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Evaluating Computational and Structural Approaches to Predict Transformation Products of Polycyclic Aromatic Hydrocarbons

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Abstract

Polycyclic aromatic hydrocarbons (PAHs) undergo transformation reactions with atmospheric photochemical oxidants, such as hydroxyl radicals (OH•), nitrogen oxides (NO_x), and ozone (O₃). The most common PAH-transformation products (PAH-TPs) are nitrated-, oxygenated-, and hydroxylated-PAHs (NPAHs, OPAHs, and OHPAHs, respectively), some of which are known to pose potential human health concerns. We sampled four theoretical approaches for predicting the location of reactive sites on PAHs (*i.e.*, the carbon where atmospheric oxidants attack), and hence the chemoselectivity of the PAHs. All computed results are based on Density Functional Theory (B3LYP/6–31G(d) optimized structures and energies). The four approaches are: 1) Clar's prediction of aromatic resonance structures, 2) thermodynamic stability of all OHPAH adduct intermediates, 3) computed atomic charges (Natural Bond order, ChelpG, and Mulliken) at each carbon on the PAH, and 4) average local ionization energy (ALIE) at atom or bond sites. To evaluate the accuracy of these approaches, the predicted PAH-TPs were compared to published laboratory observations of major NPAH, OPAH, and OHPAH products in both gas- and particle-phases. We found that the Clar's resonance structures were able to predict the least stable rings on the PAHs but did not offer insights in terms of which individual carbon is most reactive. The OHPAH adduct thermodynamics and the ALIE approaches were the most accurate when

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CONFLICT OF INTEREST

The authors declare no competing financial interest.

SUPPORTING INFORMATION

The Supporting information is available free of charge:

Summarized laboratory data; example for predicting reactivity of parent-PAHs using the Clar's resonance structure; comparison of predicted reactive sites of parent-PAHs between B3LYP/6–31G(d) and other DFT methods and basis sets for thermodynamic calculations; comparison between B3LYP/6–31G(d) and other DFT methods and basis sets for atomic charge and ALIE computations; equation for OHPAH adduct stability calculation; example for predicting reactivity of parent-PAHs using OHPAH adduct stability; ALIE calculations using MultiWFN; example of graphical and data output from MultiWFN; possible PAH-TPs formed from reactions of parent-PAHs with atmospheric oxidants; PAH-TP names and abbreviations; NBO analysis partial charge for 15 parent-PAHs; Kinetics discussion; major NPAHs detected in the environment; and geometrically optimized XYZ input files of PAHs and OHPAH adducts, Tables S-1 to S-4; and, Figures S-1 to S-4.

compared to laboratory data, showing great potential for predicting the formation of previously unstudied PAH-TPs that are likely to form in the atmosphere.¹

Graphical Abstract

Keywords

PAH; NPAH; OPAH; OHPAH; density functional theory; computations; atomic charge; average local ionization energy

INTRODUCTION

Polycyclic aromatic hydrocarbons (PAHs) are ubiquitous in the environment^{2–5} and some are known to be carcinogenic, mutagenic, or toxic.^{6–8} PAHs may be produced through geological processes or incomplete combustion of organic matter.^{6,9} Atmospheric PAHs^{6,10,11} undergo long-range atmospheric transport,^{12–15} which has implications for human health worldwide.¹⁶ Furthermore, PAHs undergo phototransformation into PAH-transformation products (PAH-TPs) via reactions with atmospheric oxidants, such as hydroxyl radicals (OH•) and nitrogen oxides (NO_x). In some cases, the resulting PAH-TPs, which are primarily nitrated-, oxygenated-, and hydroxylated-PAHs (NPAHs, OPAHs, and OHPAHs, respectively), are more toxic than their respective parent PAH compounds.^{6,9,17–19} Given the impact of PAH-TPs on human health^{20–24} and modern civilization's reliance on combustion of fossil fuels, the ability to predict the formation of atmospheric PAH-TPs is important for sustainable economy and ecology.

Previous studies have reported PAH-TP formation following exposure of parent-PAHs to atmospheric oxidants.^{17,18,25–27} The identification of PAH-TPs in a laboratory setting has informed researchers of the presence of these compounds in the environment.^{17,28} Laboratory studies have also identified previously unknown PAH-TPs. For example, in a recent study by Jariyasopit *et al.*, novel high molecular weight-NPAHs were identified from the exposure of high molecular weight parent-PAHs to NO_x.¹⁷

Computational chemistry techniques have been used as a complementary approach to laboratory studies in predicting PAH-TP formations.^{29–31} Density-functional theory (DFT) has previously been applied to a number of atmospheric speciation studies.^{17,32–34} Results of these computational studies have not only elucidated elementary steps,^{35,36} but often predict which PAH-TP is favored when many potential PAH-TP product isomers are possible. Furthermore, computational chemistry can be extended for suspect screening analysis. In this framework,³⁷ computations predict the formation of PAH-TPs that would be found in a laboratory or field settings and can be combined with experiments to guide further analysis. The potential impact and promise of such computational studies in being able to predict laboratory results suggests a need for developing a comprehensive and robust prediction model for PAH-TP formation.

