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Reaction Mechanisms

The Inherent Competition between Addition and Substitution Reactions of Br_2 with Benzene and Arenes**

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Dedicated to Professor Eluvathingal D. Jemmis on the occasion of his 60th birthday.

Although the electrophilic substitution of benzene and phenyl derivatives proceeding through arenium ion intermediates is universally regarded as being the reaction mechanism paradigm for aromatic compounds generally,[1,2] the present investigation challenges these dogmas. Polybenzenoid hydrocarbons (PBHs) were recognized to undergo addition reactions in the 19th century, and the very common addition versus substitution competition of arenes has been investigated for decades.[1–20] Both phenanthrene and anthracene add Br_2 to give isolable 9,10-dibromo-9,10-dihydro products (the latter even in the presence of $FeCl_3$);[12] subsequent facile HBr elimination (rather than direct substitution) is a preparative route to both 9-bromo arenes.[5–7] Some higher PBHs also favor addition–elimination routes to substituted products.[8,9] Even the bromination of naphthalene gave 15% addition (in CCl_4 at 20–25 °C in the dark);[10] its chlorination yielded a 34% total of various addition products and was 32000 times faster than the analogous reaction with benzene in acetic acid.[11]

These fairly spectacular experimental findings and the unambiguous results of careful investigations, particularly of de La Mare et al.,[4,11–13] conflict with the overwhelmingly popular current viewpoint that while alkenes undergo double-bond addition (e.g., of bromine),[14,15] this reaction is disfavored for arenes generally since aromaticity is retained in the substitution but not in the initially formed addition products. The direct evidence provided by the preparative addition–elimination routes to substitution products discussed above reveal problems with the generality of such conventional electrophilic mechanistic interpretations.[2,5–9] As we demonstrate herein, alternative mechanisms may compete successfully with those depicted in textbooks for electrophilic substitution reactions. Moreover, the latter have serious flaws. Why do chemists believe so strongly that electrophilic aromatic substitution via arenium ion (σ-complex) intermediates is the exclusive and characteristic reaction of arenes, despite the diversity of the substrates, the electrophiles, and the experimental reaction conditions? It may be that substitution yields are optimized by using highly polar, acidic media, Lewis acid or zeolite catalysts, strong electrophiles, and by the choice of substituents.[16–20]

Rather than mimicking such condition-biased processes theoretically, we focus here on comparisons of the *inherent competition* (i.e., in isolation or in nonpolar media) between electrophilic substitution and addition mechanisms of dibromine (Br_2) reactions with four representative arenes (benzene, naphthalene, anthracene, and phenanthrene) in the absence of catalyst modeling. Our objective is to ascertain and to examine critically the basic mechanistic features and the explanations typically presented in textbooks.

The theoretical study of the competition between the direct electrophilic substitution and the addition–elimination mechanistic routes for the reaction of Br_2 with benzene was a major motivation of this paper. As this uncatalyzed reaction in nonpolar media is very slow, and the two different pathways, which both give bromobenzene, are likely to follow the same kinetics and to have similar H/D isotope effects; experimental information under such conditions is lacking. Our computations in isolation and in simulated CCl_4 solution provide dramatic evidence that addition–elimination pathways are favored kinetically (i.e., the activation energies are lower) over the conventionally assumed electrophilic substitution route. Addition–elimination processes also give the same product, a bromobenzene–HBr complex, but the rate-determining transition states are quite different. Moreover, we have identified a concerted mechanism for electrophilic substitution, which does not involve the expected Wheland type arenium ion or any other intermediate. Our computations predict that naphthalene, anthracene, and phenanthrene behave similarly and challenge the conventional interpretations of electrophilic aromatic substitution.

