Physical Chemistry

Electronic structure of polychlorophenols and their carbocations

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Polychlorophenols (PCP) with different numbers of chlorine atoms and their protonated forms have been calculated by the AM1 method with full optimization of geometry. The proton affinity of PCP with various types of coordination of the proton to the molecule has been estimated. The calculations show that the proton affinity averaged over isomers decreases monotonically as the number of chlorine atoms increases. Based on the calculations of the carbocations, the σ^+ constant of the OH-substituent at the *ipso*-position is equal to 0.69. There is fair agreement between the relative energies of the isomers of the carbocations determined from the constants of the substituents and calculated by the AM1 method. These energies can be recommended for qualitative estimation of the proton affinity in definite positions of aromatic molecules with Cl- and OH-substituents.

Key words: quantum-chemical calculations; AM1 method; polychlorophenols; protonated forms; σ^+ constant of substituent; proton affinity.

Polychloroaromatic compounds (PCAC) are the most important sources of environmental contamination with ecotoxicants such as polychlorodibenzo-*p*-dioxin (PCDD). Polychlorophenols (PCP) form PCDD in rather high yields under the conditions of pyrolysis.[1] A two-step scheme for the preparation of highly reactive 2-ketocarbenes (precursors of PCDD) from PCP has been analyzed on the basis of quantum-chemical calculations.[2] These processes may occur in alkaline media at high temperatures. It was shown that the acidity of PCP, which is characterized by the ΔH of proton detachment, increases as the number of chlorine atoms in the PCP molecules increases.

In the present work, we used quantum-chemical calculations to study the energetics of the transformations of PCP in strongly acidic media where a PCP molecule may capture a proton to form a benzenium ion. This may occur in strongly acidic solutions and at acidic centers of zeolites. The calculations were performed by the AM1 method using the AMPAC program[3] on an ES-1066 computer with full optimization of the molecular geometry.

The main results of the calculations of neutral molecules of PCP are listed in Table 1: the enthalpies of formation (ΔH_f), HOMO (higher occupied molecular orbital) and LUMO (lower unoccupied molecular or-

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Table 1. Results of calculations of PCP by the AM1 method

Compound	ΔH_f /kcal mol^{-1}	E_{HOMO} /eV	E_{LUMO} /eV	μ/D
C_6H_5OH	−22.2	−9.12	0.39	1.23
2-ClC_6H_4OH	−28.7	−9.26	0.03	0.94
3-ClC_6H_4OH	−29.2	−9.30	0.04	0.24
4-ClC_6H_4OH	−29.3	−9.13	0.10	1.47
2,3-$Cl_2C_6H_3OH$	−34.0	−9.43	−0.26	0.84
2,4-$Cl_2C_6H_3OH$	−35.0	−9.27	−0.25	0.40
2,5-$Cl_2C_6H_3OH$	−35.1	−9.41	−0.33	1.14
2,6-$Cl_2C_6H_3OH$	−32.4	−9.38	−0.27	1.78
3,4-$Cl_2C_6H_3OH$	−34.6	−9.26	−0.20	1.36
3,5-$Cl_2C_6H_3OH$	−35.4	−9.54	−0.29	1.41
2,3,4-$Cl_3C_6H_2OH$	−38.9	−9.38	−0.47	1.01
2,4,5-$Cl_3C_6H_2OH$	−40.0	−9.39	−0.56	1.31
2,4,6-$Cl_3C_6H_2OH$	−38.3	−9.39	−0.50	1.06
2,5,6-$Cl_3C_6H_2OH$	−37.3	−9.54	−0.56	2.01
3,4,5-$Cl_3C_6H_2OH$	−39.2	−9.42	−0.47	2.06
3,5,6-$Cl_3C_6H_2OH$	−39.9	−9.59	−0.58	0.42
2,3,4,5-Cl_4C_6HOH	−43.3	−9.50	−0.75	1.22
2,3,5,6-Cl_4C_6HOH	−41.8	−9.63	−0.82	1.07
2,4,5,6-Cl_4C_6HOH	−41.7	−9.49	−0.77	1.78
2,3,4,5,6-Cl_5C_6OH	−44.7	−9.58	−0.98	1.24

bital) energies, and dipole moments. Monochlorophenols are characterized by weak dependences of ΔH_f on the position of the chlorine atom, and position 4 is the most favorable. For dichlorophenols, the 3,5-Cl_2 isomer is the most energetically stable, and the 2,5-Cl_2 isomer is the least stable. The other isomers possess intermediate energies. The 2,4,5-Cl_3 isomer is the most stable of the trichlorophenols, and 2,3,4,5-Cl_4 isomer is the most stable of the tetrachlorophenols.

