

Phenyl Radical, Cation, and Anion. The Triplet–Singlet Gap and Higher Excited States of the Phenyl Cation

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Abstract: High-level ab initio molecular orbital calculations have been carried out for the phenyl cation (**1**), the phenyl radical (**2**), and the phenyl anion (**3**). Our best estimate for the heat of formation ($\Delta H_{f,298}$) of the phenyl radical is 340 kJ mol⁻¹, corresponding to 476 kJ mol⁻¹ for the 298 K C–H bond dissociation energy in benzene. The calculated $\Delta H_{f,298}$ of the phenyl anion is 224 kJ mol⁻¹, leading to an electron affinity for the phenyl radical of 116 kJ mol⁻¹, and a gas-phase acidity for benzene of 1671 kJ mol⁻¹. The ground state of the phenyl cation is found to be a singlet (**1**⁻¹A₁, $\Delta H_{f,298} = 1134$ kJ mol⁻¹), with the triplet (**1**⁻³B₁, $\Delta H_{f,298} = 1237$ kJ mol⁻¹) lying significantly higher in energy (by 103 kJ mol⁻¹). The energies of the **1**⁻¹A₁ and **1**⁻³B₁ states of the phenyl cation at the phenyl radical geometry are much closer, but **1**⁻¹A₁ remains the energetically lowest electronic state. The essentially isoenergetic **1**⁻³A₂ and **1**⁻¹A₂ states lie about 25 kJ mol⁻¹ higher in energy than **1**⁻³B₁, while **1**⁻¹B₁ is nearly 60 kJ mol⁻¹ higher in energy. The implications of these results with respect to recent spectroscopic studies of the phenyl radical and the role of the triplet phenyl cation in the dissociation of benzene cation are discussed.

Introduction

Even though more than 50 years have passed since Waters² postulated the intermediacy of aryl cations, and phenyl cations in particular, in the decomposition of benzenediazonium salts, this interesting class of reactive intermediates continues to attract a great deal of attention.³ Initially, even the very existence of aryl cations was debated,⁴ until Swain⁵ provided compelling evidence for the generation of the phenyl cation in solution.⁶

An issue that has been the focus of many studies is the electronic character of the ground state of the phenyl cation, namely whether it is a triplet (as Taft first proposed⁷) or a singlet.⁸ While it is now generally believed that the singlet is the ground state,⁹ the triplet–singlet (T-S) gap has not been unequivocally established. Experimental data from an early photoionization study of the phenyl radical¹⁰ were interpreted^{10,11} in favor of a significant T-S splitting (96 kJ mol⁻¹). This is in agreement with early estimates (of 84 kJ mol⁻¹) based on ab initio molecular orbital calculations.¹² On the other hand, a more

recent analysis of the photoelectron spectrum of the phenyl radical proposed that the singlet phenyl cation lies just 31 kJ mol⁻¹ in energy below the triplet,¹³ which was also supported by ab initio calculations based on multiconfiguration (MC) wave functions.¹⁴ Recent ab initio calculations based on a multireference (MR) approach with limited configuration interaction return to the higher estimate of 79 kJ mol⁻¹.¹⁵ The large discrepancy between the two sets of values for the T-S gap in the phenyl cation is clearly an undesirable state of affairs. Besides its intrinsic interest, a quantitative knowledge of the T-S splitting is very important for the kinetic modeling of the unimolecular dissociation of benzene cation and related systems with use of statistical theories.¹⁶ While the theoretical estimation of T-S splittings, even in smaller systems such as methylene, is not a trivial task,¹⁷ current computational methods should certainly be able to differentiate between two sets of values that differ by more than 50 kJ mol⁻¹. Accordingly, we have used high levels of ab initio molecular orbital theory to examine various electronic states of the phenyl cation, and the results are reported in this paper.

In addition to the phenyl cation (**1**), the phenyl radical (**2**) and phenyl anion (**3**) are also fundamental species of significant interest. The heat of formation¹⁸ and infra-red spectrum at low temperature¹⁹ of the phenyl radical have been the subject of

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recent experimental studies, while for the phenyl anion experimental attention has been mainly focussed on its gas-phase formation from benzene.^{18,20} We have included both species in the present work, and we report here on the heats of formation of the phenyl radical and the phenyl anion, the ionization energies and electron affinity of the phenyl radical, and the C–H bond dissociation energy and gas-phase acidity of benzene.

