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Prediction of radical reaction site(s) of polycyclic aromatic hydrocarbons by atomic charge distribution calculation using the DFT method

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ABSTRACT

The atomic charge distributions on each atom of the PAHs were obtained using the CHelpG and MK methods with the optimized structural parameters determined by DFT calculation at the level of BLYP/6-311++G(d,p). By comparing the experimentally obtained oxidation position(s) and the calculated atomic charges on carbon atoms of PAHs, we found that the oxidation reaction mainly occurred at the carbon(s) having the higher atomic charges.

1. Introduction

Polycyclic aromatic hydrocarbons (PAHs) in the environment are harmful to humans and animals because of their biological toxicity and recalcitrant and bio-contamination properties.[1,2] On the other hand, in term of theoretical studies, a few quantum mechanical approaches have been used to study the decomposition mechanism of recalcitrant materials such as PAHs.[3,4] Reports have shown the following: the C–Cl bond dissociation energy calculation during the ultraviolet decomposition of pentachlorophenol[3]; the electron-beam decomposition mechanism of pentachlorobenzene using the B3LYP and cc-pVTZ ground state calculation[4]; the ultraviolet decomposition mechanism of mono-, di-, and tri-chlorophenol using the density functional theory (DFT) methods[5] and the Frontier electron density calculation by the PM3 method.[6] However, quantum mechanical studies have never been carried out on the position where the decomposition on the objective materials occurs, except our previous[6] study.

PAHs exist as various types of compounds. If we accurately examine the relationship between PAHs and the decomposed products of PAHs by the quantum mechanical method, the result will be very useful to predict the radical reaction product(s) of many other PAHs. Therefore, we investigated the position(s) of the radical reaction site(s) on PAHs and why the reaction occurs at those specific positions using atomic charge distribution calculations for the first time. The results of this study are reported herein.

2. Results and discussions

2.1. Products of Fenton oxidation of PAHs

Fenton oxidation occurs when the reagent is attacked by radicals, such as $^{\cdot}OH$ and $^{\cdot}O_2H$, which are produced during a consecutive Fenton reaction such as the following.[7]

The result of Fenton oxidation on benzo(a)pyrene (BAP), which is the most recalcitrant and carcinogenic compound[8] in this study, is represented in Figure 1. The GC–MS total ion chromatography (TIC) of Fenton-oxidized BAP is shown in Figure 1a, and the sub-fragment patterns of the strongest peak at a retention time of 28.9 min of Figure 1a are shown in Figure 1b. The analysis of the fragment pattern of Figure 1b revealed three products of BAP oxidation: benzo(a)pyrene-1,6-dione, benzo(a)pyrene-3,6-dione, and benzo(a)pyrene-6,12-dione.

For qualitative analysis, we confirmed these products by conducting a spike test using both the GC–MS and HPLC-UV methods. We also analyzed the resultants of the Fenton oxidation on acenaphthylene (ACEL), fluorene (FLU), anthracene (ANT), and benz(a)anthracene (BAA) in the same way. The products of Fenton oxidation of each PAH were examined as quinine-type compounds. The results resembled those of one of author's previous study.[6] The experimental results are summarized in Table 1.