The objectives of this study were to evaluate various theoretical and computational approaches used in the literature to predict the reactive sites of parent-PAHs, and determine which approach is the most accurate and efficient. Four approaches were evaluated: (1) Clar's aromatic π -sextet^{38,39}, (2) OHPAH radical adduct thermodynamic stability, (3) computed (Natural Bond Order (NBO), ChelpG, and Mulliken) atomic charges, and (4) average local ionization energy (ALIE). The accuracy of each approach was evaluated based on corroboration with published laboratory results. While these approaches have previously been used to predict the reactivity of several parent-PAHs, the advantages and weaknesses of the models have yet to be explored and compared. In particular, the ALIE approach has never been applied to predict the reactivity of atmospheric parent-PAHs. We sought to demonstrate an integrated approach, which encompasses analytical and computational chemistry, adding to our understanding of atmospheric PAH-TP formations and providing a new and robust path for discovery of PAH-TPs yet to be studied in field or laboratory settings.

EXPERIMENTAL SECTION

Data Mining from Published Laboratory Results

We evaluated 59 laboratory studies in which gas- and particle-phase parent-PAHs were exposed to OH•, NOx (NO₂, NO₃, and N₂O₅), and O₃ (Table S-1). We initially focused on the 16 United States Environmental Protection Agency (U.S. EPA) priority pollutant parent-PAHs (naphthalene [NAP], acenaphthylene [ACY], acenaphthene [ACE], fluorene [FLO], phenanthrene [PHE], anthracene [ANT], fluoranthene [FLT], pyrene [PYR], benz[*a*]anthracene [BaA], chrysene [CHR], benzo[*b*]fluoranthene [BbF], benzo[*k*]fluoranthene [BkF], benzo[*a*]pyrene [BaP], dibenz[*a,h*]anthracene [DBaA], benzo[*ghi*]perylene [BghiP], and indeno[1,2,3-*cd*]pyrene [IcdP]). After we compiled our sources, we found no laboratory studies that used DBaA and IcdP as parent-PAHs. A single study included BbF,⁴⁰ but the identities of the resulting PAH-TPs were not verified. Therefore, DBaA, IcdP, and BbF were excluded from our study. In addition to the priority pollutants, we included two parent-PAHs with molecular weight 302 a.m.u (MW302-PAHs): dibenzo[*a,l*]pyrene (DBaIP) and dibenzo[*a,j*]pyrene (DBaJP). Both have been shown to react with atmospheric oxidants, resulting in the formation of NPAHs.¹⁷ Furthermore, DBaJP is suspected to be more carcinogenic than BaP,^{41,42} and MW302-PAHs are of environmental

concern.⁴³ The structures of the 15 parent-PAHs and their numberings are available in Figure 1.

Criteria for PAH-TPs Selection

We were specifically interested in primary NPAH, OPAH, and OHPAH products due to their potential human health effects. We limited the PAH-TPs in this study to those: 1) that had laboratory data, 2) in which the structures and identities were reported (Table S-1), and 3) validated via purchased or synthesized standards, MS, or computations (Table S-1). In several studies, not every possible PAH-TP was studied.^{17,44–46}

Clar's Aromatic π -Sextet

Clar's aromatic π -sextet approach has been used to explain the reactivity of aromatic compounds.^{28,47–51} Clar's set of aromatic π -sextet rules provide guidelines for the relative stability of a given resonance structure for polycyclic aromatic ring systems.^{28,38,39} Clar postulates that the most stable Kekulé resonance structure of a PAH compound is the one with the largest number of possible aromatic π -sextet rings (see illustration with PHE, Figure S-1).^{28,38,39} It follows that the most reactive rings are the ones that do not contain the aromatic π -sextet.

We used Clar's π -sextet method to identify the most reactive carbons in the 15 parent-PAHs. We hypothesize that the least stable ring in each parent-PAH would contain the carbon that reacts most readily with OH•, NO_x, or O₃.

