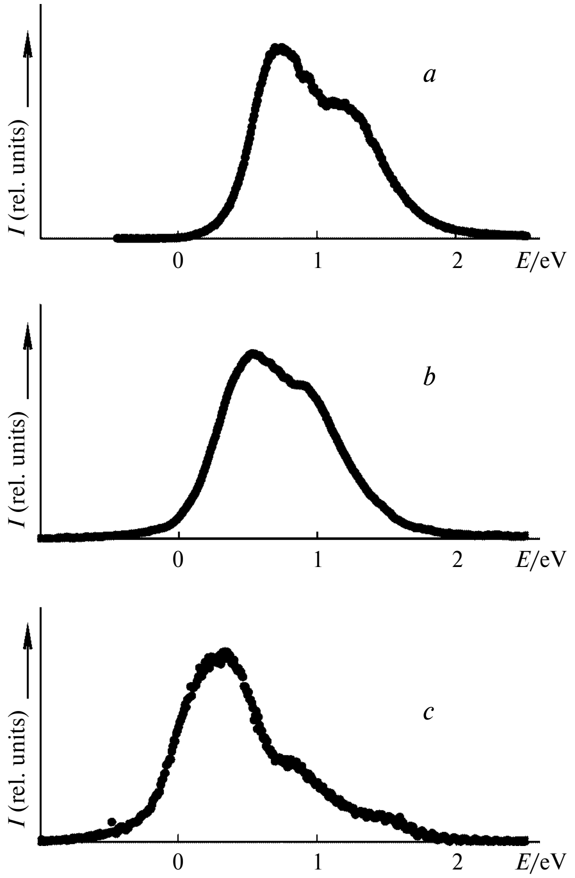

Fig. 2. Effective yield curves of Cl^- ions from *o*-chlorophenol (*a*), 1-chlorodibenzo-*p*-dioxin (*b*), and 1,3,7,8-tetrachlorodibenzo-*p*-dioxin (*c*) in the energy region 0—2.5 eV.

In the next DEA energy region (3—4 eV) the most intense peaks originate from the $[M - H]^-$ and Cl^- negative ions (see Fig. 1). These energies allow molecules to be excited to the triplet and singlet states. Indeed, the energies of maxima of the peaks of these NI exhibit a good correlation with the energies of maxima of the long-wavelength bands in the UV spectra[14] of CDD (in most cases, the deviation is at most 0.3 eV, see Table 1). It should be emphasized that both data sets show a trend toward a shift of the corresponding maxima to the low-energy range with an increase in the number of Cl atoms, though this trend is less pronounced compared to the case of the shape resonances (see above). The above-mentioned UV bands correspond[15] to four $^1[\pi\pi^*]$-excited states, so as-

Table 1. Energy correlation between the resonance peaks of the $[M - H]^-$ and Cl^- negative ions and the band maxima in the UV spectra*

Compound	Negative ion peak maximum energy, $[M - H]^-/Cl^-$	UV band maximum energy[14]
	eV	
1	4.5/—	4.23
2	4.3/4.2	4.22
3	4.2/4.2	4.15
4	4.2/4.1	4.08
5	4.0/3.9	—
6	3.8/3.7	4.00
7	3.9/3.8	—
8	3.9/3.5	3.90

* UV absorption spectra were recorded in a chloroform solution.[14]

signment of the corresponding resonance peak to a particular excited state (or states) is ambiguous. Nevertheless, here we can establish the electron attachment mechanism. Such resonances, whose energies are related to the energies of singlet-excited states of the molecules, were interpreted[16] as inter-shell resonances; namely, an incident free electron excites the molecule, loses its own energy, and is attached to the diffuse totally symmetric s-orbital, which is formed in the field of the singlet-excited molecule. Therefore, formally the singlet-excited state of the molecule serves as the parent state of the $^2[\pi\pi^*s]$-resonance.

We also observed a similar correlation for the series of benzene, phenol, chlorobenzene, and chlorophenol isomers.[7] The above-mentioned types of the resonances were also detected for substituted anizoles and thioanizoles[17] as well as for chlorinated and brominated toluene derivatives.[18] Taken altogether, these data suggest that the inter-shell $^2[\pi\pi^*s]$-resonances are typical of all compounds whose molecules contain aromatic fragments.

The assumption[19] of singlet-excited nature of the resonances in the region between 3 and 4 eV had no substantiation for CDD as yet. In this work it was substantiated using the experimental data obtained by UV spectroscopy. We can assume that it is possible for analogous resonant states to occur at higher energies; however, detection of these states among a large number of closely lying diffuse resonance peaks (see Fig. 1) is still a stubborn problem.

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