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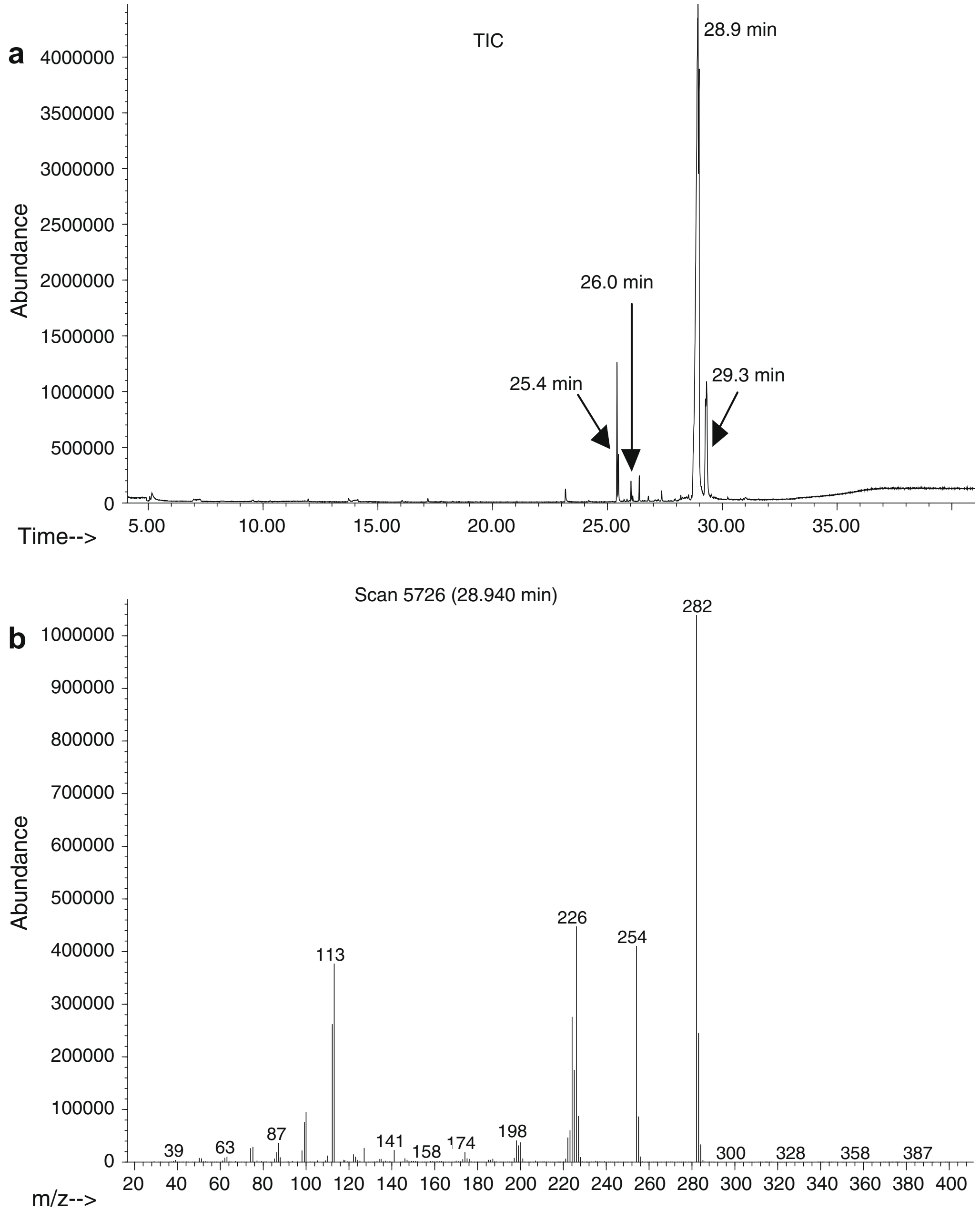


Figure 1. (a) TIC of GC–MS after Fenton oxidation of BAP and (b) library comparison of peaks at retention time of 28.9 min.

2.2. Calculated atomic charges of carbons in PAHs

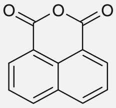
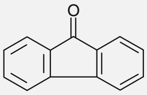
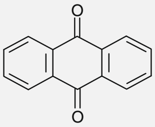
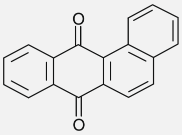
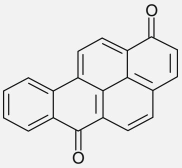
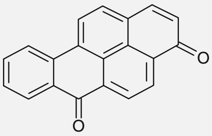
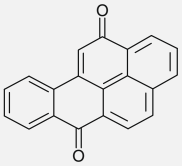
It would be very useful to predict where the Fenton oxidation site(s) will be by merely looking at the electron density of each carbon in PAH. Therefore, we investigated the charge distributions on the carbons in the molecules by atomic charge distribution calculations. Table 2 shows the atomic charges of carbon atoms that were determined by the BLYP/6-311++G(d,p) level calculation for all five PAHs considered. The atomic charges were calculated using both the BLYP and B3LYP methods with the 6-311++G(d,p) basis set, and the resulting atomic charges were similar in both calculations. Therefore, we only report the values of BLYP/6-311++G(d,p) herein.

In Table 2, the Merz-Singh-Kollman (MK) charges of positions 1 and 2 of ACEL are higher than those of the other positions. Therefore, oxidation can occur more easily at positions 1 and 2 of ACEL. This finding agrees with the experimental results where the ACEL Fenton oxidation produced 1,8-naphthalic anhydride.

In the case of FLU, the previous Frontier electron density calculation[6] results in the highest f_r values at positions 2 and 7 and did not agree with the experimental results. However, in this study, we found that the MK charge of position 9 was higher than those of the other positions. This result completely coincides with the experimentally obtained 9-fluorenone, which is the product of FLU oxidation. The MK and CHelpG charges of positions 9 and 10 of ANT and positions 7 and 12 of BAA showed higher absolute values than those of others. These results also completely coincide with the experimentally obtained 9,10-anthracenedione and benz(a)anthracene-7,12-dione, which were the products of ANT and BAA oxidation, respectively.