Computational Methods

Geometry optimizations and thermal corrections were computed using density functional theory (DFT) B3LYP^{52–54} and M06–2X functional,⁵⁵ with the 6–31G(d) basis set⁵⁶ as employed in Gaussian 09.⁵⁷ The geometries of all reactants, intermediates, and products were optimized in the gas-phase. Both functionals consistently predicted the same reactive carbons. Given that PAHs and PAH-TPs are composed of primarily main-group elements, B3LYP/6–31G(d) was deemed a suitable level of theory for this study, with little trade-off between computational cost and accuracy (see Table S-2 and SI for further discussions).

Three theoretical approaches were employed to predict the reactivity of the 15 parent-PAHs. In the first approach, we calculated the thermodynamic stability of each OHPAH adduct intermediate because we hypothesize that this regiochemical preference should dictate the site of substitution on a parent-PAH¹⁷ (Figure S-2). The change in Gibbs free energy (G_{rxn}) for the formation of the OHPAH adduct was calculated for every unique adduct position to determine the reactive site thermodynamic preference.

In the second approach, the partial atomic charges were computed for each unique carbon on the 15 parent-PAHs. Our hypothesis was that the most negatively charged carbon (also the most electron-rich) has the greatest affinity to atmospheric radicals which are highly electrophilic due to the presence of radicals on electronegative atoms. We used the popular natural bond orbital (NBO) analysis,⁵⁸ the electrostatic mimicking ChelpG method,⁵⁹ and the Mulliken population analysis.⁶⁰

In the third approach, we computed the average local ionization energy (ALIE) using MultiWFN^{61,62} to predict the reactivity of the 15 parent-PAHs. ALIE is the average energy required to remove an electron locally.^{63–65} The site with the lowest ALIE value is the most reactive site for electrophilic or free radical attack.^{63–65} The ALIE approach provides a localized reactive site prediction, which may be on either an atom, bond, or both (see SI and Figure S-3). Prior studies have determined the ALIE of several PAHs,^{63,65} but not for all 16 PAHs included in the U.S. EPA priority list. We have applied ALIE prediction to focus on atmospheric oxidant reactions, which has yet to be explored using this method.

RESULTS AND DISCUSSION

Atmospheric PAH-TPs Formed in the Laboratory

The combined results of the different reactivity predictions and laboratory data are shown in Table 1 and illustrated in Figure 2. Based on the collated published laboratory data, NPAHs are the most commonly measured PAH-TPs. Although our study focused on the formation of mono-NPAH transformation products, di-NPAHs can also be formed (Tables S-1 and S-2). The formation of both mono- and di-NPAHs are attributed to reactions with NO_x (*e.g.*, NO₂, NO₃, and N₂O₅) or the combination of NO_x and either OH• or O₃. Several studies have suggested the formation of NPAHs from reactions with OH• alone, but this could be attributed to the presence of NO_x during the generation of OH•.^{17,66}

While some studies focus on homogeneous reactions between gas-phase parent-PAHs and atmospheric oxidants,^{67–70} others have focused on heterogeneous reactions between particle-phase parent-PAHs and atmospheric radicals.^{17,18,25,44,71} Data from the latter indicate that the products formed from heterogeneous reactions do not depend on the type of particle.

Of particular note are heterogeneous reaction studies of PAHs reacted on aerosol or secondary organic aerosol particles,^{25,72–74} the latter of which are known to trap PAHs and PAH-TPs.^{75,76} Trapped persistent PAHs can undergo global long-range transport and are predicted to increase global lung cancer risk.¹⁶ Differences in the products formed, based on the type of NO_x used in the reactions, were not further explored because the experiments often exposed parent-PAHs to some or all of the NO_x simultaneously.

PAH-TPs from eight parent PAHs exist in both gas- and particle-phases, and seven exist in particle-phase only (Table S-1). For FLT and PYR, some of their PAH-TPs only exist in one phase. In the laboratory, the major products for FLT were 2- and 3-nitrofluoranthene (2- and 3-NFLT, respectively) (Table 1, Table S-3). 2-NFLT is primarily in the gas-phase, while 3-NFLT is primarily in the particle-phase. However, Ringuet *et al.* has reported particle-phase 2-NFLT in their study.²⁵ For PYR, the major reported products are 1- and 4-nitropyrene (1- and 4-NPYR, respectively) (Table 1, Table S-3). 1-NPYR is primarily in the gas-phase, while 4-NPYR is primarily in the particle-phase.

