Physical Chemistry

Theoretical study of radical anions of polychlorodibenzo-*p*-dioxins

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The electronic and energetic properties of radical anions of dibenzo-*p*-dioxins with different number and positions of chlorine atoms in the molecules are investigated by the AM1 method. The stability of radical anions regarding the elimination of chloride anion is studied. There is no obvious difference in dissociation energies of α- and β-chlorinated dioxins. Isomeric structure of polychlorinated dibenzo-*p*-dioxins influences electron affinity, β-chlorinated dioxins having higher values.

Key words: polychlorodibenzo-*p*-dioxins, electron affinity, eliminaton of chloride anion.

The detoxication of hazardous waste such as dioxins and their congeners is a matter of greater significance at present. The toxicity of dioxin mixtures with different derivatives of polychlorodibenzo-*p*-dioxins (PCDD) can be decreased by changing the number of chlorine atoms in their molecules (*e.g.*, by dechlorination[1,2]). The formation of radical anions (RA) of PCDD is conditoned by their high electron affinity. PCDD are also known to act as electron acceptors in a charge-transfer complex with a receptor in living cells.[3,4] This information has been employed to investigate the electronic structure of PCDD's RA with different numbers and positions of chlorine atoms as well as the stability of RA regarding the elimination of chloride anion. The electronic and energetic properties of PCDD's RA were calculated by the AM1 method. All computations were carried out in Dewar's "half electron" approximation[6,7] using the optimized geometry of the neutral molecules (NM).

1. The electronic characteristics of radical anions of polychlorodibenzo-*p*-dioxins

Polychlorodibenzo-*p*-dioxins (DD) with different number and positions of chlorine atoms in the molecules were examined to study their acceptor properties: unsubstituted DD, 1-monochlorodibenzo-*p*-dioxin (MCDD), 2-MCDD, 2,7-dichlorodibenzo-*p*-dioxin (2,7-DCDD), 2,3-DCDD, 2,3,7,8-tetrachlorodibenzo-*p*-dioxin (2,3,7,8-TCDD), 1,4,6,9-TCDD, 1,2,3,4,6,7,8,9-octachlorodibenzo-*p*-dioxin (OCDD).

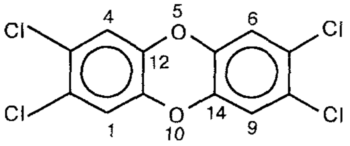

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Table 1. Effective atomic charges in NM and RA calculated by the AM1 method (in units of electron charge)

Atom	DD		2,3-DCDD		2,7-DCDD		2,3,7,8-TCDD	
	NM	RA	NM	RA	NM	RA	NM	RA
C(1)	−0.12	−0.10	−0.11	−0.07	−0.11	−0.09	−0.11	−0.09
C(2)	−0.13	−0.21	−0.06	−0.15	−0.06	−0.14	−0.06	−0.13
C(3)	−0.13	−0.21	−0.06	−0.15	−0.12	−0.20	−0.06	−0.13
C(4)	−0.12	−0.10	−0.11	−0.07	−0.11	−0.09	−0.11	−0.09
O(5)	−0.14	−0.14	−0.13	−0.13	−0.13	−0.13	−0.12	−0.13
C(6)	−0.12	−0.10	−0.11	−0.12	−0.11	−0.09	−0.11	−0.09
C(7)	−0.13	−0.21	−0.12	−0.19	−0.06	−0.14	−0.06	−0.13
C(8)	−0.13	−0.21	−0.12	−0.19	−0.12	−0.20	−0.06	−0.13
C(9)	−0.12	−0.10	−0.11	−0.12	−0.11	−0.09	−0.11	−0.09
O(10)	−0.14	−0.14	−0.13	−0.13	−0.13	−0.13	−0.12	−0.13
C(11)	0.02	−0.10	0.03	−0.08	0.02	−0.08	0.03	−0.05
C(12)	0.02	−0.21	0.03	−0.08	0.03	−0.04	0.03	−0.05
C(13)	0.02	0.21	0.02	−0.03	0.02	−0.07	0.03	−0.05
C(14)	0.02	0.10	0.01	−0.03	0.03	−0.04	0.03	−0.05
X(1)	0.15	0.11	0.17	0.13	0.16	0.12	0.18	0.14
X(2)	0.14	0.09	0.02	−0.07	0.00	−0.09	0.02	−0.06
X(3)	0.14	0.09	0.02	−0.07	0.16	0.11	0.02	−0.06
X(4)	0.15	0.11	0.17	0.13	0.17	0.13	0.18	0.14
X(6)	0.15	0.11	0.16	0.12	0.16	0.12	0.18	0.14
X(7)	0.14	0.09	0.14	0.10	0.00	−0.09	0.02	−0.06
X(8)	0.14	0.09	0.14	0.10	0.16	0.11	0.02	−0.06
X(9)	0.15	0.11	0.16	0.12	0.17	0.13	0.18	0.14