Computational Procedures

Ab initio molecular orbital calculations²¹ were carried out with the GAUSSIAN 94,²² GAMESS,²³ MOLPRO,²⁴ ACES II²⁵ and DALTON²⁶ programs. Optimized geometries for the lowest singlet (1^1A_1) and triplet (1^3B_1) states of the phenyl cation (**1**) and for the ground states of the phenyl radical (**2**) and the phenyl anion (**3**) were obtained at various levels of theory, including B3-LYP/6-31G(d),^{22,27} CASSCF/6-31G(d), and RCCSD(T)(full)/6-31G(d). Key geometrical parameters are summarized in Figure 1. Results at other levels of theory are presented in Table S1 of the Supporting Information. The nature of the stationary points was characterized by frequency calculations at all levels of theory except RCCSD(T). Energies are reported at the G2(MP2,B3LYP,RCC) and CAS-MP2^{28,29} levels of theory. G2(MP2,-B3LYP,RCC) corresponds effectively to calculations at the RCCSD(T)/6-311+G(3df,2p) level on B3-LYP/6-31G(d) optimized geometries, incorporating scaled B3-LYP/6-31G(d) zero-point vibrational energies and a so-called higher level correction (HLC). It is a modification of the recently proposed G2(MP2,B3LYP,CC) model,³⁰ the only difference being that for open-shell species the single-point coupled-cluster calculations are based on an ROHF (RCCSD(T)) rather than a UHF (UCCSD(T)) reference wave function. The active space for the CASSCF wave functions consists of seven orbitals: the six π orbitals (two a_2 and four b_1) and the σ orbital (a_1) that corresponds to the

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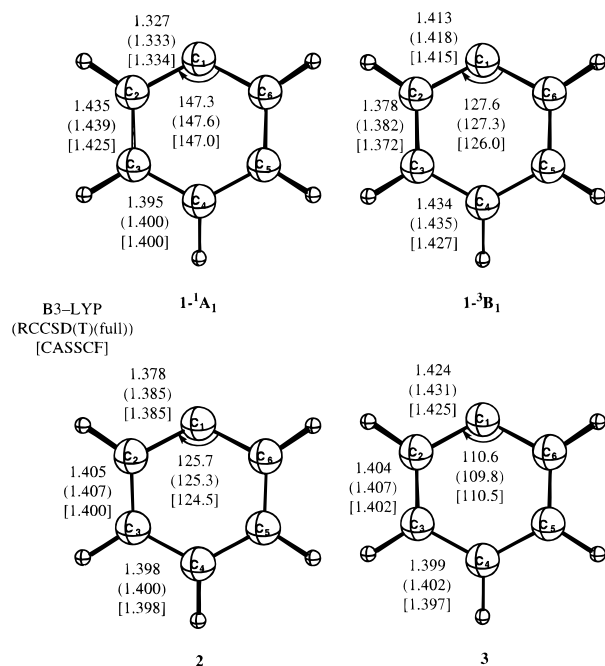
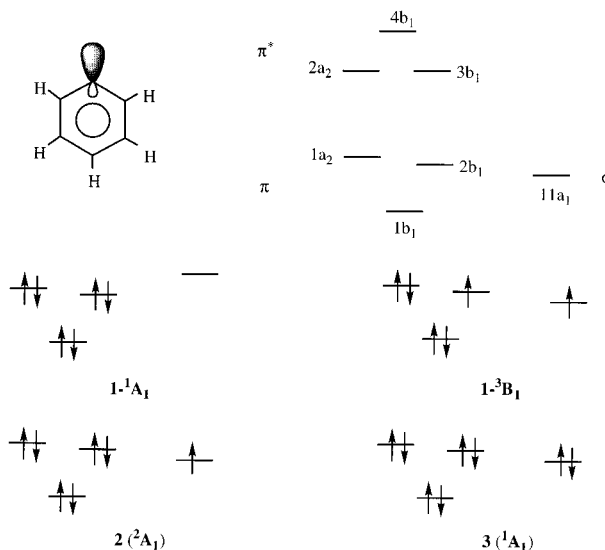


Figure 1. Bond lengths (Å) and $\angle C_2C_1C_6$ bond angles (°) for the phenyl cation (1^1A_1 , 1^3B_1), the phenyl radical (**2**), and the phenyl anion (**3**) at selected levels of theory with the 6-31G(d) basis set.

Scheme 1



"missing" C–H bond (Scheme 1). These are occupied by six (**1**), seven (**2**), or eight (**3**) electrons. Total energies at the G2(MP2,B3LYP,-RCC) level are presented in Table S2 and at the CASSCF and CAS-MP2 levels in Table S3 (Supporting Information).