The compiled data indicate that OPAHs and OHPAHs are formed as PAH-TPs, albeit not from all 15 parent-PAHs (Tables 1, S-1, and S-3). OPAHs and OHPAHs are generated by reactions between OH• or O₃ and the following PAHs: NAP,^{68,69,74,77–81} ACY,^{81–84} ACE,

83–86 PHE,^{44,87–90} ANT,^{25,44,72,91–96} PYR (OHPAH only),^{44,97–99} BaA,^{25,99} and BaP (OPAHs only).^{100,101} Although reactions between FLO, FLT, CHR, BkF, BghiP, DBaiP, or DBaP with atmospheric oxidants could also result in the formation of OPAHs and OHPAHs, these products were not reported in laboratory studies. We used the OPAH and OHPAH laboratory results as another basis to determine major NPAH products, because the oxidation sites are similar to the substitution sites measured for NPAH products (Table 1). This is particularly true for ANT, PYR, BaA, and BaP, although may be observed in the PAH-TPs for ACY, ACE, and PHE. With regards to ACY and ACE, previous laboratory studies suggest that nitration addition is not expected to occur at C1 or C2 due to selective formation of OPAHs or OHPAHs over NPAHs upon generation of OH• intermediate.^{67,102} The reactive π -bond between C1 and C2 is not involved in the aromatic delocalization. The formation of 1-nitroacenaphthylene (1-NACY) in one study was attributed to electrophilic nitration with NO₂/HNO₃ during the experiment and was not considered to be an actual gas-phase reaction product.⁶⁷ For PHE, although 9,10-phenanthrenedione (9,10-PHEdione) has been identified as the main product of the atmospheric reaction between PHE and atmospheric radicals in several studies,^{44,87,89} other studies do not indicate which OHPAH is the dominant product. These studies may have not focused on OHPAH identifications in their experiments, or they were not able to specify the identities of the OHPAHs due to the lack of availability in authentic standards.

Agreement between Clar's π -Sextet Approach and Laboratory Results

The Clar resonance structures of the 15 parent-PAHs are illustrated in Figure 3. The π -sextet ring assignments of all parent-PAHs, except for DBaiP and DBaP, were validated using the results of previous studies.^{28,39,51} Clar's π -sextet approach predicts equal reactive aromatic rings for NAP, ACY, ACE, and FLO because each of these symmetrical structures contained equivalent Kekulé structures.³⁹ Thus, the reactive carbons for these PAHs could not be validated with laboratory results. For FLO, this likely means that the fused five-membered ring of FLO is reactive, as indicated by the oxidation at C9 from permanganate oxidation of FLO, which resulted in 9-fluorenone.²⁸

The reactive carbons for PHE, ANT, and DBaiP were predicted using the Clar's aromatic π -sextet approach. In PHE, the middle ring of the Clar's π -sextet resonance structure is reactive, suggesting C9 and C10 are the most likely sites for substitution (Figure S-1 and 3). This prediction agrees with laboratory data, as 9-nitrophenanthrene (9-NPHE) is the major NPAH formed by the transformation of PHE (Table 1). The prediction for ANT is in agreement with laboratory results, as 9-nitroanthracene (9-NANT) is the major transformation product of ANT (Table 1). Clar's π -sextet resonance structure correctly predicts the reactive rings for DBaiP because 5-nitrodibenzo[*a,l*]pyrene (5-NDBaiP) is the major transformation products of DBaiP.¹⁷ In a laboratory setting, observed OPAH and OHPAH transformation products also support our predictions for these two compounds. The laboratory experiments observed mono- and di-OPAH products of ANT indicate C9 and C10 (ANT) are the most reactive carbons.

The Clar's structure prediction is useful to predict reactive carbon rings, but it does not always predict specific reactive carbons. For example, for FLT, C1, C2, and C3 were all

predicted to be equally reactive, while for CHR, both C5 and C6 were expected to be equally reactive (Figure 3). While these carbons are located within the correct rings that were predicted to be reactive, the lack of specificity of the Clar's aromatic π -sextet reactivity approach was evident because 1-NFLT is not a major product for FLT. The prediction for CHR matched with the laboratory result of 6-nitrochrysene (6-NCHR) as the major product of CHR. The lack of specificity from the Clar's aromatic π -sextet reactivity approach was also observed in the case of BkF. The predominant laboratory NPAH major product, 7-nitrobenzo[*k*]fluoranthene (7-NBkF), was not correctly predicted by the Clar's π -sextet approach. The second most abundant laboratory NPAH product is 3,7-dinitrobenzo[*k*]fluoranthene (3,7-DiNBkF), which is consistent with the prediction of the two reactive rings in the Clar's resonance structure in BkF. However, the Clar's resonance structure does not indicate which specific carbon is expected to be most reactive. When compared to laboratory determined PAH-TPs, Clar's aromatic π -sextet approach also incorrectly predicted the transformation products of BaA, BaP, BghiP, and DBaP.

