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A Linear Energy Relationship between Activation Energy and Absolute Hardness: A Case Study with the O(^{3}P) Atom-Addition Reactions to Polyaromatic Hydrocarbons

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A new linear relationship between absolute hardness and global activation energy of O-addition reaction to a series of aromatic hydrocarbons (benzene, naphthalene, phenanthrene, and pyrene) is presented. A total of seventeen O(^{3}P)-addition reactions were evaluated. Thermal rate constants were calculated for each elementary reaction and used to estimate the total rate constants. This information was employed to obtain the global activation energy. A new linear relationship is shown and is estimated that it can be used within the RC-TST framework to predict relative rate constants for any reaction within an O-addition to PAH class from just absolute hardness values.

Introduction

Polycyclic aromatic hydrocarbons (PAH) are precursors to soot formation in combustion processes. PAH formed during combustion reactions are in a reaction media of a pool of radicals such as O(^{3}P), $^\bullet$OH, $^\bullet$H, and $^\bullet$HO$_2$. The competitiveness of the formation/oxidation reactions of PAH depends on several factors such as temperature, pressure, and species concentrations and either one can be predominant depending on the region analyzed in the combustion system.[1] There have been a significant amount of reports about the chemistry of the PAH formation.[2] However, relatively much less is known about the oxidation of PAHs. Wang and co-workers determined global oxidation rates of some PAHs in the afterburner of a two-stage batch-combustion system of polystyrene,[3] but it was not possible conclude about the mechanisms and the differences on the rate oxidation of the PAHs. There have been a number of experimental studies[4,5] and theoretical investigations[6] of the reaction $C_6H_6 + O(^3P)$, a model reaction of PAH oxidation by oxygen atom. Chai and co-workers[7] found that under fuel-lean and stoichiometric equivalence ratio combustion conditions, a large fraction of the chemical decomposition of benzene into smaller hydrocarbons proceeds through the reactions: phenyl + O_2 and benzene + O(^{3}P). One can expect that the reactivity of PAH's toward oxygen is different when the reacting system has more than one aromatic ring. However, very little information is available for these reactions. In some cases the kinetic rate data for oxidation of naphthalene has been often assumed to be equal to that of benzene. In naphthalene oxidation experiments, Shaddix and co-workers[8] found that under a slightly rich stoichiometric combustion conditions the O-addition pathway, by analogy with benzene decomposition was expected to contribute significantly to naphthalene consumption. The rate of the naphthalene + O(^{3}P) reaction was estimated to be approximately twice the rate of $C_6H_6 + O(^3P)$.[8] Though, the reason for such an increase in the reactivity of naphthalene was not provided.

Kinetic models for many combustion systems often consist of numerous elementary reactions for which the kinetic parameters are usually unknown or are just estimated from those available for similar reactions. It is impractical to carry out calculations of thermal rate constants for each reaction even using the simplest transition state theory (TST). To obtain a set of kinetic parameters for a large number of reactions, a common practice, besides to assign the unknown kinetic parameters to those of a similar reaction, is to employ the Brønsted−Evans−Polanyi (BEP) linear free-energy relationship between the activation energies and bond dissociation energies (BDE) or heats of reaction of similar reactions to estimate the unknown activation energies.[9] Zhang and Truong,[10] have shown that within the reaction class TST framework (RC-TST), relative rate constants for any reaction in a given class can be predicted from just its reaction energy by the use of a linear energy relationship (LER) between the classical barrier heights and reaction energies determined from a subset of reactions in such a class. Preliminary results indicate that the barrier heights do not show a strong linear correlation with the corresponding reaction energies for the O-addition reactions to PAH's thus its use in the RC-TST framework is limited and alternative LER is needed. Our research interest is to employ absolute hardness as a reactivity parameter that can be correlated with the RC-TST/LER approach to provide kinetics of O-addition reactions to PAH's.

In this Letter, we report a new LER between the global-reaction activation energies and the absolute hardness reactivity parameter, η of the PAH's that can be used within the RC-TST framework.

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TABLE 1: List of $O(^3P)$-Addition Reactions to Benzene (C_6H_6), Naphthalene ($C_{10}H_8$), Anthracene ($C_{14}H_{10}$), Phenanthrene ($C_{14}H_{10}$), Naphthacene ($C_{18}H_{12}$) and Pyrene ($C_{16}H_{10}$) at Different Sites According with Their IUPAC Nomenclature

