insoluble molecules with dextran is effective as a method to confer water solubility. The method should be available for studies of a variety of water-insoluble molecules in aqueous solution.

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Gas-Phase Reactions of Benzenoid Hydrocarbon Ions with Hydrogen Atoms and Molecules: Uncommon Constraints to Reactivity

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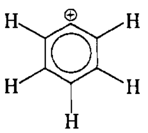
The hydrogen atom, the simplest chemical after the proton, displays in its reactions a selectivity surprising in such a small species. This is evident, for example, in reactions of hydrogen atoms with small hydrocarbon ions which are of fundamental importance in the chemistry of flames, of planetary atmospheres, and of the universe in general where hydrocarbon ions may catalyze the recombination of hydrogen atoms.[1-3] We report here results for the reactions of the benzenoid hydrocarbon ions $C_6H_n^+$ (n = 5–7) with atomic and molecular hydrogen. Remarkably, only two of this series of six reactions, all of which have exothermic channels, were observed to proceed with measurable rates, $C_6H_6^{\bullet+}$ + $H^\bullet$ and $C_6H_5^+$ + H_2, both giving the adduct $C_6H_7^+$. Such constraints to reactivity are most intriguing, particularly from the mechanistic and energetic point of view. Here we shall show that they are consistent with the structures and energies of the benzenoid ions and their possible collision complexes.

Reactions of $C_6H_n^+$ with $H^\bullet$ and H_2 were studied using the SIFT (selected ion flow tube) technique[4,5] at 297 ± 3 K and 0.35 ± 0.01 Torr of helium, unless specified otherwise. Atomic hydrogen was produced in a microwave discharge of H_2 (2–4%) in He.[6,7] $C_6H_5^+$ was generated by 50 eV electron impact upon chlorobenzene or benzene. $C_6H_6^{\bullet+}$ was generated by electron impact upon benzene. $C_6H_7^+$ was formed by proton transfer from CO_2H^+ to benzene introduced into the flow tube and was also formed in the reaction of $C_6H_6^{\bullet+}$ with $H^\bullet$. For these ions, the cyclic structures I–III related to benzene are the lowest energy isomers known[8] and should thus account for most of the $C_6H_n^+$ ion signal in question. For $C_6H_5^+$, two components of differing reactivity were present in accordance with previous studies;[9-11] there was no evidence for the presence of higher energy forms of $C_6H_6^{\bullet+}$ and $C_6H_7^+$.

Table I. Reactions of $C_6H_n^+$ (n = 5–7) with H and H_2

reactants	products	k_{obsd}[a]	k_L[b]	$-\Delta H°_{trf}$[c]	$-\Delta H°_{assn}$[d]
c-$C_6H_5^+$ + H		<0.01	1.9	9	88
l-$C_6H_5^+$ + H		<0.005	1.9	3[e]	42[e]
$C_6H_6^+$ + H	$C_6H_7^+$	0.25[f]	1.9	16	81
$C_6H_7^+$ + H		<0.01	1.9	23	41[g]
c-$C_6H_5^+$ + H_2	$C_6H_7^+$	0.05	1.5		65
l-$C_6H_5^+$ + H_2		<0.001	1.5		24[h]
$C_6H_6^{\bullet+}$ + H_2		<0.001	1.5		18[g]
$C_6H_7^+$ + H_2		<0.001	1.5		13[i]

[a] Observed rate coefficient in units of 10^{-9} cm^3 molecule^{-1} s^{-1}. The accuracy of the rate coefficients is estimated to be ±50% for reactions with H-atoms and ±30% for reactions with H_2. [b] Calculated Langevin collision rate coefficient, in units of 10^{-9} cm^3 molecule^{-1} s^{-1}. [c] Exothermicity of H-atom transfer, $C_6H_x^+ + H \rightarrow C_6H_{x-1}^+ + H_2$, in kcal mol^{-1}. [d] Exothermicity of association, in kcal mol^{-1}. [e] Calculated using $\Delta H°_f(CH_2CCHCHCCH^+)$ = 284 kcal mol^{-1}.[7,12] [f] Invariant over the pressure range 0.2–0.6 Torr. [g] For formation of ionized 1,3-cyclohexadiene. [h] For formation of protonated $CH_3C{\equiv}CC{\equiv}CCH_3$. [i] For formation of protonated 1,3-cyclohexadiene.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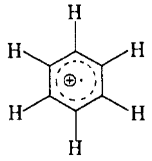
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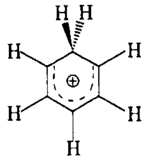
III