Thermodynamic Stability OH-PAH Adduct Reactions

We used quantum-mechanical computations to predict the thermodynamic stability of all possible OHPAH radical intermediate adducts for each of the 15 parent-PAHs included in this study (Figure 4). With few exceptions, the OHPAH thermodynamic stability predicted the most reactive site on the PAH. This reactive site is the location of substitution for either a hydroxy or nitro group. The OHPAH adduct thermodynamic stabilities correctly predicted NPAH products for all PAHs in this study except for ACY, ACE, and FLO (Table 1, Figure 4). Based on prior computational results for NAP,^{103,104} PHE,^{105,106} and ANT,¹⁰⁷ the G_{rxn} of OHPAH adducts accurately predicted the most abundant OPAH and OHPAH products (*i.e.*, 1-naphthol (1-OHNAP), 9,10-PHEdione, and 9,10-anthracenedione (9,10-ANTDione)) (Tables 1 and S-3). Recent computational predictions of heterogeneous reaction between ANT and PHE with NO₃ also suggested that C9 (ANT) and C9 and C10 (PHE) were the most thermodynamically favorable sites for PAH-TP formations.¹⁰⁸ The BaP, BghiP, DBaP, and DBaP results are in agreement with previous study.¹⁷

This approach correctly predicted the formation of both mono- and di-NPAH products of BkF. 3- and 7-OHBkF adducts are the most thermodynamically favorable ($G_{rxn} = -19.5$ and -17.5 kcal/mol, respectively). In a previous laboratory study, Jariyasopit *et al.* reported 7-nitrobenzo[*k*]fluoranthene (7-NBkF), not 3-nitrobenzo[*k*]fluoranthene (3-NBkF), as the major mono-NPAH product.¹⁷ However, further nitration occurred at 3-OHBkF adduct, resulting in the formation of 3,7-dinitrobenzo[*k*]fluoranthene (3,7-DiNBkF) as the major di-NPAH product.¹⁷

In cases where the PAH-TPs observed in gas- and particle-phase differ, the thermodynamics only predicts the outcome of one of the phases, not both. The computed FLT PAH-TP thermodynamics agree with the particle-phase results, but not the gas-phase (Table 1). The 3-OHFLT adduct is predicted to be the most thermodynamically stable ($G_{rxn} = -19.1$ kcal/mol), and indeed, laboratory data shows 3-NFLT as the major *particle-phase* FLT TP. However, 2-NFLT is the major *gas-phase* FLT TP (Tables 1 and S-3), even though the 2-OHFLT adduct is the least thermodynamically favorable ($G_{rxn} = -10.0$ kcal/mol).

Conversely, the computed thermodynamics of PYR PAH-TPs agree with the gas-phase observations, but not the particle-phase.

The OHPAH adduct thermodynamic stability approach performed poorly for ACY, ACE, and FLO. In the case of ACY, the most stable OHPAH adduct was C1 ($G_{rxn} = -29.0$ kcal/mol, Figure 4), followed by C5. However, 4-nitroacenaphthylene (4-NACY) is the major NPAH product (Tables 1 and S-3), even though the OHPAH adduct at this carbon is predicted to be the least stable ($G_{rxn} = -10.3$ kcal/mol). The same trend was also observed for ACE and FLO.

Partial Atomic Charges as a Predictor for PAH Reactivity

The partial atomic charges of the 15 parent-PAHs were predicted based on partial atomic charges, using Mulliken population analysis. We employed the rationale that the more negative the partial atomic charge, the higher the electron density of the carbon, which makes the carbon more susceptible to attack by electron-poor atmospheric radicals. The popular NBO analysis only correctly predicted experiments for two of the 15 PAHs (Figure S-4), and ChelpG charges were similarly ineffective. Mulliken produced results that were in much better agreement with laboratory data than the previous two methods.

Specifically, the predictions for PAH reactivity based on the Mulliken charges were accurate for 9 of the 15 parent-PAHs, including NAP, ANT, PYR (gas-phase), BaA, CHR, BkF, BaP, DBaP, and DBaP (Figure 5). For BaP, both the Mulliken charges and OHPAH adduct stability approaches identified C6 as the most reactive carbon. The reactivity of C6 was demonstrated by the formation of oxygenated-BaP degradation products in a previous study¹⁰⁹ in which all laboratory products were formed by oxidation at C6. The predicted reactivity of C9 and C10 in ANT, and C7 and C12 in BaA (Figure 5), based on Mulliken charges, are in agreement with previous computational prediction for the same two parent-PAHs.¹⁰⁹ The Mulliken analysis for BkF predicted C7 to be the most reactive site, consistent with 7-NBkF being the major mono-NPAH product of BkF (Tables 1 and S-3).

