J. Am. Chem. Soc. **2000,** *122,* 11203−11211 11203

Synthesis, Characterization, and Reactivity of the *m*-Xylylene Anion in the Gas Phase. The Enthalpy of Formation of *m*-Xylylene

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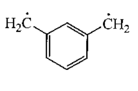
Received June 14, 2000

Abstract: The enthalpy of formation of *m*-quinodimethane (*m*-xylylene) has been determined using two different gas-phase approaches. The first involves combining the electron affinity of the biradical (0.919 ± 0.008 eV, Wenthold, P. G.; Kim, J. B.; Lineberger, W. C. *J. Am. Chem. Soc.* **1997**, *119*, 1354) with the acidity of the 3-methylbenzyl radical. The acidity of the 3-methylbenzyl radical was determined by bracketing the proton affinity of *m*-xylylene ion, prepared from the reaction of *m*-xylene and atomic oxygen ions in a flowing afterglow triple quadrupole apparatus. Deuterium labeling and reactivity studies show that 75% of the H_2^+ abstraction product formed in the reaction is the *m*-xylylene ion, with the rest being 3-methyl-α,*n*-dehydrotoluene ions resulting from [α, ring] hydrogen abstraction. The *m*-xylylene negative ion underwent reactions similar to those observed for 3-methylbenzyl anion and for other open-shell ions. The *m*-xylylene ion also reacted with mesitylene by H_2^+ transfer. The acidity of the 3-methylbenzyl radical was 382.5 ± 2.1 kcal/mol, which leads to an enthalpy of formation of *m*-xylylene of 80.1 ± 3.8 kcal/mol. The enthalpy of formation of *m*-xylylene was also determined to be 81.2 ± 3.0 kcal/mol using collision-induced dissociation (CID) threshold energy measurements with the 3-(chloromethyl)benzyl ion. The measured enthalpies of formation indicate a second C−H bond dissociation energy in *m*-xylene of 90.7 ± 2.9 kcal/mol, only slightly higher than the first (90.1 ± 1.7 kcal/mol). The fact that the strength of the second C−H bond in the 3-methylbenzyl radical is essentially the same as that in *m*-xylene indicates that the interaction between the two unpaired electrons is negligible, as would be expected for a triplet biradical.

m-Xylylene (*m*-quinodimethane, **1**)[1] has been the subject of considerable interest for several years. Because it is a non-Kekule molecule with a triplet ground state, **1** has attracted significant attention as a building block for paramagnetic materials. Subsequently, there have been many experimental and theoretical studies into the structure and reactivity of this biradical and its derivatives. In 1915, Schlenk[2] reported the first derivative of *m*-xylylene, **2**, as an isolable crystalline substance. The electron spin resonance (ESR) spectrum of Schlenk's biradical was determined in 1970,[3,4] and indicated a ground-state triplet. The ESR spectrum of **1**, obtained in 1983 by Platz and co-workers,[5] confirmed the triplet ground state in the unsubstituted biradical. These observations agree with the theoretical predictions based on a simple electron-repulsion model[6] and high-level molecular orbital calculations.[7,8]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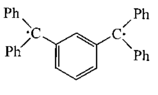
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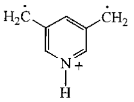
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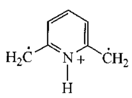
3b

Studies have been carried out to probe the reactivity of the biradical. Goodman and Berson examined the reactions of **1** with organic reagents.[9−11] They observed that **1** reacts with conjugated dienes to give indanes and *m*-cyclophenes,[11] and reactions with deuterium-labeled starting materials indicated a symmetric intermediate.[9] Kenttämaa and co-workers have described the gas-phase reactivity of charged derivatives of *m*-xylylene, including the 3,5- and 2,6-bis-methylenepyridinium ions (**3a** and **3b**, respectively).[12] They found contrasting reactivity for the two isomers, and attributed it to different spin states of the ions. Whereas ion **3a** undergoes hydrogen abstraction reactions, consistent with the behavior expected for a triplet, **3b** yields reaction products similar to those obtained for the related closed-shell singlet cation, the 2-methyl-6-methylenepyridine cation, as would be expected for a singlet biradical. The inferred spin states are consistent with those predicted for **3a** and **3b** by Dougherty and co-workers.[13] The reactivity of other *m*-xylylene derivatives has also been investigated.[14]

Recently, Wenthold et al.[15] reported the photoelectron spectrum of the *m*-xylylene negative ion, $\mathbf{1}^-$. In the spectrum, they observed the $^3B_2$ ground state and singlet states, corresponding to the $^1A_1$ and $^1B_2$ states, which were 9.6 ± 0.2 and <21.5 kcal/mol higher in energy, respectively. Moreover, they found the electron affinity (EA) of **1** to be 0.919 ± 0.008 eV.