Let's dwell on the charge distribution in PCDD's RA. For this purpose compare atomic charges of four molecules mentioned above: DD, 2,3-DCDD, 2,7-DCDD and 2,3,7,8-TCDD. The values of effective atomic charges of NM and their RA are shown in Table 1. According to Table 1 charge localization in RA is observed mainly at carbon atoms in lateral positions (C(2), C(3), C(7), C(8)), at atoms of the dioxin cycle (C(11), C(12), C(13), C(14) and chlorine atoms as well. There are no obvious changes at carbon atoms C(1), C(4), C(6) and C(9) upon addition of an electron into DD molecules, while the charges at lateral carbon atoms increase 1.5—2.0 fold.

Such behaviour in changing the atomic charges doesn't depend on the number of chlorine atoms in PCDD molecule and its isomeric structure. Similar charge redistribution is even typical of unsubstituted DD.

2. The electron affinity of polychlorinated dioxins

Electron affinity (EA) is a real energetic characteristic of formation of the RA by addition of an electron to a neutral molecule. EA is expressed as the difference of formation enthalpy (ΔH_f) of NM and RA according to the equation

$$\mathrm{EA} = \Delta H_f^{\mathrm{NM}} - \Delta H_f^{\mathrm{RA}} \qquad (1)$$

Formation enthalpies ΔH_f^{RA} were calculated in Dewar's "half electron" approximation using configuration interaction (200 configurations). Table 2 shows that with an increase in the number of chlorine atoms in DD the electron affinity increases too, this relathionship being practically linear. It should be noted that isomeric structure of dioxins also influences EA, β-chlorinated dioxins having higher values. For example, EA equals 22.7 and 26.8 kcal/mol for 1,4,6,9- and 2,3,7,8-TCDD, respectively; the difference of EA values for monochlorinated DDs is small (less than 1 kcal/mol). Calculated values of ΔH_f^{NM}, ΔH_f^{RA} and EA are presented in Table 2.

3. The stability of radical anions of polychlorinated dioxins regarding the elimination of chloride anion

The relative stability of PCDD's RA can be estimated by elimination reaction

$$\mathrm{RX}^- \rightarrow \mathrm{R}\cdot + \mathrm{X}^- + \Delta H_{\mathrm{D_1}}, \qquad (2)$$

where RX⁻ is a radical anion of PCDD; X⁻ is the

Table 2. Formation enthalpies of NM and RA (ΔH_f^{NM} and ΔH_f^{RA}) and electron affinity (EA) of polychlorinated dioxins (kcal/mol)

Molecule	ΔH_f^{NM}	ΔH_f^{RA}	EA
DD	−8.3	−14.1	5.7
1-MCDD	−12.9	−23.3	10.5
2-MCDD	−15.4	−26.5	11.1
2,3-DCDD	−18.7	−37.1	18.4
2,7-DCDD	−21.1	−38.2	17.1
2,3,7,8-TCDD	−29.2	−56.1	26.8
1,4,6,9-TCDD	−22.8	−45.5	22.7
1,2,3,4-TCDD	−22.1	−48.7	26.6
OCDD	−34.7	−71.7	37.1