Results and Discussion

Theoretical Aspects. A recent analysis³¹ of the relative merits of UHF and ROHF wave functions within the CCSD formalism suggested that modest spin-contamination of the reference UHF wave function should generally not affect the performance of the corresponding CCSD wave function (UCCSD). While the comparison of the two reference wave functions in this analysis was based largely on the spin purity of the resulting coupled cluster wave function, one would expect that this conclusion should also carry over to the relative energies of the RCCSD and UCCSD wave functions. Indeed, we find

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that in most cases the CCSD and the CCSD(T) energies are not very sensitive to whether ROHF or UHF is used as the reference wave function (Table S4, Supporting Information). A notable exception, however, is the phenyl radical where the RCCSD(T) energy is 9 kJ mol⁻¹ below the UCCSD(T) value.³² However, in this case the spin contamination of the UHF wave function (as judged by its spin-squared expectation value of 1.4) can hardly be regarded as modest. In order to treat the systems in the present study in as uniform a way as possible, we have modified the original G2(MP2,B3LYP,CC) method as described above, using RCCSD(T) in place of UCCSD(T).³³

Several methods were examined for optimizing the geometries of **1–3**. The UHF wave function for **1-³B₁** exhibits artificial symmetry breaking, predicting one imaginary frequency (along a b₂ mode) for the C_{2v} stationary point. Minimization under C_s symmetry results in a planar structure distinctly different from that of the C_{2v} stationary point, but with essentially the same energy. At the UMP2(full) level of theory, a C_{2v} minimum is found, but one of the vibrational modes (the same b₂ mode) is associated with an unreasonably high frequency (>6000 cm⁻¹).³⁴ On the other hand CASSCF, B3-LYP, and QCISD(T)(full)/3-21G methods all predict a C_{2v} minimum with all vibrational frequencies appearing reasonable. B3-LYP/6-31G(d) gave results for **1–3** that were consistently close to those obtained at the RCCSD(T)(full) level of theory (Figure 1). In addition, limited testing indicated that G2(MP2,B3LYP,RCC) energies calculated at the B3-LYP and RCCSD(T)(full) geometries are very close to one another (generally within 4 kJ mol⁻¹), with the B3-LYP geometry consistently providing the lower energies.³⁵

Perhaps the most notable geometric difference in the four species shown in Figure 1 is the size of the angle at the dehydro carbon (∠C₂C₁C₆). Increased occupation of the σ (11 a₁) molecular orbital results in a narrowing of the angle, which is presumably associated with an increase in the s character of the σ orbital.^{12,13} There is also a systematic increase in the C₁–C₂ (C₁–C₆) bond length, and to a lesser extent a systematic decrease in the C₂–C₃ (C₅–C₆) bond length as one proceeds from **1-¹A₁** to **2** and **3**.¹²

The choice of an active space of seven orbitals for the CASSCF calculations was based on what we considered to be the minimum active space necessary for a balanced treatment of the phenyl radical, the phenyl anion, and the various low-lying states of the phenyl cation. However, having settled on this active space it is quickly clear that the CASSCF level of theory itself is inadequate even for a qualitative treatment of the ionization energies of the phenyl radical. The relative energies of **1** and **2** are not well described at the CASSCF/6-311G(d,p) level and are hardly improved in expanding the basis set to 6-311+G(3df,2p) (Table S3, Supporting Information). Furthermore, the electron affinity of the phenyl radical is calculated to be negative.

The picture changes dramatically when dynamic electron correlation is taken into account (CAS-MP2). A more reasonable estimate for the T-S gap in the phenyl cation is obtained and the phenyl anion (**3**) is predicted to be bound with CAS-MP2/6-311G(d,p). Thus, the T-S gap obtained directly from

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CAS-MP2/6-311+G(3df,2p) total energies (Table S3, Supporting Information) is 83 kJ mol⁻¹, which is somewhat lower than our best estimate of 103 kJ mol⁻¹ (see below). Inclusion of dynamic correlation and the use of a large basis set are essential in the challenging case of the vertical ionization energies of **2**, to predict the correct order of relative stabilities for the ¹A₁ and ³B₁ states. Our results show that it is the **1-¹A₁** state that preferentially benefits when dynamic correlation is included in the CASSCF treatment. Preferential stabilization of **1-¹A₁** also results from improvement of the basis set in the CAS-MP2 treatment. On the other hand, the relative energies of **1-³B₁**, **1-¹B₁**, **1-³A₂**, and **1-¹A₂** are reasonably well described even at the CASSCF level of theory. A possible rationalization comes from observing that the last four states all have five π electrons whereas **1-¹A₁** has six π electrons. A balanced description is therefore achievable at a lower level of theory for the five-π-electron states.