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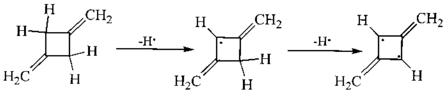
This value can be used to calculate the C−H bond dissociation energy (BDE) in 3-methylbenzyl radical (i.e., the second C−H bond dissociation energy in *m*-xylene) using the relationship shown in eq 1. However, the quantity $\Delta H_{acid}(3\text{-}CH_2C_6H_4CH_3)$ has not been measured, so the second BDE in *m*-xylene is not known.

$$\mathrm{BDE}(3\text{-}CH_2C_6H_4CH_2{-}H) = \mathrm{EA}(\mathbf{1}) + \Delta H_{acid}(3\text{-}CH_2C_6H_4CH_3) - \mathrm{IP}(H) \quad (1)$$

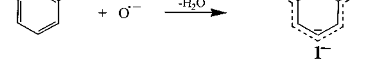
The second C−H BDEs for systems such as these are important because the difference between it and the first BDE provides a measure of the interaction between the unpaired electrons in the biradical. For example, the C−H BDEs in the phenyl radical (i.e., the second C−H BDEs in benzene) in the *ortho*, *meta*, and *para* positions to form the singlet benzynes have recently been measured to be lower than that in benzene by 36.0, 20.7, and 4.8 kcal/mol, respectively.[16,17] The difference between the first and second bond dissociation enthalpies in benzene reflect the extent of interaction between the unpaired electrons in the biradicals through either direct overlap of the nonbonding atomic orbitals (*ortho*, *meta*) or indirect interaction via through-bond coupling (*para*).[17]

The BDEs also reflect the electronic structure in triplet biradicals. For example, the experimental BDEs for the formation of the *triplet* benzynes are all ~113 kcal/mol,[17] the same as that in benzene, indicating little interaction between the two unpaired electrons. Similarly, the recently reported enthalpy of formation of triplet trimethylenemethane agrees with the value predicted using simple bond additivity.[18,19] However, Hill and Squires have recently found that the second C−H BDE in 1,3-bis-methylenecyclobutane, which leads to the formation of the triplet biradical (eq 2), is 16 kcal/mol higher than the first.[20] Zhang and Borden[21] have shown that the second BDE is higher because, unlike the radical, the triplet is not stabilized by delocalization throughout the cyclobutane system. Delocalization does not occur in the biradical because it would involve a nonfavorable, cyclobutadiene-like configuration. Therefore, the enthalpies of formation for triplet biradicals are not always equal to bond additivity.



(2)

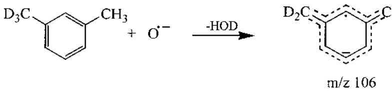
For the photoelectron experiments described above, $\mathbf{1}^-$ was generated by H_2^+ abstraction from *m*-xylene by the atomic oxygen ion, $O^{\bullet-}$ (eq 3), a reaction first reported by Jennings and co-workers.[16]



(3)

$\mathbf{1}^-$

To verify the structure of the ion, Bruins et al.[22] carried out the reaction using d_3-labeled *m*-xylene, as shown in eq 4.



(4)

For this reaction, they observed the transfer of HD^+ but did not see any D_2^+, and concluded that the abstraction takes place from each of the two methyl groups, forming the *m*-xylylene ion. Surprisingly, although it has been almost 25 years since Bruins et al.[22] first reported the formation of $\mathbf{1}^-$, the ion has not been fully characterized or studied. Among the information that could be obtained from such a study is the proton affinity of the ion [i.e., $\Delta H_{acid}(3\text{-}CH_2C_6H_4CH_3)$], which can be used along with the recently determined EA of **1** to calculate the second C−H BDE in *m*-xylene.

In this work, we describe the measurement of the enthalpy of formation of *m*-xylylene from which the second C−H BDE in *m*-xylene can be calculated. Two approaches are used to determine the enthalpy of formation of **1**. First, we use proton-transfer reactions to bracket the proton affinity of $\mathbf{1}^-$. However, because these experiments are complicated by the presence of competing reaction pathways, we also measure $\Delta H_{f,298}(\mathbf{1})$ using the collision-induced dissociation (CID) threshold approach developed by Squires and co-workers.[16,23] We find that the second C−H BDE in *m*-xylene agrees with the first, within error, indicating little interaction between the electrons, as expected for a triplet biradical.[24,25]

