

Communications

Prediction of Reaction Intermediate(s) of Pentachlorophenol Degradation: An Application of Atomic Charge Distribution Calculations

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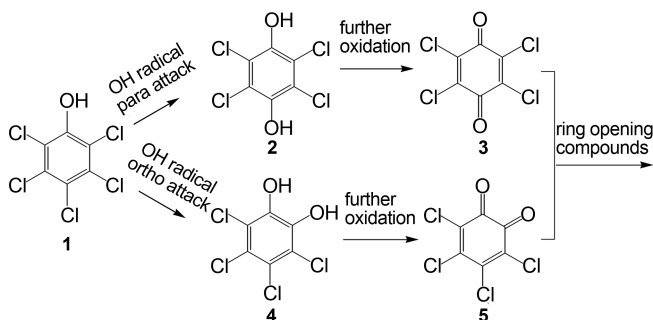
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With the availability of rapid *ab initio* calculations for molecules with small computers, it is now possible to obtain very accurate molecular structural parameters, total energies and atomic charges with relatively high basis sets. It was very valuable to predict the reaction site(s) of oxidation reactions with these data.^{1,2} Through the previous studies^{1,2} we recognized that atomic charge distribution calculations could be useful for predicting reaction intermediate(s) and mechanism as demonstrated in this paper.

Pentachlorophenol (PCP, **1**) has been widely used throughout the world as preservative and biocide and has been known as an acute toxic material.³ The degradation of PCP was extensively investigated by various methods⁴⁻¹⁰ and the degradation pathway of PCP under ozonation and the resulting intermediates were well identified.^{6,7}

In this study, we report an application of atomic charge distribution calculations, especially CHelpG¹¹ and MK^{12,13} (Merz-Singh-Kollman) methods, to predict the intermediates produced during the degradation of PCP. These calculations will also provide us deeper understanding of reaction intermediates. In order to predict the most possible intermediates at the early steps of the oxidation on PCP, we initially established the reaction pathways of PCP oxidation referring to the results of a previous study.⁶ This is summarized in



Scheme 1. Proposed reaction pathways for PCP.

Table 1. Calculated total energies and atomic charges of PCP and its radical reaction products^a

Compound	E^b	Position	Charges	
			MK	CHelpG
 1	-2605.481703 (-2605.427849)	1	0.491	0.351
		2	-0.234	-0.126
		3	0.102	0.136
		4	-0.056	-0.038
		5	0.082	0.096
		6	-0.160	-0.051
 2	-2221.118890 (-2221.052036)	1	0.419	0.308
		2	-0.186	-0.081
		3	-0.062	-0.009
		4	0.410	0.312
		5	-0.179	-0.085
		6	-0.066	-0.006
 3	-2219.896058 (-2219.851662)	1	0.774	0.607
		2	-0.185	-0.092
		3	-0.185	-0.091
		4	0.774	0.607
		5	-0.187	-0.091
		6	-0.187	-0.092
 4	-2221.118710 (-2221.051496)	1	0.140	0.153
		2	-0.095	-0.039
		3	0.052	0.023
		4	-0.011	0.060
		5	-0.113	-0.069
		6	0.370	0.309
 5	-2219.882211 (-2219.838367)	1	0.463	0.452
		2	-0.110	-0.111
		3	0.020	0.073
		4	0.017	0.073
		5	-0.108	-0.111
		6	0.463	0.452

^aCharges in electron, energies in Hartree. ^bThe values of energy in parentheses are the ones of zero-point correction.

Scheme 1.

The plane figures of all the compounds in Scheme 1 were drawn using the ChemDraw program and the three-dimensional features of these figures were confirmed with the Chem3D program using the CS Chem3D program package.¹⁴ Using this Chem3D program, the Gaussian input files were created to run the Gaussian-03 program.¹⁵ We carried out the density functional theory calculations with the Becke's exchange functional (BLYP)^{16,17} to obtain the optimized structures of molecules at the level of BLYP/6-311++G(d,p). The atomic charge distributions were calculated using the CHelpG¹¹ and MK^{12,13} methods with these optimized structural parameters. The calculated atomic charges on the atoms at important positions are listed in Table 1.

In Table 1 the carbon atoms at *ortho*- and *para*-positions of PCP have negative charges. Therefore the electrophilic attack can be occurred at *ortho*- and/or *para*-position of PCP. If the oxidation occurred at *para*-position, the product will be 2,3,5,6-tetrachloro-*p*-hydroquinone (**2**) and 2,3,5,6-tetrachloro-*p*-benzoquinone (**3**). If the oxidation occurred at *ortho*-position, the product will be 2,3,4,5-tetrachlorocatechol (**4**) and 2,3,4,5-tetrachloro-*o*-hydroquinone (**5**).

The atomic charges of PCP were obtained as -0.126 and -0.234 for position 2, -0.051 and -0.160 for position 6 as -0.038 and -0.056 for position 4 of the benzene ring from CHelpG and MK calculations, respectively. With these values the electrophilic attack on the carbon atom of position 2 or 6 could be more favorable than on that of position 4. Otherwise, the zero-point correction energies of compound **4** and **5** are higher than those of compound **2** and **3** by 0.338 and 8.34 kcal/mol. This means the oxidation at position 4 is little more favorable than at position 2 with the aspect of the stabilization by enthalpy effect. Therefore in a kinetically favorable reaction condition, the oxidation at position 2 would be more advantageous. And in an energetically favorable reaction condition, the oxidation at position 4 is more advantageous. This well coincides with the results of Benitez *et al.*⁶ Benitez *et al.* had shown the OH radical addition at the *ortho*-position of PCP was more favorable than the *para*-position in UV irradiated reaction. But in a high pressure ozone condition, the OH radical addition at *para*-position was advantageous. These results show that the atomic charge distribution calculation, in addition to enthalpy difference information of molecules, can provide us with a more profound understanding about reaction pathways and can be a useful tool for predicting reaction

intermediate(s) and final product(s), especially for the competitive reaction.

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