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Critical structures along the reaction paths for the bromination of benzene, naphthalene, anthracene, and phenanthrene were optimized initially at the RB3LYP/6-311 + G(2d,2p) level of theory (as implemented in Gaussian 03).[21] The results for benzene and naphthalene were verified by full reoptimization of all stationary-point structures using the double hybrid RB2-PLYP/6-311 + G(2d,2p) method[22] and the Gaussian 09 program.[23] The B2-PLYP functional includes second-order perturbation theory corrections (PT2) for the correlation energies[22] and has been shown to improve the reliability of quantitative predictions of various molecular properties, including barrier heights, considerably.[24,25] Furthermore, the DFT-D3 dispersion corrections introduced by Grimme et al. were also applied to the energies of all optimized structures.[26,27] Bulk solvation effects on the reactions of benzene with dibromine in CCl_4 were simulated by applying the IEFPCM method,[28] as implemented in the Gaussian 09 program.[23] We verified a referee's suggestion that **TS1**–**TS6** (Figure 1) had singlet diradical character by carrying out unrestricted broken-symmetry wave-function optimizations at the UBS-B3LYP/6-311 + G(2d,2p) level of theory. The $\langle S^2 \rangle$ values of **TS1**–**TS6** ranged from 0.205 to 0.861 but were zero for the other species. The resulting geometries were employed for single-point UBS-B2-PLYP/6-311 + G(2d,2p) energy evaluations in simulated CCl_4. The spin-projection method of Yamaguchi et al.[29] eliminated the spin contamination of singlets arising from admixture of high spin states. Data at this most comprehensive level are representative and are presented in column **C** of Table 1. The Supporting Information gives full details of the theoretical methods employed. (Energies for the benzene–Br_2 potential energy surface (PES) at UBS-M062X will be included in a subsequent full paper.)

Table 1: Relative energies ($E + ZPE + E_{disp}$ in kcal mol^{-1}) of species in the benzene–Br_2 reaction. Data for RB2-PLYP/6-311 + G(2d,2p) optimizations in isolation (gas phase, **A**) and in simulated CCl_4 (**B**) and spin-projected UBS-B2-PLYP/6-311 + G(2d,2p)//UBS-B3LYP/6-311 + G(2d,2p) data in simulated CCl_4 (**C**).

Species	**A** Gas phase	**B** CCl_4 solvent	**C** CCl_4 solvent
π complex	−5.14	−5.06	−4.90
TS1	44.97	41.77	42.98
TS2	42.73	39.35	38.79
TS3	37.70	36.15	34.93[a]
TS4	44.89	36.39	35.83
TS5	38.05	32.51	32.56
TS6	43.58	35.34	34.99
TS7	33.82	29.19	29.44
TS8	30.11	25.98	26.42
TS9	26.19	24.06	24.46
P1	−17.68	−17.61	−17.68
P2	7.91	7.35	7.31
P3	4.76	4.09	4.03
P4	3.00	2.56	2.60
P5	4.37	3.79	3.70

[a] The **TS3** geometry was optimized at UBS-M062X/6-311 + G(2d,2p).

Figure 1 summarizes the main part of the potential energy surface (PES) of the benzene–Br_2 reaction in simulated CCl_4 solution computed at the RB2-PLYP/6-311 + G(2d,2p) level of theory. The effect of a nonpolar, noncomplexing solvent medium on the inherent competition between substitution and addition–elimination benzene–Br_2 reactions was examined by IEFPCM computations at the more sophisticated RB2-PLYP hybrid functional level.[22,25] CCl_4 was chosen as the appropriate medium, since it was used for the chlorination of benzene and higher arenes in the studies by de La Mare et al.[4,11–13] and has been employed for the bromination of naphthalene[10] and of benzenes with electron-donating substituents.[30–32] The computed PES in CCl_4 (Figure 1) shows clearly that two addition–elimination pathways (via $\mathbf{TS2}_{CCl_4}$ and $\mathbf{TS3}_{CCl_4}$ as the rate-limiting steps) leading to bromobenzene–HBr product ($\mathbf{P1}_{CCl_4}$) are more favorable kinetically than the alternative direct substitution route.