R1	$C_6H_6 + O(^3P) \rightarrow {}^{\bullet\bullet}C_6H_6O^{\bullet}$
R2	$C_{10}H_8 + O(^3P) \rightarrow {}^{\bullet}1{*}C_{10}H_8O^{\bullet}$
R3	$C_{10}H_8 + O(^3P) \rightarrow {}^{\bullet}2{*}C_{10}H_8O^{\bullet}$
R4	anth + $O(^3P) \rightarrow {}^{\bullet}$1*anth-$O^{\bullet}$
R5	anth + $O(^3P) \rightarrow {}^{\bullet}$2*anth-$O^{\bullet}$
R6	anth + $O(^3P) \rightarrow {}^{\bullet}$9*anth-$O^{\bullet}$
R7	phen + $O(^3P) \rightarrow {}^{\bullet}$1*phen-$O^{\bullet}$
R8	phen + $O(^3P) \rightarrow {}^{\bullet}$2*phen-$O^{\bullet}$
R9	phen + $O(^3P) \rightarrow {}^{\bullet}$3*phen-$O^{\bullet}$
R10	phen + $O(^3P) \rightarrow {}^{\bullet}$4*phen-$O^{\bullet}$
R11	phen + $O(^3P) \rightarrow {}^{\bullet}$10*phen-$O^{\bullet}$
R12	$C_{18}H_{12} + O(^3P) \rightarrow {}^{\bullet}1{*}C_{18}H_{12}O^{\bullet}$
R13	$C_{18}H_{12} + O(^3P) \rightarrow {}^{\bullet}2{*}C_{18}H_{12}O^{\bullet}$
R14	$C_{18}H_{12} + O(^3P) \rightarrow {}^{\bullet}12{*}C_{18}H_{12}O^{\bullet}$
R15	$C_{16}H_{10} + O(^3P) \rightarrow {}^{\bullet}1{*}C_{16}H_{10}O^{\bullet}$
R16	$C_{16}H_{10} + O(^3P) \rightarrow {}^{\bullet}2{*}C_{16}H_{10}O^{\bullet}$
R17	$C_{16}H_{10} + O(^3P) \rightarrow {}^{\bullet}10{*}C_{16}H_{10}O^{\bullet}$

Computational Approach

The absolute hardness, η is a global property of the system which measures the resistance of a system to change its electronic distribution. Within the DFT theoretical formalism,[11] the global hardness η, is defined as

$$\eta = \frac{1}{2}\left(\frac{\partial \mu}{\partial N}\right)_v \approx \frac{\varepsilon_L - \varepsilon_H}{2} \qquad (1)$$

where μ is the chemical potential and N is the total electron number. The η value can be approximated from the HOMO and LUMO energies, ε_H and ε_L, respectively, as shown in eq 1. For the PAH's considered in this study, benzene has larger η parameters and is consistent with experimental observation that these species are quite stable, whereas "linear" acenes such as anthracene and naphthacene are much more reactive.

In this study we examined the $O(^3P)$-addition reactions to benzene (C_6H_6), naphthalene ($C_{10}H_8$), anthracene ($C_{14}H_{10}$), phenanthrene ($C_{14}H_{10}$), naphthacene ($C_{18}H_{12}$) and pyrene ($C_{16}H_{10}$). This leads to the total of seventeen different reactions for O-addition to different sites as shown in Table 1. The geometries and frequencies of equilibrium and transition state structures were calculated using the B3LYP density functional theory method (DFT),[11] with the 6-311g(d,p) basis set. Optimized transitions states were verified by normal-mode analyses to ensure the eigenvector of the only one imaginary frequency corresponding to the $O(^3P)$-addition reaction. Animation of this normal-mode corresponding to the imaginary frequency was done to each reaction to confirm the right transition state. Additionally, intrinsic reaction coordinate (IRC)[12] calculations were performed just at **R1**, **R2** and **R3** transitions states to establish the correct connections between reactants and products. The B3LYP method is known to give rather accurate reaction energies, geometries and vibrational frequencies of aromatics hydrocarbons and their radicals.[13] However, B3LYP has been known to underestimate the reaction activation energies.[14] To improve the accuracy of the calculated barrier heights, single-point energy calculations at a higher level of theory is often employed. Due the number of reactions and the size of the reactants considered here, single point calculations at the BH&HLYP/6-31G(3d,3p) level of theory were carried out. The calculated potential surface information was used to predict thermal rate constants using the conventional TST. Rate calculations with the harmonic approximation for the vibrational partition functions were done using the web-based kinetics module TheRate[15] within the Computational Science and Engineering online suite of programs.

Results and Discussion

Nguyen and co-workers[6] found that the O-addition reaction to benzene can proceed via two different triplet electronic states, $^3A'$ and $^3A''$, with the former being the lowest-energy state. Their calculations were carried out at CBS-QB3 level. The BH&HLYP/6-31G(3d,3p)//B3LYP/6-311G(d,p) methodology was reliable for the analysis of the O-addition reaction to benzene because the results are in good agreement with high-level calculation reports.[6] This approach was used to calculate the potential energy profiles of the **R1**−**R17** O-addition reactions shown in Table 1S of the Supporting Information. Attack of the oxygen atom at a C atom at any of the other PAHs considered in this work takes place at the ^3A electronic state belonging to C_1 point group (see Table 1S), except for pyrene at the position 2, **R16**, where the transition states for both the $^3A'$ and $^3A''$ electronic states were found. It was not possible to determine transition states structures for the O-addition to the C9-anthracene (**R6**) and to the C12-naphthacene (**R14**) at B3LYP/6-311G(d,p) level of theory. Relaxed scans indicated that such reactions proceed without transition state.