Experimental Section

All the gas-phase experiments described in this paper were carried out in a flowing afterglow, triple quadrupole instrument described elsewhere.[26,27] For the present studies, helium buffer gas was maintained in the 1 m × 7.3 cm flow reactor at a total pressure of 0.4 Torr, with a flow rate of 200 STP cm^3/s and bulk flow velocity of 9700 cm/s. The primary reactant ions $O^{\bullet-}$, and OH^-, are produced by electron ionization (EI) of N_2O and a N_2O/CH_4 mixture, respectively, in the upstream end of the flow tube. We find that the yield of $O^{\bullet-}$ is significantly enhanced if a small electrostatic potential ($-5 - -10$ V) is placed on the cross region, which is electrically isolated from the rest of the flowing afterglow. Once formed, the ions are transported down the tube by the flowing helium, where they are allowed to react with neutral reagent vapors introduced through leak valves. Reaction rates can be determined by monitoring signal depletion as a function of neutral reagent flow, where the neutral reagent vapors are added through a ring inlet at a fixed distance from the flow reactor. The ions in the flow tube, thermalized to ambient temperature by $\sim 10^5$ collisions with the helium buffer gas, are extracted from the flow tube through a 1-mm orifice and then focused into an EXTREL triple quadrupole analyzer.

The CID studies are carried out by selecting the ion with the desired mass-to-charge ratio using the first quadrupole (Q1), and then injecting them into the second quadrupole (Q2, radio frequency only), where they undergo collision with an argon target. For energy-resolved CID studies, the cross sections for product formation are measured while the Q2 rod offset is scanned. The reactant and product ions are analyzed with the third quadrupole (Q3) and are detected with an electron multiplier operating in pulse-counting mode. Absolute cross sections are calculated using $\sigma_p = I_p/INl$, where I_p and I are the intensities of

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the product and reactant ions, respectively, N is the number density of the target, and l is the effective length of the collision cell, calibrated to be 24 ± 4 cm. The CID cross sections are measured at different pressures and extrapolated to $p = 0$, such that they correspond to single collision conditions.

The center of mass collision energies are calculated using $E_{CM} = E_{lab}[m/(M + m)]$, where E_{lab} is the collision energy in the laboratory frame of reference, and m and M are the masses of the target and the ion, respectively. Determination of the ion kinetic energy origin and beam energy spread is accomplished by retarding potential analysis, with Q2 serving as the retarding field element. Ion beam energy distributions are found to be Gaussian in shape, with a typical full width at half-height (fwhm) of 0.5−1.5 eV (laboratory frame).

Energy-resolved cross sections are fit using the assumed model shown in eq 5,[28−30] where E is the energy of the ion, E_i is the vibrational energy, E_T is the dissociation energy, n is an adjustable parameter, and σ_o is a scaling factor.

$$\sigma(E) = \sigma_0 \sum_i \left[\frac{g_i P_D(E,E_i,\tau)(E + E_i - E_T)^n}{E} \right] \tag{5}$$

Modeling is carried out by minimizing the deviation between the model function and the steeply rising portion of the appearance curve just above threshold. The modeling also accounts for the ion energy distribution and Doppler broadening due to thermal motion of the target.

Also incorporated into the analysis are the dissociation rates of the ions, P_D, calculated using Rice−Ramsperger−Kassel−Marcus (RRKM) theory, to account for potential kinetic shifts that result from slow dissociation on the instrumental time scale ($\tau = \sim 30\ \mu s$). The dissociation reactions are assumed to have loose, product-like transition states that correspond to the "phase-space limit," and are calculated using the approach described by Rodgers et al.[31] Physical parameters for the reactants and products, including vibrational frequencies, rotational constants, and polarizabilities, are calculated at the Becke3LYP/6-31+G* level of theory.[32] Vibrational frequencies are scaled by 0.965 to account for anharmonicities. Dissociation energies obtained from the fitting procedures correspond to the 0 K energies. These values are converted to the 298 K bond dissociation enthalpies, DH_{298}, using the integrated heat capacities. All analyses are carried out using the CRUNCH program developed by Armentrout and co-workers.[28−31]

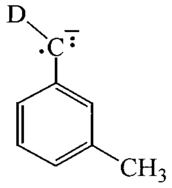
Materials. The labeled *m*-xylenes, d_3 and d_6, were prepared from the reaction of CD_3I with the Grignard reagents prepared from *m*-bromotoluene and *m*-dibromobenzene, respectively, in tetrahydrofuran at room temperature, and were purified by column chromatography. The d_2-chloro-*m*-xylene was prepared by the reduction of the corresponding methyl carboxylate with lithium aluminum deuteride,[33] followed by chlorination with $SOCl_2$.[34] All other reagents were obtained from commercial sources and were used as supplied. Gas purities were as follows: He (99.995%), NO_2 (99.5%), and CH_4 (99%).