The rate coefficients for the observed reactions are detailed in Table I. Our results for the reactions of $C_6H_5^+$ and $C_6H_6^{\bullet+}$ with H_2 agree with those of Giles et al.,[9] although we favor the assignment of the phenylium ion as the reactive isomer in the reaction of $C_6H_5^+$ with H_2, rather than one of the higher energy linear isomers.[11]

Association is the only exothermic channel for the reactions with H_2. The observed association of c-$C_6H_5^+$ and H_2 can be rationalized as an insertion process involving the H–H bond and the vacant sp^2 orbital on the ipso carbon of the phenylium ion. This association reaction has also been observed at low pressures in FT-ICR experiments, with a rate coefficient $k = 1.5 \times 10^{-11}$ cm^3 molecule^{-1} s^{-1},[11] and thus appears to contain measurable bimolecular and termolecular components, although we have not attempted to verify this experimentally. The absence of association with H_2 for the other ions studied here can be understood since these ions do not have any entirely vacant orbitals or such a localized positive charge.

The reactions with $H^\bullet$ are still more intriguing. Association is more strongly exothermic for c-$C_6H_5^+$ than for $C_6H_6^{\bullet+}$, and yet is seen only in the latter case. Why should c-$C_6H_5^+$, which adds efficiently to H_2 and to many other neutrals,[11] not add detectably to $H^\bullet$? $C_6H_6^{\bullet+}$ possesses more vibrational/rotational degrees of freedom than c-$C_6H_5^+$, but this factor[13] seems insufficient to account for the observed trend in efficiency of association. Furthermore, hydrogen atom transfer reaction 1 is exothermic for all four of the reactant ions included in our study, and yet is not observed for any of these ions.

$$C_6H_n^+ + H^\bullet \rightarrow C_6H_{n-1}^{\bullet+} + H_2 \tag{1}$$

The absence of H-atom transfer from $C_6H_5^+$ to $H^\bullet$ is consistent with the likely collision complex (IV) in which the reacting hydrogen atom never gets sufficiently close to any of the C–H bonds in order to break them and form H_2. The inefficiency of association in this system may arise because the initial collision complex involves an interaction of the hydrogen atom's electron with the vacant σ-orbital upon I, leading to an excited electronic state of the benzene cation. Formation of the ground state requires re-

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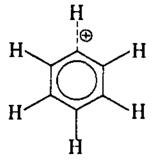
location of a π-electron to this σ-orbital before dissociation of the collision complex. The complex lifetime partially depends upon the depth of the potential well accessible to reactants: this potential well will be much shallower than is suggested by the heat of formation of ground-state $C_6H_6^{\cdot+}$. The threshold for the electronically forbidden ${}^2E_{2g}(\sigma-1) \leftarrow {}^2E_{1g}(\pi-1)$ transition has been assigned at 502 nm,[14] corresponding to an energy difference of 57 kcal mol^{-1}. The potential well depth of the collision complex IV thus cannot exceed 31 kcal mol^{-1}, leading to a substantially reduced complex lifetime consistent with the observed lack of association.