For benzene, the total temperature-dependence rate constant k_{tot} was computed as a sum of the thermal rate constants of each electronic state. The global activation energy of the benzene reaction here calculated is 4.45 kcal/mol, which is in good agreement with published values between 4 and 5 kcal/mol.[4−6,16] The global rate constants (k_{tot}) of the $O(^3P)$-addition reaction to the other PAHs selected were estimated as follows. As a case example, naphthalene has a total of 10 carbon positions available for addition of one oxygen atom. These positions can be divided into three groups by symmetry: group i, carbons 1, 4, 5 and 8; group ii, carbons 2, 3, 6 and 7; group iii, carbons 4a and 8a according with their IUPAC nomenclature (see Figure 1S of the Supporting Information). When a reaction takes place at one of these groups, the rate constant expressions are represented as k_1, k_2 and k_3 for groups i, ii and iii, respectively. Thus, the total thermal rate constant value to the $O(^3P)$-addition reaction of naphthalene was calculated from eq 2

$$k_{tot} = \frac{1}{10}(4k_1 + 4k_2 + 2k_3) \approx \frac{1}{10}(4k_1 + 4k_2) \qquad (2)$$

because the barrier for which k_3 is calculated is 13.04 kcal/mol as compared to 2.0 kcal/mol for k_1 and 3.2 kcal/mol for k_2 (see Figure 2S).

The global rate constants k_{tot} of the O-addition reactions calculated using the methodology above-described were fitted to the modified Arrhenius equation, $k_{tot} = AT^n \exp(-E_a/RT)$, to find the global activation energy, E_a. For the naphthalene reaction the global activation energy value calculated was 2.0 kcal/mol, which is in good agreement with published values (1.8 kcal/mol).[16] Employing this methodology, it was not possible calculate the global rate constants of anthracene and naphthacene because it was not possible to determine the transition state for O-additions at the carbon positions 9 (anthracene) and 12 (naphthacene) at the level of theory here employed. The linear relationship found between the global hardness η and the global activation energy, E_a, is depicted in Figure 1, which corresponds to the equation $E_a = 2.82\eta - 5.0$, with units of kcal/mol for E_a and eV for η. This linear relationship was used to predict the global activation energy of the O-addition reaction to biphenyl (2.58 kcal/mol), triphenylene

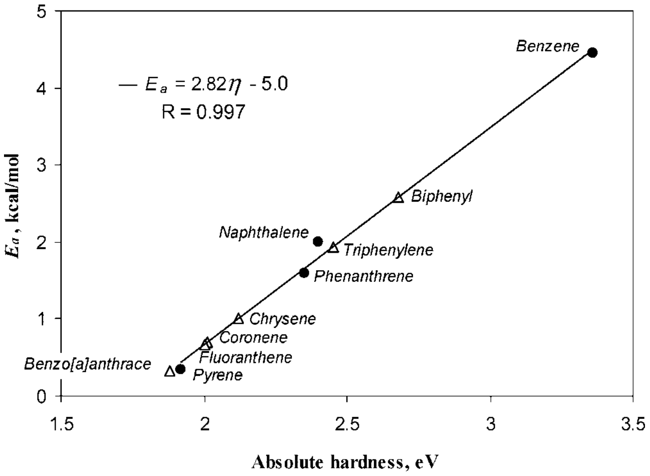

Figure 1. Linear correlation between activation energy, E_a and absolute hardness, η. The correlation coefficients (R) have been determined from linear regression analysis of the benzene, naphthalene, phenanthrene and pyrene data ("•"). The activation energies of biphenyl (2.58 kcal/mol), triphenylene (1.94 kcal/mol), chrysene (1.0 kcal/mol), coronene (0.69 kcal/mol), fluoranthene (0.66 kcal/mol) and benzo[*a*]anthracene (0.33 kcal/mol) have been determined from the absolute hardness ("△").

(1.94 kcal/mol), chrysene (1.0 kcal/mol), coronene (0.69 kcal/mol), fluoranthene (0.66 kcal/mol) and benzo[*a*]anthracene (0.33 kcal/mol) just from a simple calculation of the hardness parameter. These results are also plotted in Figure 1. The activation energy found for biphenyl is very close to the value published by Frerichs et al., 2.9 kcal/mol.[16] To our knowledge there are no available kinetic data reported for the others PAHs that allow us to validate the predicted values. The above-described methodology using only information on global hardness is a practical way to obtain unknown kinetic parameters, such as the activation energies of global O-addition reactions of importance in combustion systems. Additionally, the new LER here shown can be used within the RC-TST framework to predict relative rate constants for any reaction within an O-addition to PAH class from just its absolute hardness.

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Supporting Information Available: List of the polycyclic aromatic hydrocarbons considered in Figure 1S with their corresponding IUPAC nomenclature. Table 1S of relative energy values (kcal/mol) of the O-addition reaction calculated with BH&HLYP/6-31G(3d,3p)//B3LYP/6-311G(d,p). Table 2S of kinetic parameters of the thermal rate constants with Eckart corrections of O-addition reactions between 298 and 2998 K. Figure 2S showing the small effect of k_3 on k_{tot} for O-addition to naphthalene (O-add to carbon-8a). Table 3S of absolute hardness values of all aromatic compounds. This information is available free of charge via the Internet at http://pubs.acs.org.

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