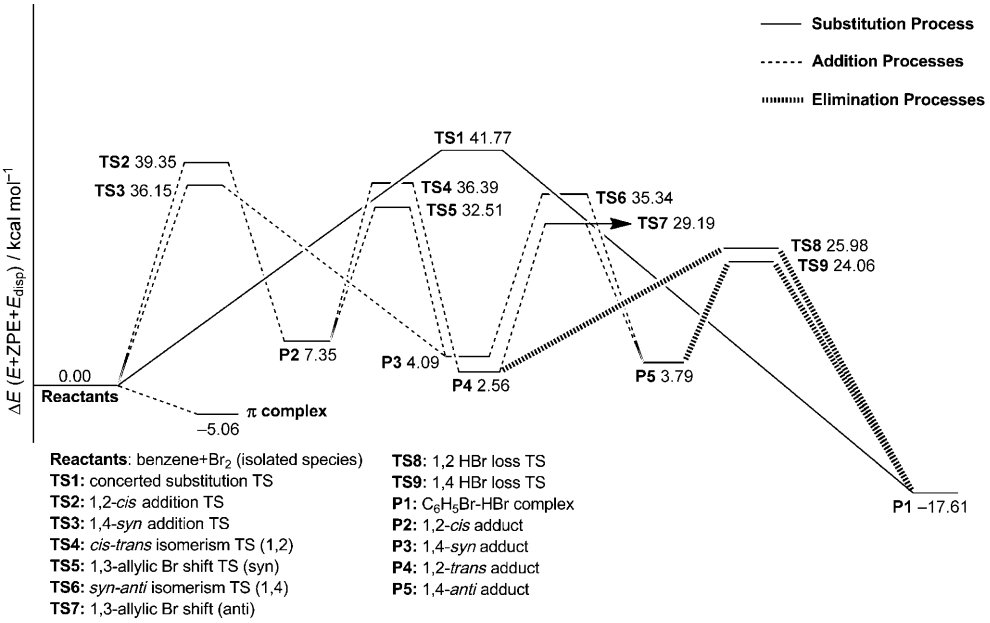

Figure 1. Computed potential energy surface (PES) for benzene–Br_2 reactions[39] in simulated CCl_4 solution at the RB2-PLYP/6-311 + G(2d,2p) level of theory. See also Table 1, column **B**, and Figure 2. The structures of the π complex and **P1**–**P5** are shown in the Supporting Information. ZPE = zero-point energy, E_{disp} = dispersion energy.

The features of Figure 1 as well as the structures of key stationary points (shown in Figure 2) are quite different from expectations. There is no Wheland intermediate akin to $\mathbf{WI}^{+}_{CCl_4}$ (which could only be optimized to a minimum as an isolated positively charged species in the absence of a counterion).[33] When the

