Specific features of resonance electron capture by the molecules of dibenzo-*p*-dioxin and its monochlorinated derivatives

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Derivatives of dibenzo-*p*-dioxins are highly toxic and can be accumulated in human and animal tissues.[1] Therefore, it seems urgent to study them by physical, chemical, and biological methods with the purpose of revealing the relation of the steric and electronic structure of these molecules to their biological activity. We studied the dissociative electron capture (DEC) by the molecules of dibenzo-*p*-dioxin (**1**) and 1- (**2**) and 2-monochlorodibenzo-*p*-dioxins (**3**).

The experiment was carried out on an MI-1201 mass spectrometer re-equipped for generation and detection of negative ions under the following conditions: accelerating voltage 4 kV and energy resolution of the electron beam at the half-width 0.4 eV for an electron current of 1 μA.

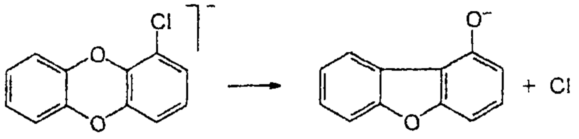
The DEC mass spectrum of compound **1** in the energy region of at least 8 eV is presented by the lines of 17 ions (*m/z* 183, 181, 108, 91, 41, 80, 75, 65, 155, 49, 93, 101, 117, 76, 182, 154, and 141), which sharply distinguishes it from the spectra of condensed aromatic compounds containing a single peak of the fragmentary ions $[M - H]^-$.[2] Another specific feature is the multichannel fragmentation in the energy region of 4 eV (ions with *m/z* 183, 181, 108, 91, and 41 were detected), which is not characteristic of naphthalene, anthracene, and phenathrene.[2] These distinctions are due to the presence of O atoms in the structure of molecule **1** and the possibility of the formation of oxyanions.

The monochlorinated derivatives of **2** and **3** are also characterized by multichannel fragmentation under DEC conditions (Table 1). The spectra of the isomers exhibit substantial differences in the intensities of the peaks of the Cl^- ions (in the energy regions of 0.5 eV and 4 eV they differ by 7 and 2 times, respectively) and $[M - Cl]^-$ (in the energy region of 4 eV they differ by 30 times) (see Table 1). These facts can be explained by a hypothesis about the rearrangement of the molecular ions through the migration of the O atoms to position 1 followed by isomerization of the dioxin framework to the dibenzofuran system (Scheme 1). The elimination of the chlorine atom (ion) results in the formation of the stable oxyanion (oxyradical). In the case of compound **3**, these structures cannot exist due to the low probability of the migration of the O atom to position 2. Analysis of alternative structures of oxyanions and oxyradicals, for example, with an open benzene ring, shows their insolvency because of the too high enthalpy of formation.[3]

Table 1. Relative intensities (I_{rel}) of the yield of ions from compounds **2** and **3** normalized by the intensities of the peaks of the $[M - H]^-$ ions in the region of 8 eV. The maxima of the curves of the effective yield in the energy scale (E_{max}) are given in parentheses.

Ion	I_{rel} (rel. units) (E_{max}/eV)	
	2	**3**
$[M - H]^-$	3.0 (4.4), 1.0 (8.4)	4.7 (4.1), 1 (8.2)
$[M - Cl]^-$	22 (4.5)	0.80 sh (4.0), 2.1 (5.3), 1.1 (7.3)
$[M - HCl]^-$	0.4 (4.3), 0.3 (6.8)	0.9 (3.8)
$C_6H_3O_2Cl^-$	0.3 (4.9), 0.1 (8.8)	0.2 (4.5)
$C_6H_4O_2^-$	0.9 (4.6)	1.1 (4.4)
Cl^-	8700 (0.6), 110 (4.3)	1200 (0.4), 50 (4.0)

Scheme 1



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