Heats of Formation. As we have noted recently,³⁶ G2 and G2(MP2)³⁷ atomization energies lead to an overestimation of the heat of formation of benzene (by 16 and 21 kJ mol⁻¹, respectively). However, much better agreement with experiment is found when the G2-type total energies are employed with isodesmic and/or isogyric reactions. Therefore, it seems reasonable to follow a similar procedure here, and use benzene as our reference system, for the estimation of heats of formation. Along these lines, we have used the calculated energies of reactions 1–7 (Table 1) in conjunction with experimental data^{38–40} for all the species involved except for the species of interest to estimate the heats of formation of the phenyl radical (**2**), the phenyl anion (**3**), and the singlet and triplet phenyl cations (**1-¹A₁** and **1-³B₁**).

According to our calculations the C–H bond dissociation energy (BDE) in benzene is 476 kJ mol⁻¹, which is 10 kJ mol⁻¹ greater than that in ethylene (reactions 1 and 2 in Table 1). This leads to predicted values of 340–341 kJ mol⁻¹ for the heat of formation of the phenyl radical, in close agreement with other recent computational findings.^{33,41}

The C–H bond dissociation energy in benzene and the heat of formation of **2** have been the subject of a recent elegant and detailed experimental study.¹⁸ From the analysis of the experimental data, a C–H BDE of 475 ± 2 kJ mol⁻¹ for benzene and a heat of formation for **2** of 339.7 ± 2.5 kJ mol⁻¹ have been proposed. These results are in excellent agreement with our calculated values (476 and 340 kJ mol⁻¹, respectively), but this agreement appears to be partly fortuitous, since the experimental quantities that were used to derive the C–H BDE of benzene, namely the gas-phase acidity of benzene and the electron affinity of the phenyl radical, are themselves not in quite as good agreement with theory. The acidity of benzene at 298 K was determined in flowing afterglow/selected ion flow tube experiments¹⁸ as 1681 ± 2 kJ mol⁻¹ whereas we calculate a value of 1671 kJ mol⁻¹ at 298 K. Interestingly, our calculated

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Table 1. Calculated Reaction Energies (ΔH_f , kJ mol⁻¹) and Derived Thermochemical Quantities (kJ mol⁻¹) at 298 K Relating to the Phenyl Cation (**1**), the Phenyl Radical (**2**), and the Phenyl Anion (**3**)^a

		ΔH_f	ΔH_f 298	
(1)	$C_6H_5^+ + C_2H_4 \rightarrow C_6H_6 + C_2H_3^+$	-10	2	340 ^{b,c}
(2)	$C_6H_5^+ + H^+ \rightarrow C_6H_6$	-476		341 ^b
(3)	$C_6H_5^+ + e^- \rightarrow C_6H_5^-$	-118 ^d	3	
(4)	$C_6H_5^- + H^+ \rightarrow C_6H_6$	-1671 ^e		223
(5)	$C_6H_5^- + C_2H_4 \rightarrow C_6H_6 + C_2H_3^-$	42 ^f		225
(6)	$C_6H_5^+(^1A_1) + H^- \rightarrow C_6H_6$	-1196 ^g	1-¹A₁	1134 ^{b,g}
(7)	$C_6H_5^+(^3B_1) + 2C_2H_4 \rightarrow C_6H_6 + C_2H_4^{++} + C_2H_3^+$	106	1-³B₁	1239 ^{b,c}
(8)	1-³B₁ + ¹ CH ₂ → 1-¹A₁ + ³ CH ₂	-137	$C_6H_5^+(T-S)$	99 ^h

^a At the G2(MP2,B3LYP,RCC) level of theory. ^b Using data from ref 38, unless otherwise noted. ^c ΔH_f for $C_2H_3^+$ taken from ref 39. ^d 105.7 kJ mol⁻¹ from electron detachment experiments.⁴² ^e 1681 kJ mol⁻¹ from flowing afterglow/selected ion flow tube experiments.¹⁸ ^f ΔH_f for $C_2H_3^-$ taken from ref 39. ^g Obtained by using the exact value (-0.52539 hartree) for the energy of H^- .⁴⁰ ^h Obtained by using singlet-triplet splitting for methylene from ref 43.