The dipole moments of PCP isomers differ significantly: for example, they vary from 0.42 to 1.06 D for trichlorophenols. A simple analysis of Table 1 shows that the dipole moments lie in the range 1.2—1.5 D for the most stable PCP isomers.

In the series of compounds considered, the value of E_{HOMO} varies irregularly as the number of chlorine atoms in the PCP molecule increases, while E_{LUMO} decreases regularly. The range of the variation of E_{LUMO} is ~1.4 eV from phenol to pentachlorophenol.

The protonation energies of PCP molecules were calculated according to the scheme

$$PCP + H^+ \rightarrow PCP \cdot H^+ + \Delta H_p \qquad (1)$$

by the AM1 method with the full optimization of geometric parameters, and different types of proton attachment were considered. The binding of the proton with the oxygen atom of the OH group is extremely unfavorable and therefore, will not be discussed. The calculated energies of the protonation of PCP at the carbon atoms of the aromatic cycle are listed in Table 2. For simplicity, the formulas of the compounds in Table 2 are given in an abbreviated form. For example, the 3-H,1-OH,2,4,5-$Cl_3C_6H_2^+$ arenium ion is designated as 3-H,2,4,5-Cl_3, and 2-H,1-OH,$C_6H_5^+$ is denoted as 2-H.

In all of the cases, as has been observed for arenium ions of polychlorobenzenes[4] and polyfluorobenzenes,[5] the carbon atom to which the proton is attached becomes approximately sp^3-hybridized, and the substituents at this C-atom (H, Cl or OH) are situated on different sides of the plane of the aromatic molecule. The energy of PCP protonation (ΔH_p) decreases monotonically as the number of chlorine atoms in the molecule increases. This behavior is exactly the opposite to that of polychlorobenzenes (PCB), whose proton affinity[4] increases as the number (n) of chlorine atoms increases from 1 to 5. It is interesting to compare some quantitative parameters. The decrease in ΔH_p for PCP on going from $n = 1$ to $n = 5$ is 19 kcal mol^{-1}, whereas the corresponding increase in ΔH_p for PCB is close to 10 kcal mol^{-1}.

Like in the case of polyfluorobenzenes,[5] let us try to determine the constants of substituents at the *ipso*-position from the quantum-chemical calculations of the relative energies of the isomers of benzenium ions. These constants are absent in the works on the correlation analysis (see, *e.g.*, Ref. 6). Using the formula

$$\frac{\Delta E}{RT} \log e = \rho \sum_i \sigma_i , \qquad (2)$$

where ΔE is the difference between the energies of formation of the benzenium ion isomers and $\rho = 11.7871$ at $T = 263$ K,[5] we found $\sigma^+_{ipso} = 0.69$ for the OH-substituent. Now, using the values of σ^+ for Cl and OH in different positions, which have been partly determined previously[6] ($\sigma^+_{p,Cl} = 0.11$; $\sigma^+_{m,Cl} = 0.40$; $\sigma^+_{o,Cl} = 0.18$; $\sigma^+_{ipso,Cl} = 0.60$; $\sigma^+_{p,OH} = -0.92$; $\sigma^+_{m,OH} = 0.12$; and $\sigma^+_{o,OH} = -0.80$) and were partly established by formula (2) taking into account $\sigma^+_{ipso,OH} = 0.69$ and ΔE from the calculations by the AM1 method, one can estimate the relative energies of the isomers of benzenium ions of PCP by the correlation

$$\Delta E_{ca} = 14.2759 \sum_i \sigma_i , \qquad (3)$$

to which $T = 273$ K corresponds. Table 2 attests that ΔE_{ca} calculated by this correlation analysis agree well with those calculated by the AM1 method (ΔE_{AM1}).