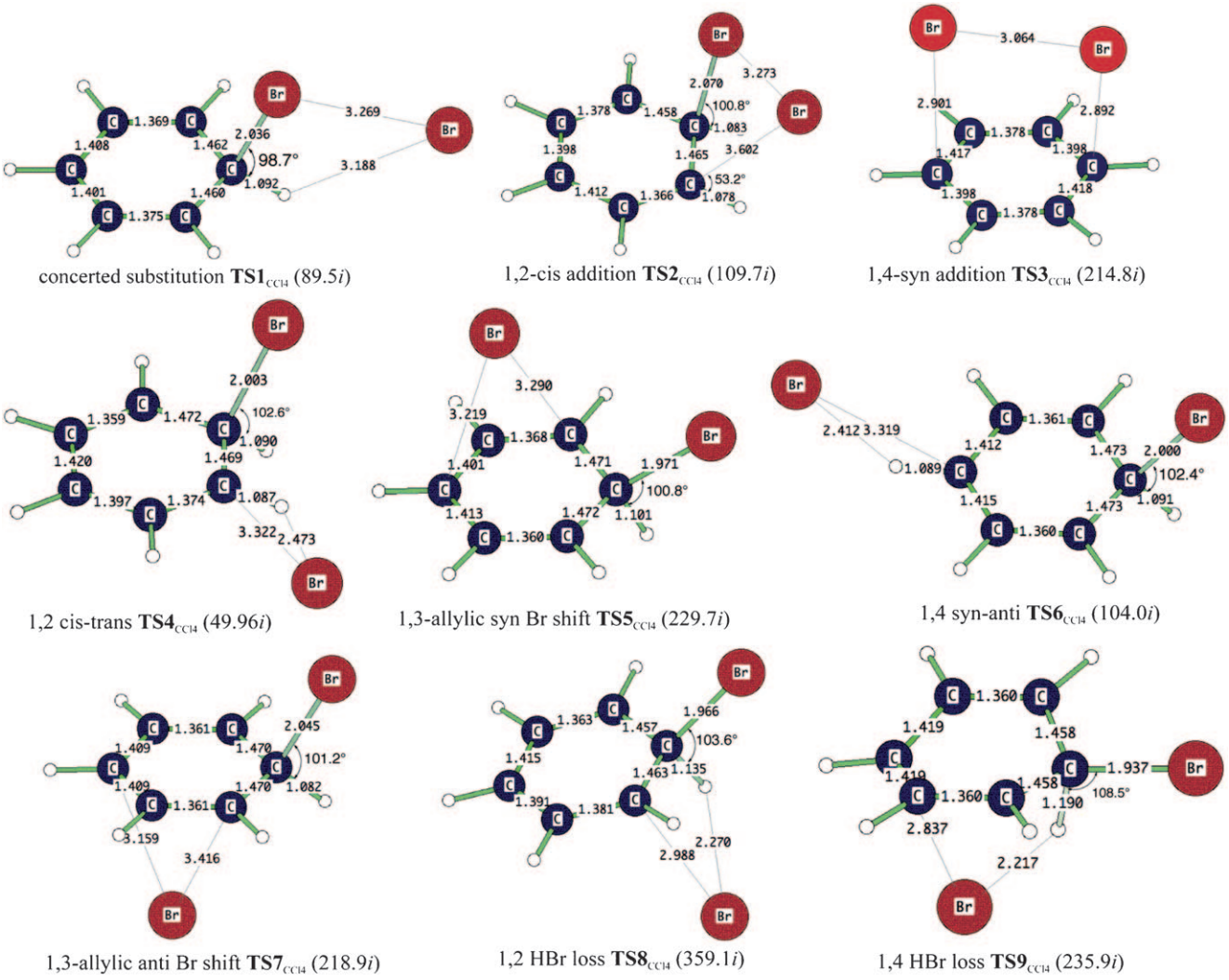

Figure 2. Geometries of $\mathbf{TS1}_{CCl_4}$ – $\mathbf{TS9}_{CCl_4}$ in simulated CCl_4 solvent at the RB2-PLYP/6-311 + G(2d,2p) level of theory. Bond lengths are given in Å, bond angles in degrees. Note that $\mathbf{TS1}_{CCl_4}$, $\mathbf{TS2}_{CCl_4}$, and $\mathbf{TS4}_{CCl_4}$ – $\mathbf{TS8}_{CCl_4}$ ion pairs have some $\mathbf{WI}^{+}_{CCl_4}$ character but are not intermediates. The geometries of the $C_6H_6Br^+$ Wheland arenium ion $\mathbf{WI}^{+}_{CCl_4}$ and $\mathbf{P1}_{CCl_4}$ – $\mathbf{P5}_{CCl_4}$ are given in the Supporting Information.

second bromine atom was included as the counterion, no minimum in that region of the PES was located. Instead of an intermediate, the computations revealed a transition state ($\mathbf{TS1}_{CCl_4}$) for a concerted substitution process. But this ion-pair process follows a direct pathway and does not involve a Wheland (benzenium-type) or any other intermediate at all! Only the transition structure $\mathbf{TS1}_{CCl_4}$ associated with the direct ion-pair substitution mechanism has a $C_6H_6Br^+$ moiety with arenium ion character, although the C–Br distance is lengthened (2.036 Å for $\mathbf{TS1}_{CCl_4}$ vs. 2.005 Å in $\mathbf{WI}^{+}_{CCl_4}$) and the *ipso* ∡Br-C-H bond angle is smaller (98.7° in $\mathbf{TS1}_{CCl_4}$ vs. 102.9° in $\mathbf{WI}^{+}_{CCl_4}$). In the presence of, for example, Lewis acid catalysts, Wheland intermediates may indeed be viable, since the counterions are complexed and interact with the arenium ion moieties less strongly.[19]