Table 2. Best Theoretical Estimates of Heats of Formation (ΔH_f) at 0 and 298 K for the Phenyl Cation (**1**), Radical (**2**), and Anion (**3**) and Derived Adiabatic (IE_a) and Vertical (IE_v) Ionization Energies and Electron Affinities (EA) at 298 K (kJ mol⁻¹)^a

species		ΔH_{f0}	ΔH_{f298}	IE_a^b	IE_v^c	EA ^d
1-¹A₁	$C_6H_5^+$	1146	1134 ^e	794	881	
1-³B₁	$C_6H_5^+$	1250 ^f	1237 ^f	897	915	
2-²A₁	$C_6H_5^*$	354	340 ^g			
3	$C_6H_5^-$	237 ^h	224 ^h			116
T-S (phenyl cation)				103 ⁱ	(34)	

^a Estimated uncertainties of 5 and 10 kJ mol⁻¹, respectively, are associated with the calculated heats of formation on the one hand and ionization energies and electron affinities on the other. ^b Adiabatic ionization energy of the phenyl radical to the specified state of the phenyl cation. ^c Vertical ionization energy of the phenyl radical to the specified state of the phenyl cation. ^d Electron affinity of the phenyl radical to produce the phenyl anion. ^e The recommended experimental value from gas-phase appearance energies is 1127 kJ mol⁻¹.³⁸ ^f Derived from our best estimates for $\Delta H_f(1-^1A_1)$ and the T-S splitting. ^g The recommended experimental value is 339.7 ± 2.5 kJ mol⁻¹.¹⁸ ^h Estimated as the average of the $\Delta H_f(3)$ derived from reactions 4 and 5 of Table 1. ⁱ Experimental values for the adiabatic triplet-singlet splitting of 96 and 31 kJ mol⁻¹ have been suggested (refs 10 and 13, respectively).

acidity of benzene at 600 K of 1676 kJ mol⁻¹ is in close agreement with a previous 600 K experimental value of 1677 ± 3 kJ mol⁻¹.²⁰ Our best estimate for the electron affinity of the phenyl radical is 116 kJ mol⁻¹ (Table 2) compared with the experimental value of 105.7 ± 0.6 kJ mol⁻¹.⁴² Thus our underestimation compared with the most recent experimental results of the acidity of benzene, when combined with our overestimation of the EA of the phenyl radical, leads to the apparent excellent agreement as far as the heat of formation of **2** and the C-H BDE in benzene are concerned. While the discrepancies are not very large, their source is presently unclear. In this context it is interesting to note that our calculated EA of the vinyl radical and the gas-phase acidity of ethylene (67 and 1712 kJ mol⁻¹, respectively) are in very good agreement with the corresponding experimental quantities (64 ± 2 and 1713 ± 3 kJ mol⁻¹, respectively) as reported³⁹ by the same group that carried out the experimental measurements on the EA of the phenyl radical and the acidity of benzene.

In a similar fashion, using reactions 6 and 7 (Table 1) we obtain 1134 and 1239 kJ mol⁻¹ for the ΔH_{f298} of the singlet (**1-¹A₁**) and the triplet (**1-³B₁**) phenyl cation, respectively. The calculated value for **1-¹A₁** is in good agreement with the recommended heat of formation of the phenyl cation based on a review of gas-phase appearance energies (1127 kJ mol⁻¹),³⁸ indicating that under these conditions the phenyl cation is observed in its singlet state.

(42) Gunion, R. F.; Gilles, M. K.; Polak, M. L.; Lineberger, W. C. *Int. J. Mass Spectrom. Ion Proc.* **1992**, *117*, 601.

Excited States of the Phenyl Cation and the Ionization Energies of the Phenyl Radical. The T-S gap obtained by directly comparing the G2(B3LYP,MP2,RCC) total energies of the triplet (**1-³B₁**) and the singlet (**1-¹A₁**) cation is 110 kJ mol⁻¹ (Table S2, Supporting Information). However, it is likely that, even at this high level of theory, the computational treatment of these two species is not perfectly balanced.¹⁷ A better estimate is likely to be arrived at if the T-S gap of the phenyl cation is compared with that of methylene, which is known very accurately from spectroscopic measurements.⁴³ This comparison (reaction 8) leads to a "corrected" theoretical value of 99 kJ mol⁻¹ for the T-S splitting in the phenyl cation. A third estimate of the T-S gap, calculated from the ΔH_{f298} values derived for **1-³B₁** and **1-¹A₁** in Table 1, is 105 kJ mol⁻¹. This leads to a (subjective) average of 103 kJ mol⁻¹ as our best approximation to the T-S splitting in the phenyl cation.