The σ^+ constants of the substituents (Cl and OH) presented above can be used for the analysis of more complex protonated systems. Let us consider, for example, the directions of the most favorable protonation for 2,3,7,8-TCDD (tetrachlorodibenzo-*p*-dioxin) (**1**), 1,4,6,9-TCDD (**2**), and 2,3,7,8-TCDF (tetrachlorodibenzofuran) (**3**). Let us assume in the determination of σ^+ that the oxygen atom in dioxins and dibenzofurans is equivalent to a OH-group. Then the method of the correlation analysis shows that the proton affinity is higher for compound **1** (positions 1, 4, 6, or 9) than for derivative **2** (positions 2, 3, 7, and 8). In molecule **3**, position 4 is the most favorable for proton attachment.

Table 2. Relative protonation energies of PCP according to the data of the AM1 method and correlation analysis

Ion of PCP	ΔE_{AM1} /kcal mol^{-1}	ΔE_{ca}	Ion of PCP	ΔE_{AM1} /kcal mol^{-1}	ΔE_{ca}
1-H	23.0	23.0	1-H,4-Cl	15.2	17.1
2-H	3.1	1.7	2-H,4-Cl	0.0(−133.1)	0.0
3-H	13.8	14.9	3-H,4-Cl	7.7	10.0
4-H	0.0(−141.0)	0.0	4-H,4-Cl	3.0	1.1
1-H,2-Cl	19.3	19.8	1-H,3-Cl	25.9	25.4
2-H,2-Cl	8.9	4.6	2-H,3-Cl	3.6	1.0
3-H,2-Cl	11.3	11.7	3-H,3-Cl	24.0	20.1
4-H,2-Cl	0.0(−136.4)	0.0	4-H,3-Cl	0.1	−0.7
5-H,2-Cl	11.5	10.7	5-H,3-Cl	17.3	17.3
6-H,2-Cl	0.7	1.7	6-H,3-Cl	0.0(−138.7)	0.0
1-H,2,3-Cl_2	22.0	22.3	1-H,3,4-Cl_2	21.0	21.3
2-H,2,3-Cl_2	9.4	3.9	2-H,3,4-Cl_2	3.2	1.0
3-H,2,3-Cl_2	21.0	17.0	3-H,3,4-Cl_2	19.8	17.0
4-H,2,3-Cl_2	0.1	−0.7	4-H,3,4-Cl_2	5.6	2.1
5-H,2,3-Cl_2	14.5	13.1	5-H,3,4-Cl_2	14.1	14.1
6-H,2,3-Cl_2	0.0(−135.2)	0.0	6-H,3,4-Cl_2	0.0(−134.6)	0.0
1-H,2,6-Cl_2	14.4	16.7	1-H,2,5-Cl_2	21.9	23.0
2-H,2,6-Cl_2	8.7	4.6	2-H,2,5-Cl_2	7.7	3.6
3-H,2,6-Cl_2	6.9	7.6	3-H,2,5-Cl_2	14.0	14.8
4-H,2,6-Cl_2	0.0(−131.9)	0.0	4-H,2,5-Cl_2	0.0(−134.2)	0.0
5-H,2,6-Cl_2	7.7	7.6	5-H,2,5-Cl_2	21.2	17.4
6-H,2,6-Cl_2	6.2	4.6	6-H,2,5-Cl_2	0.8	1.7
1-H,2,4-Cl_2	14.1	14.0	1-H,3,6-Cl_2	20.4	23.0