In the case of BAP, the MK and CHelpG charges at position 6 were remarkably higher, at −0.562 and −0.383, respectively, than

Table 1
PAHs and products of Fenton oxidation on PAHs

PAH	Reaction product	
Acenaphthylene	1,8-Naphthalic anhydride	
Fluorene	9-Fluorenone	
Anthracene	9,10-Anthracenedione	
Benz(a)anthracene	Benz(a)anthracene-7,12-dione	
Benzo(a)pyrene	Benzo(a)pyrene-1,6-dione	
	Benzo(a)pyrene-3,6-dione	
	Benzo(a)pyrene-6,12-dione	

those of the other positions. The charges of positions 1, 3, and 12 were the second highest ones in the range of −0.263 to −0.308 in MK and −0.258 to −0.273 in CHelpG. These findings lead us to conclude why BAP has three kinds of oxidized products: (1) the carbon at position 6 can be predominantly attacked by radicals because of its exceedingly high atomic charge; (2) because the carbons at positions 1, 3, and 12 have enough charges to attract the radicals and keep the radicals from carbon 6, these carbons can be attacked by radicals secondly; and (3) after one of the carbons at positions 1, 3, and 12 is attacked by radicals, the other positions lose their chance to be attacked by radicals because of their proximity.

3. Conclusions

Even though the Frontier electron density calculation was fairly good to predict the oxidation position of PAHs, it failed to predict the oxidation position of FLU.[6] However, in this study, the carbons showing higher MK and/or CHelpG atomic charges of PAHs, such as ACEL, ANT, FLU, BAA, and BAP, all corresponded to the experimentally obtained Fenton oxidation positions. Therefore, one can assume that determining the MK and/or CHelpG charges of PAHs will be a more promising method for predicting the oxidation position on PAHs. Additionally, we also found that the Mulliken method did not give suitable atomic charge data for this study.

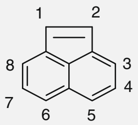
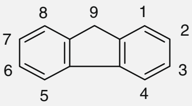
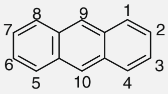
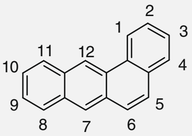
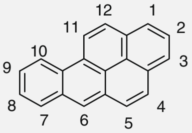
4. Experimental

The plane figures of all the molecules in this study 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.[9] With the Chem3D program, the GAUSSIAN input files were created to run the GAUSSIAN 98 program.[10]

In this study we carried out density functional theory calculations with the Becke's exchange functional (BLYP)[11,12] using the GAUSSIAN 98 program. The energy minima with respect to the nuclear coordinates were obtained by the simultaneous relaxation of all the geometrical parameters of the molecule using the gradient method.[13] With these optimized structures of molecules, the atomic charge distributions were calculated using the Mulliken,[14] CHelpG,[15] and MK[16,17] methods.

The Fenton oxidation was previously[6] performed on ethanol solutions containing ACEL, FLU, ANT, BAA, PYN, and BAP. These PAHs were identified by GC–MS and HPLC. The reagents, experimental procedures, and analytical conditions are described in reference.[6]

Table 2
Calculated Atomic Charge Distributions of PAHs[*]

Position	ACEL 			FLU 			ANT 			BAA 			BAP 		
	Mulliken	CHelpG	MK	Mulliken	CHelpG	MK	Mulliken	CHelpG	MK	Mulliken	CHelpG	MK	Mulliken	CHelpG	MK
1	−0.316	−0.202	−0.261	−0.294	−0.156	−0.263	−0.123	−0.217	−0.240	−0.700	−0.120	−0.186	−0.322	−0.273	−0.303
2	−0.316	−0.200	−0.257	−0.247	−0.061	−0.090	−0.281	−0.051	−0.120	−0.590	−0.127	−0.145	−0.274	0.014	−0.052
3	−0.154	−0.223	−0.241	−0.248	−0.076	−0.164	−0.281	−0.051	−0.120	−0.238	−0.010	−0.088	−0.119	−0.262	−0.263
4	−0.283	0.032	−0.103	−0.447	−0.138	−0.172	−0.123	−0.217	−0.240	−0.370	−0.196	−0.257	−0.301	−0.197	−0.213
5	0.134	−0.287	−0.266	−0.447	−0.138	−0.161	−0.123	−0.217	−0.224	−0.529	−0.176	−0.343	−0.239	−0.170	−0.250
6	0.134	−0.287	−0.260	−0.248	−0.074	−0.147	−0.281	−0.051	−0.119	−0.393	−0.195	−0.212	−0.219	−0.383	−0.562
7	−0.283	0.032	−0.105	−0.247	−0.065	−0.120	−0.281	−0.051	−0.119	−0.153	−0.382	−0.456	−0.303	−0.215	−0.265
8	−0.154	−0.230	−0.261	−0.294	−0.152	−0.225	−0.123	−0.217	−0.224	−0.084	−0.216	−0.226	−0.296	−0.041	−0.117
9	–	–	–	−0.189	0.105	−0.382	−0.013	−0.406	−0.322	−0.295	−0.061	−0.142	−0.365	−0.083	−0.142
10	–	–	–	–	–	–	−0.013	−0.406	−0.322	−0.259	−0.050	−0.115	−0.812	−0.157	−0.188
11	–	–	–	–	–	–	–	–	–	0.052	−0.220	−0.252	−1.007	−0.078	−0.157
12	–	–	–	–	–	–	–	–	–	−0.228	−0.306	−0.308	−0.612	−0.258	−0.308

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[*] Charges in electron.

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