Our best estimates of the heats of formation of the species discussed above are shown in Table 2. From these values the two lowest adiabatic ionization energies (IE_a) of the phenyl radical, corresponding to the formation of **1-¹A₁** and **1-³B₁**, respectively, are readily obtained. We have also calculated the total energies of **1-¹A₁** and **1-³B₁** at the phenyl radical geometry, and in a manner similar to that used for the IE_a s, we have arrived at our best estimates for the two lowest vertical IEs (IE_v , Table 2). Due to the differences between the geometries of **1-¹A₁** and **2**, the vertical IE for the formation of **1-¹A₁** is significantly higher than the adiabatic IE (by 87 kJ mol⁻¹). In the case of **1-³B₁**, the difference between vertical and adiabatic IEs is much smaller at 18 kJ mol⁻¹. However, due to the initial large T-S gap (103 kJ mol⁻¹), we find that even at the phenyl radical geometry **1-¹A₁** is still lower in energy than **1-³B₁**, by 34 kJ mol⁻¹.⁴⁴

Other excited states of the phenyl cation were examined at the CAS-MP2 level. Optimization of **1-¹A₂**, **1-³A₂**, and **1-¹B₁** states subject to C_{2v} -symmetry constraints leads to structures that were all found to be higher-order stationary points,⁴⁵ and their possible adiabatic formation from **2** was not considered any further. However, we calculated the energies of these states at the phenyl radical geometry, corresponding to vertical

(43) McKellar, A. R. W.; Bunker, P. R.; Sears, T. J.; Evenson, K. M.; Saykally, R. J.; Langhoff, S. R. *J. Chem. Phys.* **1983**, *79*, 5251.

(44) In contrast, the MR-CIS calculations¹⁵ predict that vertical ionization to the triplet is lower in energy than vertical ionization to the singlet by 74 kJ mol⁻¹. Similarly, calculations using a limited type of configuration interaction including single and double excitations¹³ also find **1-³B₁** to be lower in energy than **1-¹A₁**. We have found this same (incorrect) ordering of states at the CISD/6-31G(d) level of theory even when the Davidson correction for quadruple excitations was included. This is somewhat surprising given that the MP2 level of theory correctly predicts the opposite order of states. This is a manifestation of the sensitivity to the level of theory of the calculated vertical T-S gap.

(45) The two A₂ states were found to be first-order saddle points, while **1-¹B₁** was found to be a second-order saddle point.

Table 3. Energies (ΔE , kJ mol⁻¹) of Selected Electronic States of the Phenyl Cation Relative to the $1\text{-}^3\text{B}_1$ State at the CAS-MP2 Level of Theory^{a,b}

species	ΔE
$1\text{-}^3\text{B}_1^c$	0
$1\text{-}^3\text{A}_2$	24
$1\text{-}^1\text{A}_2$	26
$1\text{-}^1\text{B}_1$	59 ^d

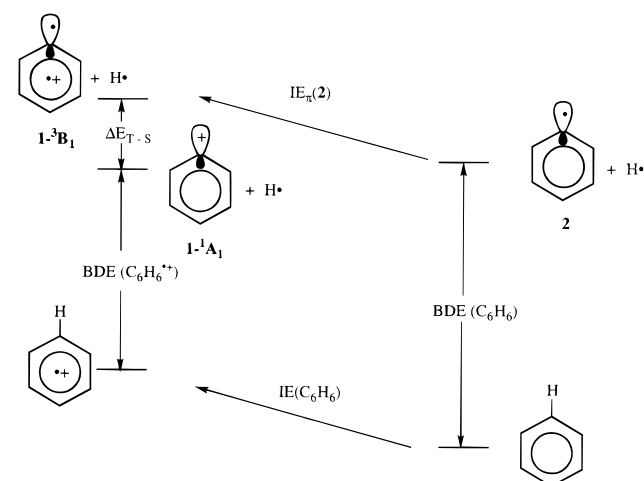
^a At the B3LYP/6-31G(d) optimum geometry of the phenyl radical, corresponding to vertical ionization. ^b With the 6-311+G(3df,2p) basis set, unless otherwise noted. ^c Relative to -230.75437 hartrees. ^d With the 6-311G(d,p) basis set.

ionization (Table 3).⁴⁶ The two A₂ states, which are energetically almost degenerate, are predicted to lie approximately 25 kJ mol⁻¹ higher in energy than $1\text{-}^3\text{B}_1$, i.e. 60 kJ mol⁻¹ higher than $1\text{-}^1\text{A}_1$. On the other hand, $1\text{-}^1\text{B}_1$ is predicted to be about 59 kJ mol⁻¹ higher than $1\text{-}^3\text{B}_1$ at the phenyl radical geometry. The finding that the two A₂ states are nearly degenerate, whereas the triplet B₁ state is significantly lower in energy than the singlet B₁ state, can be rationalized by taking into account the topological properties of the singly occupied molecular orbitals (SMO). In both cases, the σ SMO is an a₁ orbital largely localized on the dehydro carbon. The other SMO is a π MO. In the case of the A₂ states, the a₂ SMO has a node on the dehydro carbon and therefore the direct interaction between the two odd electrons is minimized. On the other hand, the b₁ SMO has significant density on the dehydro carbon causing a larger interaction between the two electrons. As expected under such circumstances, the B₁ triplet state is calculated to lie well below the B₁ singlet.