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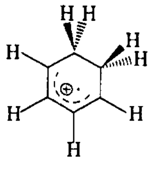

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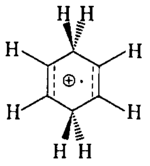
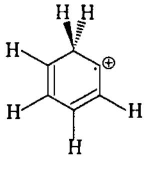


VI

The apparent saturation (as inferred by the lack of pressure dependence)[15] of the association reaction of $C_6H_6^{\cdot+}$ with $H^\cdot$ is consistent with conservation of spin in this reaction. The association is seen to occur at $k/k_c = 0.13 \pm 0.07$, reasonably close to that fraction ($^1/_4$) of the collision rate which would be expected for formation of singlet products. The lowest lying triplet state of $C_6H_7^+$, if bound, presumably is sufficiently far above the ground singlet state to render the triplet association channel much less efficient; alternatively, triplet association may fall upon a repulsive curve. H-atom transfer does not occur because essentially all collisions leading to the singlet potential surface result in association, while H-atom transfer on the triplet potential surface is presumably endothermic: the highest level theoretical calculation performed on the singlet–triplet separation in $C_6H_5^+$ places the B_1 level at 5 ± 15 kcal mol^{-1} above the $^1A_1$ level.[17] The uncertainty of this calculation is sufficient to permit the endothermicity of this channel. The lack of association of $C_6H_7^+$ with $H^\cdot$ is consistent with the shallower potential well for this reaction. The absence of H-atom transfer is more surprising, since the arguments presented above for $C_6H_5^+$ and $C_6H_6^{\cdot+}$ clearly do not apply to the reaction of $C_6H_7^+$ with $H^\cdot$. Two collision complexes, V and VI, can be formed corresponding to the dominant centers of charge localization in structure III. Loss of H_2 by 1:1 elimination from these complexes would give the isomers VII and VIII, respectively, whose heats of formation are not known but are probably sufficiently high that their production in this reaction is endothermic. (1,2)- and (1,4)-hydrogen shifts would convert VII and VIII, respectively, to II; the absence of H-atom transfer in $C_6H_7^+ + H^\cdot$ suggests that a barrier prevents their occurrence concomitantly with H_2 loss.[18]



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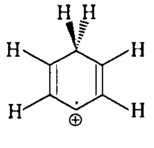

VIII

In summary, we have measured rate coefficients for reactions of $H^\cdot$ and H_2 with several hydrocarbon ions generated from benzene and have proposed mechanisms to account for the observed reactivities. These results appear to preclude a catalytic role in H-atom recombination for all three of the benzenoid hydrocarbon ions as well as the linear $C_6H_5^+$ isomer investigated in this study.

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[15] The observation of apparent saturation suggests the occurrence of a saturated termolecular reaction in which the $C_6H_7^+$ is stabilized by collisions with the He buffer gas, but it does not rule out the possibility of bimolecular radiative association[16] or, indeed, the occurrence of a combination of the two.

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Endocyclic Restriction Test: Experimental Evaluation of the Transition Structure Geometry of a Nucleophilic Substitution at Trivalent Phosphorus

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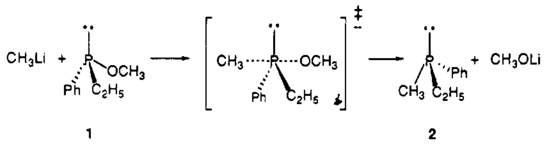
The generally accepted mechanism for nucleophilic substitution at trivalent phosphorus is the S_N2 in-line process.[1,2a,b,3] The reaction of **1** with methyllithium to give **2** is illustrative of these reactions, which have been found to proceed with inversion of configuration at phosphorus.[1-4] We wish to report an evaluation of the transition structure geometry for a nucleophilic substitution of an alkoxyl group by an aryllithium at trivalent phosphorus. Our results rule out a classic S_N2 in-line mechanism for the system we have studied.



1 2

In an application of the endocyclic restriction test, we have investigated the conversion of **3** to **4**.[5] If a geometry is required for substitution in which the entering and leaving groups are simultaneously in the apical positions of a trigonal bipyramid about phosphorus, this conversion would be intermolecular because a 180° disposition of the entering and leaving groups would not be possible within the five-membered endocyclic ring required for an intramolecular reaction. However, if the reaction can proceed by a different pathway, an intramolecular process could be observed.

3 4

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