2-H,2,4-Cl_2	8.0	2.9	2-H,3,6-Cl_2	3.4	1.7
3-H,2,4-Cl_2	7.6	6.9	3-H,3,6-Cl_2	18.6	16.7
4-H,2,4-Cl_2	5.4	1.1	4-H,3,6-Cl_2	0.0(−134.2)	0.0
5-H,2,4-Cl_2	8.0	5.9	5-H,3,6-Cl_2	13.2	14.8
6-H,2,4-Cl_2	0.0(−131.2)	0.0	6-H,3,6-Cl_2	5.1	3.6
1-H,3,5-Cl_2	28.5	29.6	1-H,2,4,6-Cl_3	6.1	8.1
2-H,3,5-Cl_2	2.4	1.0	2-H,2,4,6-Cl_3	4.7	0.1
3-H,3,5-Cl_2	26.5	24.3	3-H,2,4,6-Cl_3	0.0(−123.7)	0.0
4-H,3,5-Cl_2	0.0(−136.4)	0.0	4-H,2,4,6-Cl_3	2.0	−1.6
1-H,2,3,4-Cl_3	17.4	18.1	1-H,3,5,6-Cl_3	23.1	26.1
2-H,2,3,4-Cl_3	8.8	3.9	2-H,3,5,6-Cl_3	2.5	0.7
3-H,2,3,4-Cl_3	17.1	13.8	3-H,3,5,6-Cl_3	21.4	19.8
4-H,2,3,4-Cl_3	5.5	2.1	4-H,3,5,6-Cl_3	0.0(−133.0)	0.0
5-H,2,3,4-Cl_3	11.5	10.0	5-H,3,5,6-Cl_3	22.7	20.8
6-H,2,3,4-Cl_3	0.0(−131.3)	0.0	6-H,3,5,6-Cl_3	5.1	3.6
1-H,2,4,5-Cl_3	16.9	17.1	1-H,2,5,6-Cl_3	17.0	19.8
2-H,2,4,5-Cl_3	7.2	1.9	2-H,2,5,6-Cl_3	7.6	3.6
3-H,2,4,5-Cl_3	10.2	10.0	3-H,2,5,6-Cl_3	9.8	10.7
4-H,2,4,5-Cl_3	5.1	1.1	4-H,2,5,6-Cl_3	0.0(−130.9)	0.0
5-H,2,4,5-Cl_3	17.2	11.8	5-H,2,5,6-Cl_3	16.9	13.6
6-H,2,4,5-Cl_3	0.0(−130.0)	0.0	6-H,2,5,6-Cl_3	6.0	4.6
1-H,2,3,5-Cl_3	24.6	25.4	1-H,2,3,6-Cl_3	17.0	19.8
2-H,2,3,5-Cl_3	8.0	2.9	2-H,2,3,6-Cl_3	9.1	4.6
3-H,2,3,5-Cl_3	23.6	20.1	3-H,2,3,6-Cl_3	15.9	13.6
4-H,2,3,5-Cl_3	0.01	−0.7	4-H,2,3,6-Cl_3	0.0(−131.0)	0.0
5-H,2,3,5-Cl_3	24.1	19.1	5-H,2,3,6-Cl_3	10.7	10.7
6-H,2,3,5-Cl_3	0.0(−133.1)	0.0	6-H,2,3,6-Cl_3	5.0	3.6
1-H,3,4,5-Cl_3	21.3	24.4	1-H,2,3,5,6-Cl_4	19.5	23.0
2-H,3,4,5-Cl_3	0.0(−130.9)	0.0	2-H,2,3,5,6-Cl_4	7.8	3.6
3-H,3,4,5-Cl_3	19.9	20.1	3-H,2,3,5,6-Cl_4	18.7	16.7
4-H,3,4,5-Cl_3	2.9	2.1	4-H,2,3,5,6-Cl_4	0.0(−129.8)	0.0
1-H,2,3,4,5-Cl_4	20.1	21.3	1-H,2,4,5,6-Cl_4	7.2	12.8
2-H,2,3,4,5-Cl_4	7.8	2.9	2-H,2,4,5,6-Cl_4	2.2	0.7
3-H,2,3,4,5-Cl_4	19.6	17.0	3-H,2,4,5,6-Cl_4	1.3	4.7
4-H,2,3,4,5-Cl_4	5.2	2.1	4-H,2,4,5,6-Cl_4	0.0(−121.8)	0.0
5-H,2,3,4,5-Cl_4	20.5	16.0	5-H,2,4,5,6-Cl_4	8.2	7.6
6-H,2,3,4,5-Cl_4	0.0(−130.1)	0.0	6-H,2,4,5,6-Cl_4	0.1	1.7