Phenyl Cation: Comparison of Theoretical Findings with Experimental Data. A photoionization mass spectrometry (PIMS) study of the phenyl radical concluded that the first and second adiabatic ionization energies of the phenyl radical differ by 96 kJ mol⁻¹.¹⁰ The lowest IE_a was measured at 782 ± 10 kJ mol⁻¹ and assigned to the formation of $1\text{-}^1\text{A}_1$, while the second ionization (878 ± 10 kJ mol⁻¹) was postulated to be due to the formation of $1\text{-}^3\text{B}_1$.^{10,11} While our calculated IE_as are individually higher by 12–19 kJ mol⁻¹, the agreement is sufficient to strongly support the above interpretation.

Some time ago the photoelectron (PE) spectrum of the phenyl radical (prepared from the reaction of atomic fluorine with benzene) was analyzed with the help of ab initio calculations.¹³ It was proposed that the adiabatic IE corresponding to the formation of the singlet cation takes place at 772 ± 10 kJ mol⁻¹ (not observed in the experimental spectrum), while two peaks observed at 803 ± 4 and 837 ± 4 kJ mol⁻¹ were assigned to the adiabatic and vertical ionization, respectively, to form $1\text{-}^3\text{B}_1$. This interpretation is not compatible with our findings, since our calculations indicate that significantly greater energy is required for the (adiabatic or vertical) formation of $1\text{-}^3\text{B}_1$ from the phenyl radical. In addition, the calculated difference between the adiabatic and vertical ionization energies for the formation of $1\text{-}^3\text{B}_1$ is somewhat smaller (18 kJ mol⁻¹). From our results alone an unambiguous interpretation of the spectrum is not possible. However, we note that the experimentally measured distance between the two peaks (34 kJ mol⁻¹) closely matches our calculated vertical T-S gap. While this may be purely coincidental, it does suggest the possibility that what is actually observed is the vertical spectrum from the vibrationally excited (by ca. 80 kJ mol⁻¹) phenyl radical to $1\text{-}^1\text{A}_1$ and $1\text{-}^3\text{B}_1$.⁴⁷

(46) At the phenyl radical geometry, further electronic states like $1\text{-}^3\text{B}_2$, $1\text{-}^1\text{B}_2$ and $1\text{-}^3\text{A}_1$ are found to be significantly higher in energy than $1\text{-}^3\text{B}_1$ (by 252, 297 and 409 kJ mol⁻¹, respectively, at the CAS-MP2/6-311G(d,p) level).

Scheme 2

In a recent study of the unimolecular dissociation of the benzene cation within the framework of transition-state theory, it was suggested that at the transition state the surface corresponding to the triplet phenyl cation might lie below that of the singlet, thereby providing the dominant contribution to the reaction rate.^{16c} In this connection, it is relevant to note that it is the electronic structure of the *triplet* phenyl cation that correlates with the ground state of the benzene cation.^{16c} While our calculations do not directly address this issue, a comparison between our estimated heats of formation and the experimental results¹⁶ makes it clear that the phenyl cation is produced in its ground (singlet) state. In other words, during the dissociation of the benzene cation intersystem crossing takes place at some point along the reaction coordinate.⁴⁸ The high T-S splitting predicted by the current calculations suggests that the relative contribution of the triplet and singlet states to the reaction rate should be re-evaluated.

It might also be helpful to add a qualitative explanation as to why the T-S splitting in the phenyl cation might be expected to be large. Chen has used a valence bond promotion energy argument to relate T-S gaps in biradicals with differences in relevant BDEs.¹¹ Along similar lines, one can argue that the C–H BDE in the benzene radical cation should be smaller than the C–H BDE in benzene by an amount that is similar to the T-S gap in the phenyl cation (Scheme 2). Our calculations find the bond in the radical cation to be weaker by 109 kJ mol⁻¹. Similarly, available experimental data³⁸ show that the C–H BDE in the benzene radical cation is around 370 kJ mol⁻¹, or 105 kJ mol⁻¹ less than the corresponding BDE of benzene. In other words, according to the valence bond picture of Scheme 2, one expects the T-S gap in the phenyl cation to be of the order of 100 kJ mol⁻¹. Implicit in this argument is the assumption that ionization from the π system of the phenyl radical, corresponding to the formation of $1\text{-}^3\text{B}_1$ (IE _{π} (2), Scheme 2), is similar to the IE of benzene. This assumption, which was applied in the analysis of the PIMS data, is also justified by our data. The calculated energy for the adiabatic formation of the triplet phenyl cation from **2** (897 kJ mol⁻¹) compares favorably with the known IE_a of benzene (892.09 kJ mol⁻¹).³⁸

(47) The observed IEs are not far from our calculated adiabatic IE for the formation of $1\text{-}^1\text{A}_1$. While it is still possible that one of the observed peaks is associated with the adiabatic formation of $1\text{-}^1\text{A}_1$, it would be hard to explain the other signal. Furthermore, as has already been noted,¹³ the Franck–Condon factor for the (adiabatic) formation of $1\text{-}^1\text{A}_1$ is expected to be very small.