Mulliken population analysis was the best approach for predicting the oxidation sites of PAHs with aliphatic fused five-membered rings, based on the results for ACE and FLO. Mulliken population analysis allows inclusion of all carbons, including aliphatic carbons, which is a limitation of the other methods. Mulliken population analysis predicted the aliphatic carbons to have the highest electron densities (Figure 5) and are consistent with laboratory data reported for ACE and FLO based on OPAH degradation products of these PAHs following oxidation by permanganate.²⁸ OPAH transformation products of ACE were reported in the collected laboratory data (Tables 1 and S-3). No OPAH transformation product of FLO was found in the collected laboratory data, although 9-fluorenone has been commonly measured in air samples collected from the environment.^{6,110}

ALIE-based Prediction of PAH Reactivity

ALIE predicts the most reactive carbon in each parent-PAHs. The lowest ALIE value indicates the site where an electron is the most easily removed, donated, or shared. Figure 6 shows the ALIE results for the 15 parent-PAHs. ALIE categorizes reactive sites into three groups: atom, bond, or both atom and bond sites. For PAHs where the reactive site is on the

atom, the location of the carbon with the lowest ALIE value determined the major NPAH product of the parent compound. PAHs in this group include ANT, BaA, BaP, BghiP, DBaIP, and DBaIP. The formation of 9-NANT, 7-NBaA, and 6-nitrobenzo[*a*]pyrene (6-NBaP) corresponded well with the carbons having the lowest ALIE values in these PAHs. The lowest ALIE values are found at C9 in ANT, C7 in BaA, and C6 in BaP. The presence of the OPAH and OHPAH products of ANT and BaA were also accurately predicted by ALIE in these PAHs—9,10-ANTDione and anthrone (9-ANTOne) for ANT, and 7,12-benzo[*a*]anthracenedione (7,12-BaADione) and 7,12-hydroxybenz[*a*]anthrone (7,12-OHBaAOne) for BaA. C12 was the only other reactive atom site in BaA, as indicated by the predicted formation of 7,12-BaADione and 7,12-OHBaAOne (Figure 6). The C1-C2 bond in ANT and C4-C5 bond in BaP were also predicted to be reactive, which explains the formation of both 1- and 2-nitroanthracene (1- and 2-NANT, respectively), and 4,5-benzo[*a*]pyrenedione (4,5-BaPDione) in laboratory (Table 1).

For the majority of the remaining parent-PAHs, ALIE predicts reactive bond sites (Figure 6). PAHs in this group included NAP, ACY, ACE, PHE, FLT, and CHR. With the exception of PHE where the two atoms are symmetry equivalent or FLT where both atoms reacted, the substitution occurs on one carbon, but not the other. The reasons for this are as yet unknown. In such cases, the OHPAH adduct thermodynamics may be required to distinguish between the two carbons of the reactive bond.

ALIE results show that C1-C2 bond in NAP, C9-C10 in PHE, and C5-C6 in CHR were the most reactive bonds, and these results agree with the observed major NPAH products (*i.e.*, 1-NNAP, 9-NPHE, and 6-NCHR, respectively) (Table 1). Moreover, the formation of 2-nitronaphthalene (2-NNAP) and 9,10-PHEDione in laboratory could also be explained by the ALIE predictions.

In cases where the ALIE results indicate that a PAH possesses a reactive atom and a bond, the laboratory results are consistently in agreement with the atom sites. It would be interesting to see if the PAH-TPs that correspond to the reactive bonds could also be located in laboratory settings (the C5 and C6 bond of BaA and the C3 and C4 bond of BghiP are reactive). Such is the case for PYR. The ALIE approach predicted both C1 and C4-C5 bond to be the most reactive. Both 1- and 4-nitropyrene (1- and 4-NPYR, respectively) have been detected in laboratory settings as the major products of PYR in the gas- and particle-phases, respectively. The formations of disubstituted PYR (1,3-, 1,6-, and 1,8-dinitropyrene (DiNPYR)) in the gas-phase also reflects this.

ACY appears unique its reactivity pattern. The ALIE approach predicts the C1 atom to be reactive (in actuality, the C1-C2 bond is reactive, but these atoms are symmetry equivalent). This matches the observed major OPAH and OHPAH products, but not the NPAH products (Table S-3) – oxidation occurs at the C1 and C2 sites,⁶⁷ as predicted. However, nitration occurs at C4, even though the C1-C2 bond had the lowest ALIE value (Figure 6).