Notably, the 36.2 kcal mol^{-1} barrier for 1,4-*syn* addition to benzene (via $\mathbf{TS3}_{CCl_4}$) is lower than the 39.4 kcal mol^{-1} 1,2-*cis* addition barrier (via $\mathbf{TS2}_{CCl_4}$). Both addition processes are inherently more favorable than the best substitution alternative (41.8 kcal mol^{-1} via $\mathbf{TS1}_{CCl_4}$). Although the transition states for the direct formation of 1,2-*trans* ($\mathbf{P4}_{CCl_4}$) or 1,4-*anti* ($\mathbf{P5}_{CCl_4}$) adducts were not located, $\mathbf{P4}_{CCl_4}$ (or $\mathbf{P5}_{CCl_4}$) can form from $\mathbf{P2}_{CCl_4}$ (or $\mathbf{P3}_{CCl_4}$) by *cis–trans* isomerization via $\mathbf{TS4}_{CCl_4}$ (or *syn–anti* via $\mathbf{TS6}_{CCl_4}$). Note that 1,3-allylic Br shifts may interconvert the 1,2- and 1,4-dibromides (*syn* $\mathbf{TS5}_{CCl_4}$ connects $\mathbf{P2}_{CCl_4}$ and $\mathbf{P3}_{CCl_4}$; *anti* $\mathbf{TS7}_{CCl_4}$ connects $\mathbf{P4}_{CCl_4}$ and $\mathbf{P5}_{CCl_4}$ in Figure 1). Intramolecular HBr eliminations from the 1,2-*trans* adduct ($\mathbf{P4}_{CCl_4}$, 23.4 kcal mol^{-1} barrier via $\mathbf{TS8}_{CCl_4}$) or the 1,4-*anti* adduct ($\mathbf{P5}_{CCl_4}$, 20.3 kcal mol^{-1} barrier via $\mathbf{TS9}_{CCl_4}$) are remarkably facile. The HBr elimination $\mathbf{TS8}_{CCl_4}$ has some ion-pair arenium character (1.966 Å C–Br distance and 103.6° Br-C-H bond angle). The *ipso* C–H bond is lengthened (to 1.135 Å) owing to interaction with the Br^- counterion (i.e. ion-pairing effect). The intrinsic reaction coordinate (IRC) computations confirms that the subsequent proton loss leads to the same aromatic product, bromobenzene (as its HBr complex), but these processes and the bromine addition intermediates are hidden from experimental detection, since elimination occurs too rapidly.

The computational results for the benzene–Br_2 processes in isolation (gas phase, see Table 1 and Figure S1 in the Supporting Information) confirm the major conclusions from those in simulated CCl_4 solution; only minor details vary. As expected, all transition states have distinctly lower energies in simulated CCl_4 than in isolation (Table 1), but those for the isomerization processes (**TS4** and **TS7**) are decreased the most. In contrast to the usual assumptions, the substitution mechanism in isolation also is concerted and does not involve a Wheland intermediate; moreover, the energy of the corresponding direct substitution transition state (**TS1**, 45.0 kcal mol^{-1}) is 7.3 kcal mol^{-1} higher than that for 1,4-syn addition (**TS3**) and 2.2 kcal mol^{-1} higher than that for 1,2-cis addition (**TS2**). The most favorable reaction pathway in isolation involves 1,4-syn addition via transition state **TS3** (37.7 kcal mol^{-1}); subsequent 1,4-syn–anti isomerization (**TS6**, 43.6 kcal mol^{-1}) and ready 1,4-HBr elimination (**TS9**, 26.2 kcal mol^{-1}) give the bromobenzene–HBr product. Note that the 1,2-cis-Br_2 addition route via **TS2** (42.7 kcal mol^{-1}) is also more favorable in isolation than the direct substitution pathway (via **TS1**, 45.0 kcal mol^{-1}).

The results in Figure 1 and Table 1 confirm that the energies of the various addition products **P2**–**P5** are higher (owing to aromaticity loss) that the energy of a substitution product **P1** (which preserves aromaticity). However, the substitution product **P1** can also arise from addition–elimination routes. Hence, the mere observation of substitution product does not reveal the mode of its formation. Instead, the competition among the various alternative mechanistic routes is determined by the relative activation barrier heights (i.e., kinetic rather than thermodynamic control). Our computations show that addition–elimination processes are favored kinetically in nonpolar solvents like CCl_4 as well as in isolation. However, the barriers for benzene bromination under such conditions are too high for practicable mechanistic studies and for preparative purposes.

Consequently, polar, acidic media and Lewis acid catalysis are required to accelerate the actual reactions of benzene.[16–20] Such conditions alter the mechanism and bias the interpretation. In contrast to benzene, other arenes are more reactive and their inherent addition–substitution competition is well established experimentally (see above). We stress that addition–elimination mechanistic routes also lead to substitution products, so that the usual "preservation of aromaticity" argument (based on the reaction exothermicity) does not rationalize the assumed preference of direct substitution. Aromaticity is lost in going to the transition state for direct substitution as well as to the transition states for the addition routes.