(48) CASSCF calculations indicate that this intersystem crossing does not give rise to a reverse dissociation barrier, so that dissociation of a hydrogen atom from the benzene cation proceeds monotonically uphill.

In summary, our results indicate that the ground state of the phenyl cation (1^1A_1) lies 103 kJ mol^{-1} in energy below the first excited triplet state (1^3B_1). Under conditions that promote the vertical ionization of the phenyl radical, the singlet A_1 remains the lowest energy electronic state, but three more states (1^3B_1 and the essentially degenerate 1^1A_2 and 1^3A_2) lie within approximately 60 kJ mol^{-1} . Still higher in energy there is yet another electronic state (1^1B_1). In principle, these findings should be verifiable by a high-resolution photoelectron spectrum of the phenyl radical which, as has already been suggested,¹³ is highly desirable.

After this work was substantially completed we became aware of a related study by Hrusák et al. with a rather different emphasis but with similar conclusions.⁴⁹ These authors also find a large adiabatic T-S splitting (ca. 80 kJ mol^{-1} in their work)⁵⁰ for the phenyl cation in favor of the singlet A_1 . Their calculated Frank–Condon factors for the formation of 1^1A_1 and 1^3B_1 strongly support the idea that *adiabatic* formation of 1^1A_1 was *not* observed in the PE experiments. The unsatisfactory agreement between their simulated spectra and the experimental PE spectra led Hrusák et al. also to suggest that a spectroscopic reinvestigation of the ionization of the phenyl radical is desirable.

Conclusions

Our calculated heats of formation of the phenyl radical and the singlet phenyl cation and the C–H BDE in benzene are in accordance with the most recent experimental and computational results. Furthermore, in agreement with current thinking, we find the singlet (1^1A_1) to be the ground state of the phenyl cation. Our calculated electron affinity of the phenyl radical and the acidity of benzene (both closely related to the heat of formation for the phenyl anion) are in reasonable but slightly less good agreement with experiment, differing by about 10 kJ mol^{-1} from the most recent experimental values.

(49) Hrusák, J.; Schröder, D.; Iwata, S. *J. Chem. Phys.* 1997, **106**, 7541.

(50) The main reason for the smaller T-S splitting in ref 49 appears to be associated with their use of a smaller double- ζ plus polarization basis set (cc-pVDZ) compared with the effective 6-311+G(3df,2p) basis set in our G2(MP2,B3LYP,RCC) calculations. At the RCCSD(T)/6-311G(d,p) level, we calculate a T-S splitting of 82 kJ mol^{-1} , in close agreement with their cc-pVDZ value.

The first excited state of phenyl cation is the triplet B_1 (1^3B_1) which lies 103 kJ mol^{-1} higher in energy than the singlet A_1 state, in agreement with the interpretation of photoionization mass spectrometry results. The origin of the discrepancies between our data and the most recent PE spectrum of the phenyl radical is not clear, making a high resolution PE study of this reactive intermediate highly desirable.

Our data are also consistent with the formation of *singlet* phenyl cation in the gas-phase dissociation of benzene cation. In view of the high T-S gap in phenyl cation, a re-evaluation of the relative importance of the singlet and triplet surfaces at the transition state is recommended.

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Supporting Information Available: Geometrical parameters of 1^1A_1 , 1^3B_1 , **2**, and **3** at selected levels of theory (Table S1), G2(B3LYP,MP2,RCC) total energies (Table S2), CASSCF and CAS-MP2 total energies for **1**, **2**, and **3** (Table S3), spin-squared expectation values and RCCSD, UCCSD, RCCSD(T), and UCCSD(T) total energies for the open-shell species (Table S4), B3-LYP/6-31G(d) harmonic vibrational frequencies and intensities for 1^1A_1 , 1^3B_1 , **2**, and **3** and their perdeuterated derivatives (Table S5), and archive entries for the B3-LYP/6-31G(d) optimized geometries and MP2(fc)/6-311+G(3df,2p) single-point calculations for 1^1A_1 , 1^3B_1 , **2**, and **3** (Table S6) (9 pages). See any current masthead page for ordering and Internet access instructions.

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