Table 2. *Continued*

Ion of PCP	ΔE_{AM1} /kcal mol^{-1}	ΔE_{ca}	Ion of PCP	ΔE_{AM1} /kcal mol^{-1}	ΔE_{ca}
1-H,2,3,4,6-Cl_4	7.6	12.1	1-H,3,4,5,6-Cl_4	16.2	21.2
2-H,2,3,4,6-Cl_4	3.5	1.0	2-H,3,4,5,6-Cl_4	0.0(−127.6)	0.0
3-H,2,3,4,6-Cl_4	7.3	6.9	3-H,3,4,5,6-Cl_4	15.2	16.0
4-H,2,3,4,6-Cl_4	0.3	−0.7	4-H,3,4,5,6-Cl_4	2.7	2.1
5-H,2,3,4,6-Cl_4	2.7	4.0	5-H,3,4,5,6-Cl_4	16.7	17.0
6-H,2,3,4,6-Cl_4	0.0(−122.3)	0.0	6-H,3,4,5,6-Cl_4	2.4	2.9
1-H,2,3,4,5,6-Cl_5	10.6	15.3	2-H,2,3,4,5,6-Cl_5	0.0(−122.3)	0.0
3-H,2,3,4,5,6-Cl_5	11.6	10.0	4-H,2,3,4,5,6-Cl_5	0.2	−0.7

Note. Absolute values of the enthalpies of protonation in kcal mol^{-1} are given in parentheses.

Table 3. Results of the calculations of protonated xenobiotics of the dioxin type

Arenonium ion	ΔH_f	ΔH_p
4-H,2,3,7,8-TCDD	167.0	−128.415
3-H,2,3,7,8-TCDD	171.0	−124.415
1-H,2,3,7,8-TCDF	197.9	−130.515
2-H,2,3,7.8-TCDF	204.8	−123.615
3-H,2,3,7,8-TCDF	202.9	−125.515
4-H,2,3,7,8-TCDF	200.5	−127.95

Now let us consider the quantum-chemical calculations by the AM1 method that were performed for these molecules with the full optimization of their geometry. The enthalpies of formation of the arenium ions of the xenobiotics considered and the protonation energies calculated with the use of the calculation data on neutral molecules[7] are listed in Table 3. The results of the correlation analysis agree well with those obtained by the AM1 method.

Thus, the studies performed show that the proton affinity of polychlorophenols decreases as the number of chlorine atoms increases, and the relative protonation energies determined from the correlation constants of the substituents agree well with the data of the calculations by the AM1 method. Therefore, a simple correlation analysis is suitable for quantitative estimates of the proton affinity of certain centers of aromatic molecules with Cl- and OH-substituents.

References

1. C. G. Choudhry and O. Hutzinger, *Mechanistic Aspects of the Thermal Formation of Halogenated Organic Compounds Including Polychlorined Dibenzo-p-Dioxins*, Gordon and Brech Science Publ., New York, 1983.
2. A. V. Fokin, Yu. A. Borisov, N. I. Raevskii, and A. F. Kolomiets, *Izv. Akad. Nauk, Ser. Khim.*, 1992, 1740 [*Bull. Russ. Acad. Sci., Div. Chem. Sci.*, 1992, **41**, 1346 (Engl. Transl.)].
3. QSPE program 506.
4. Yu. A. Borisov and R. M. Kurbanbaev, *Izv. Akad. Nauk, Ser. Khim.*, 1993, 1213 [*Russ. Chem. Bull.*, 1993, **42**, 1156 (Engl. Transl.)].
5. Yu. A. Borisov and R. M. Kurbanbaev, *Izv. Akad. Nauk, Ser. Khim.*, 1993, 1878 [*Russ. Chem. Bull.*, 1993, **42**, 1792 (Engl. Transl.)].
6. V. A. Koptyug, *Arenonievye iony. Stroenie i reaktsionnaya sposobnost'* [*Arenonium Ions. Structure and Reactivity*], Nauka, Novosibirsk, 1983, 269 (in Russian).
7. A. V. Fokin, Yu. A. Borisov, V. G. Enchev, N. I. Raevskii, and N. P. Vorob'eva, *Dokl. Akad. Nauk SSSR*, 1991, **316**, 1165 [*Dokl. Chem.*, 1991, **316** (Engl. Transl.)].

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