Results from BkF were unique when compared to the rest of the PAHs. ALIE reactive sites for BkF are predicted to be on both specific atom and bond sites (Table 1). While the ALIE correctly predicted the most reactive atom (C7), it incorrectly predicted the most reactive

bond site (Figure 6). Laboratory results show that C2-C3 bond reacted (major TP of BkF was 3-NBkF,¹⁷), as opposed to the C8-C9 bond as predicted by ALIE.

Predicting Reactivity of other PAHs using ALIE

Based on the success of ALIE in predicting the reactivity of 13 out of the 15 parent-PAHs in this study, we predicted the PAH-TPs of the remaining 3 PAHs from the U.S. EPA list of priority pollutants: BbF, DBaA, and IcdP (Figure 7). The reactive sites for BbF were predicted by ALIE to be on C1-C2 bond and at the C6 atom. ALIE predicted reactivity of DBaA to be on C7 and C14 atoms. For IcdP, there were multiple reactive sites for specific carbons, C12 being the most reactive carbon. The only bond site predicted to be reactive was the C1-C2 bond. The ALIE prediction for IcdP was similar to PYR, which had both reactive atom and bond sites. However, given that IcdP is likely to exist in the particle-phase,^{111–113} the C1-C2 bond is more likely to be the reactive site for the formation of PAH-TP, similar to the formation of 4-NPYR as particle-phase product of PYR. It would be of significant interest if the predictions by ALIE are proven to be accurate in the ensuing studies.

Evaluations of the Different Prediction Approaches

Of all the methods tested, Clar's aromatic π -sextet approach was the most expedient, not needing any additional computations. While clearly accurate in identifying the most stable and least stable aromatic rings, on its own, the specific reactive carbon sites were not easily identified or rationalized. Computed partial charges were not particularly effective in predicting which PAH-TPs were observed under laboratory conditions. NBO and ChelpG charges were both unable to accurately predict PAH-TPs in the vast majority of cases (>12). Mulliken analysis, which was clearly the best among computed charges, was only predictive for slightly more than half the compounds. By far, but the predictions were most accurate when using the OHPAH adduct thermodynamics or the ALIE approach (Figure 8). Computing the OHPAH thermodynamics is time and resource intensive (all possible OHPAH adducts must be computed), and the accuracy is highly dependent on the researcher's assumptions on what the mechanism of PAH-TP formation are. In this light, ALIE is a highly attractive approach. While boasting the best in predictive accuracy, ALIE is relatively efficient to compute and is able to correctly predict PAH-TPs in both gas- and particle-phases. The drawback of the ALIE approach is not being able to identify which of the two carbons would be reactive if the ALIE points to a reactive C-C bond.

Of note, no method was able to correctly predict the reactive site of FLO. We hypothesized here that the C3 site is kinetically preferred over the other sites (see discussion in SI). Alternatively, a prior computational study suggests that the presence of water might impact the formation of the NPAH products that originate from FLO.¹¹⁴ With the exception of FLO and BkF, ALIE accurately predicted the reactive sites for the 15 PAHs in this study. The ALIE prediction results from MultiWFN are in agreement with prior studies that used different software.^{63,65} In these prior publications, NAP, PHE, FLT, PYR, CHR, and BaP were studied, but the supporting nitration data was not from reactions with atmospheric oxidants,^{115–117} suggesting this study presents a novel application of ALIE in environmental reactions with PAHs.

The experimental data collected in this study were based on laboratory experiments where the atmospheric conditions and reactions were controlled. However, our computational predictions are consistent with the profile of dominant PAH-TPs that were found in the environment (Table S-4), suggesting that computational prediction is a useful tool to predict the formation of a variety of PAH-TPs in the environment. For PAHs such as BkF, BghiP, DBaIP, and DBaP, where the predicted PAH-TPs have not been detected in the environment, our computational results can serve as the basis of identifications for unknown PAH-TPs in the environment that were previously undetected.³⁶

In summary, we surveyed four approaches to predict atmospheric PAH-TP formations: Clar's aromatic π -sextet, OHPAH adduct thermodynamic stability, partial atomic charges (NBO, ChelpG, and Mulliken), and ALIE. Out of the four, we found that the adduct thermodynamics and the ALIE approaches were the most robust methods for predicting PAH reactivity. It would be of great interest to see if these methods would be as effective in predicting the reactivity of other types of PAHs, such as methylated-, halogenated- or heterocyclic-PAHs,^{22,118–121} as well as to predict PAH-TPs from reactions between PAHs with other atmospheric species such as sulfate particles and chlorine.^{122,123} More studies are also needed to determine the underlying mechanisms that result in the formation of PAH-TPs that did not match with our prediction, including the heterogeneous nitration of PYR and FLT where the NPAHs that are formed differ from NPAHs that are formed through gas-phase reaction.¹⁸ Based on this study, we conclude that the adduct thermodynamics or the ALIE approaches should serve as starting points for researchers to accurately predict the formation of PAH-TPs in the environment and subsequently assess the potential human health implications of these compounds.^{37,43}

Supplementary Material

Refer to Web version on PubMed Central for supplementary material.