The comparisons in Table 2 show that the computed barriers of various substitution and addition processes in isolation for the other arenes are substantially lower than those for benzene. Naphthalene favors 1,4-*syn* Br_2 addition and substitution at the 1-position kinetically. Indeed, both addition and substitution take place simultaneously in naphthalene.[4,10–13] The alternative naphthalene reactions, 1,2-*cis* and 1,2-*trans* addition as well as 2-substitution via a less stabilized arenium ion-like transition state, have 3–5 kcal mol^{-1} higher barriers.

Table 2: Substitution versus addition reaction barriers (rel. $E+ZPE+E_{disp}$) for bromination of benzene and naphthalene at RB2-PLYP/6-311+G(2d,2p) and anthracene and phenanthrene at RB2-PLYP/6-311+G(2d,2p)//RB3LYP/6-311+G(2d,2p) in isolation.[a]

Species	E_a (substitution) [kcal mol^{-1}]	E_a (addition) [kcal mol^{-1}]
benzene	**1-sub: 44.97**[b]	1,2-*cis*: 42.73
		1,4-*syn*: 37.70[b]
naphthalene	**1-sub: 34.72**[b]	1,2-*cis*: 37.01
	2-sub: 38.74	1,2-*trans*: 38.23
		1,4-*syn*: 31.27[b]
anthracene	1-sub: 29.74	1,2-*cis*: 34.61
	2-sub: 34.46	1,2-*trans*: 33.14
	9-sub: 26.00[b]	1,4-*syn*: 27.83
		9,10-*syn*: 23.47[b]
phenanthrene	1-sub: 35.68	1,2-*cis*: 37.41
	2-sub: 39.29	1,2-*trans*: 38.30
	3-sub: 38.22	**9,10-*trans*: 34.23**[b]
	4-sub: 34.79	
	9-sub: 33.11[b]	

[a] For computations at RB2-PLYP/6-311+G(2d,2p)//RB3LYP/6-311+G(2d,2p) the ZPE at RB3LYP/6-311+G(2d,2p) were used [b] The most favorable reactions are highlighted in bold.

The 9,10-syn Br_2 addition to anthracene (barrier 23.5 kcal mol^{-1}) is the kinetically most favorable process of all those considered in Table 2. For anthracene, only direct substitution at center-ring 9-position competes, consistent with the occurrence of both processes, but its computed barrier (26.0 kcal mol^{-1}) is 2.5 kcal mol^{-1} higher.

Although the computed direct substitution barriers for bromination at the five positions of phenanthrene gave the $9>4>1>3>2$ reactivity order (Table 2), corresponding qualitatively with the experimental product ratios for phenanthrene chlorination given by de La Mare et al.: 9-chloro (0.978) > 1-chloro (0.012) > 4-chloro (0.006) > 3-chloro (0.004) > 2-chloro (0.000),[13] the predominance of 9-product evidently is due to the long-recognized alkene-like double-bond character of the 9,10-C–C linkage of phenanthrene. The isolable but labile bromine adduct[6] gives 9-bromophenanthrene as well. Indeed, our 9,10-*trans* Br_2 addition barrier (34.2 kcal mol^{-1}) not only is lower than the 1,2-addition alternatives (Table 2) but also is competitive with the 33.1 kcal mol^{-1} barrier for direct substitution at the 9-position.

These computational results confirm experimental observations that nonradical addition reactions compete with electrophilic substitution of arenes generally, and they actually predict that benzene undergoes uncatalyzed bromine addition, both 1,2-*cis* and especially 1,4-*syn*, more rapidly than substitution in a simulated CCl_4 medium. We question the appropriateness of considering the classic S_EAr mechanism involving a Wheland intermediate to be the universally applicable aromatic reaction paradigm. Important aspects of this mechanism are not typical of arenes generally. Since many PBHs undergo addition processes (uncatalyzed dihydrogen[34] and Diels–Alder[35] additions) readily, it is not surprising that experimental observations of competition between addition and substitution are common.

We also emphasize the importance of including the counterions (i.e., ion-pairing effects)[36–38] in computational

investigations of the mechanisms of electrophilic arene reactions. At least under some reaction conditions, we find that no "σ complex" intermediates may be involved,[33] although the transition states may have some Wheland or arenium ion character.[39] Furthermore, substitution products may be formed more rapidly via stepwise addition–elimination pathways than by concerted substitution mechanisms.

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