Table 3. Energetic characteristics of dissociation of PCDD's RA (kcal/mol)

Compound	ΔH_f^{AP}	ΔH_f^R	ΔH_{D_1}
DD	−14.1	–	–
1-MCDD	−23.3	59.1	44.8
2-MCDD	−26.5	55.9	44.8
2,7-DCDD	−38.2	49.7	50.2
2,3-DCDD	−37.1	51.6	51.0
2,3,7,8-TCDD	−56.1	40.4	58.8
1,4,6,9-TCDD	−45.5	49.6	57.4
		49.4*	60.4
1,2,3,4-TCDD	−48.7		
		47.0**	58.0
		36.0*	68.4
OCDD	−71.1		
		34.6**	68.7

Note. With elimination of the chloride anion from α-(*) and β-positions (**). For chloride anion $\Delta H_f = -37.7$ kcal/mol.

chloride anion and ΔH_{D_1} is the dissociation enhthalpy (the difference of the full energies of initial RA and the reaction products). The radicals ($R^{\cdot}$) of PCDD were calculated in two steps: firstly with full geometry optimization within the framework of the unrestricted Hartree-Fock (UHF) method, and then in Dewar's "half electron" approximation using the geometry optimized in the first step and taking into account the configuration interaction. The energetic characteristics of dissociation of PCDD's RA corresponding to the Equation (2) are given in Table 3: the formation enthalpies of RA and $R^{\cdot}$ and ΔH_{D_1} values. The data in Table 3 show that ΔH_{D_1} increases with an increase in the number of halogen atoms (*i.e.*, with an increase in the electron affinity of $R^{\cdot}$).

ΔH_{D_1} values, in kcal/mol, are ~45 for MCDD, 50—51 for DCDD, 57—60 for TCDD and 68—70 for OCDD. Thus the range of change of ΔH_{D_1} values is rather wide and equals 24 kcal/mol. The data presented confirm that an increase in the number of chlorine atoms in PCDD molecule enhances its stability. In comparing dissociation energies (ΔH_{D_1}) of α- and β-chlorinated radicals of PCDD there is no obvious difference, although it is just β-chlorinated dioxins that are usually toxic. There is no difference in ΔH_{D_1} values for MCDDs at all. The largest difference in ΔH_{D_1} values is ~2 kcal/mol between α- and β-chlorinated 1,2,3,4-TCDD.

Two other alternative pathways of elimination from 2,3,7,8-TCDD as the most toxic dioxin have been also considered:

$$RX^- \rightarrow R^- + X\cdot + \Delta H_{D_2} \qquad (3)$$

$$RX^- \rightarrow R^- + H\cdot + \Delta H_{D_3} \qquad (4)$$

Both pathways of dissociation of RA proved to be thermodynamically unfavourable: dissociation energy of 2,3,7,8-TCDD in Equation (3) and (4) equals 82.5 and 93.4 kcal/mol respectively. These values considerably exceed $\Delta H_{D1} = 58.8$ kcal/mol in Equation (2).

Thus, the investigation of radical anions of PCDDs showed the following :

— elimination of radical anions of PCDDs to a radical and chloride anion is thermodynamically more preferable;

— the changes at lateral carbon atoms (2, 3, 7, 8) of phenyl rings in PCDD's RA are 1.5—2.0 times greater than those in NM;

— with an increase in the number of chlorine atoms in PCDD molecule, electron affinity increases. Isomeric structure of PCDDs also influences electron affinity: for the same number of chlorine atoms β- chlorinated DDs have higher EA values;

— there is no obvious difference in dissociation energies in α- and β- chlorinated dioxins (the largest one does not exceed 2 kcal/mol).

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