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Figure 1.

The structures and relevant numberings of the 15 parent-PAHs that have been studied in the laboratory. Hydroxylated and nitrated transformation products formed from red parent PAHs are only found in the particle phase, blue in both particle and gas phase.

- Predicted carbon with lowest OHPAH adduct stability
- Predicted with Mulliken
- Predicted carbon with lowest ALIE
- All above prediction methods applicable
- Clar's predicted reactive carbons
- Location of primary substitutions based on laboratory data

Figure 2.

Summary of nitration sites predicted by different methods and laboratory results. Location of primary substitutions based on laboratory data circled in blue. Clar's predicted reactive carbons bolded in red.

Figure 3.

The Clar's π -sextet resonance structures of the 15 parent-PAHs in this study. For parent-PAHs that can have multiple Clar structures, only a single Clar structure is indicated with the predicted reactive carbons bolded in red. Location of primary substitutions based on laboratory data are circled in blue.

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Figure 5.

Calculated Mulliken population analyses of all symmetrically unique carbon sites for all 15 parent-PAHs (B3LYP/6–31G(d)). The carbon with the highest electron density is bolded in red. Location of primary substitutions based on laboratory data are circled in blue.

Figure 6.

Calculated ALIE (eV) of all symmetrically unique carbon sites for all 15 parent-PAHs (B3LYP/6–31G(d)). Reactive bond sites are bolded and in green, while the most reactive atom sites are in red. Location of primary substitutions based on laboratory data are circled in blue.

Figure 7.

The results of predicted average local ionization energy (ALIE) (eV) for the 3 PAHs that were not studied in the laboratory (B3LYP/6-31G(d)). Reactive bond sites are bolded and in green, while the most reactive atom sites are in red.

Figure 8.
Number of correctly predicted primary substitutions out of fifteen parent-PAHs from each prediction method.

Table 1.

Tabulated data indicating the substitution sites of the 15 parent-PAHs based on laboratory data and the predictive models.

PAH	Laboratory NPAH	Laboratory OPAHs and OHPAHs	Clar's π -Sextets	OHPAH Adduct Stability	Mulliken Charges	ALIE	Laboratory Results References
NAP	C1	C1+2, C1+4; C1, C2	C1-C2*	C1	C1	C1-C2	25,68,69,74,77-81,124,125
ACY	C4	C1+2; C1; C1	C3-C5*	C1	C3	C1-C2	67,81-83,102,124,126,127
ACE	C4	C1+2; C1; C1	C3-C5*	C5	C1	C4-C5	67,83-86,124
FLO	C3	-	C1-C4*	C2, C4	C9	C4	25,124,128
PHE	C9	C1+4, C9+10; C1, C2, C3, C4, C9	C9-C10	C9/C10	C1	C9-C10	25,44,67,87-90,95
ANT	C9	C9+10; C9	C9-C10	C9/C10	C9	C9	25,44,46,67,72,91-96,124
FLT	C2/C3	-	C1-C3/C4-C6	C3	C1	C2-C3	25,27,67,70,71,124,129-133
PYR	C1/C4	C1	C4-C5/C9-C10	C1	C1	C1 and C4-C5	25,27,44-46,70,71,73,97-99,124,129,134-137
BaA	C7	C7+12	C5-C6	C7	C7	C7	25,27,45,71,99,138
CHR	C6	-	C5-C6	C6	C6	C5-C6	45,46,71,138
BkF	C7	-	C1-C3/C4-6	C3	C7	C7	17
BaP	C6	C1+6, C3+6, C6+12, C4+5	C4-C5	C6	C6	C6	17,25-27,45,46,71,73,100,101,136,138-141
BghiP	C5	-	C3-4/C11-12	C5	C7	C5	17,46
DBaIP	C5	-	C5/C8	C5	C5	C5	17
DBaIP	C10	-	C8-C9	C10	C10	C10	17

* indicates Clar's aromatic π -sextet predict equal reactive rings due to symmetrical parent-PAH structures. 2-NFLT and 4-NPYR are major particle-phase products, while 3-NFLT and 1-NPYR are major gas-phase products.