Results and Discussion

Here we describe the determination of the enthalpy of formation of *m*-xylylene, **1**. Given that our first approach involves measuring the proton affinity of the negative ion, $\mathbf{1}^-$, we first discuss its formation and characterization. We next describe proton-transfer experiments used to determine the proton affinity of $\mathbf{1}^-$ and the subsequent calculation of $\Delta H_{f,298}(\mathbf{1})$. In the last part of this section, we describe an alternate measurement of the enthalpy of formation using CID threshold measurements. Finally, the measured value for the enthalpy of formation is discussed in light of the electron − electron interaction within the biradical.

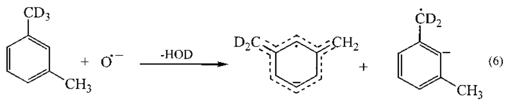
Ion Formation. The reaction of $O^{\bullet -}$ with *m*-xylene (eq 3) in the flowing afterglow gives *m/z* 104 (H_2^+ transfer) as the major product.[22] The 3-methylbenzyl anion is also observed, with the intensity of the *m/z* 105 peak ∼40% of that for *m/z* 104. The 3-methylbenzyl anion can be formed directly by deprotonation of *m*-xylene with $O^{\bullet -}$, or it can be the result of proton transfer between *m*-xylylene and hydroxide, which is formed by hydrogen atom abstraction.

To characterize the products of eq 3, we have first repeated the experiments of Bruins et al.[16] using *m*-xylene-d_3. Of the possible products, we only observe those at *m/z* 106, 107, and 108. Whereas *m/z* 107 and 108 can result from D^+ and H^+ transfer, respectively, the peak at *m/z* 106 indicates the transfer of HD^+. More importantly, the absence of a peak at *m/z* 105 rules out formation of 3-methylphenylcarbene radical anion, $\mathbf{4}^-$, the result of D_2^+ abstraction. Therefore, our results agree with those of Jennings and co-workers[22] in that the reaction of *m*-xylene-d_3 does not produce the phenylcarbene radical anion.



$\mathbf{4}^-$

Although the reaction of $O^{\bullet -}$ with *m*-xylene-d_3 rules out α,α-abstraction to form the carbene ion, the results do not require the product to be the *m*-xylylene ion. For example, the HD^+ transfer product observed in the reaction may result from [α, ring] abstraction to form a 3-methyl-α,*n*-dehydrotoluene ion, as shown for the α,2 isomer in eq 6. However, if [α, ring] abstraction is occurring, then we also expect to observe the H_2^+ transfer product (*m/z* 107). Unfortunately, this ion has the same mass as that resulting from D^+ transfer, and we cannot rule out the formation of the ring-abstracted ion using the d_3-labeled material.



Additional insight is gained from the reaction with *m*-xylene-d_6. Assuming that α,α-abstraction does not occur, potential products of the reaction are shown in Scheme 1. Formation of $\mathbf{1}^-$ is indicated by the formation of *m/z* 108, whereas 3-methyl-α,*n*-dehydrotoluene ion (shown as the α,2 isomer in Scheme 1) has *m/z* 109.

The mass spectrum of the region *m/z* 100−115 is shown in Figure 1. The main product of the reaction is the *m*-xylylene ion, with *m/z* 108. However, we also observe significant yields at *m/z* 109 and 110, resulting from HD^+ and D^+ transfer, respectively. From the relative yields of the *m/z* 108 and 109 ions, we estimate that the 75% of the H_2^+ transfer product in

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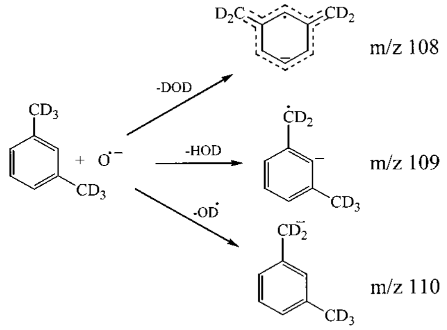
Scheme 1



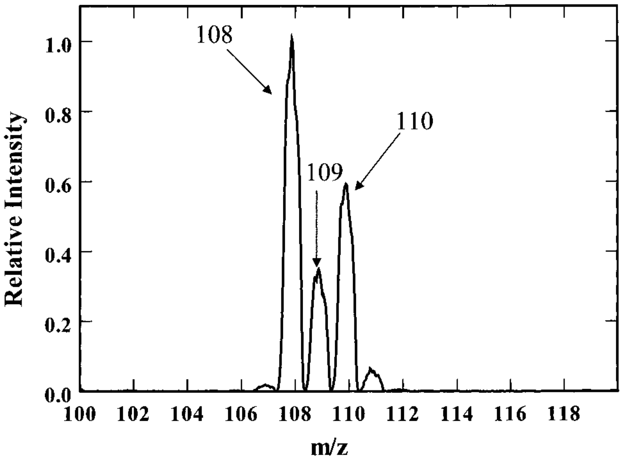


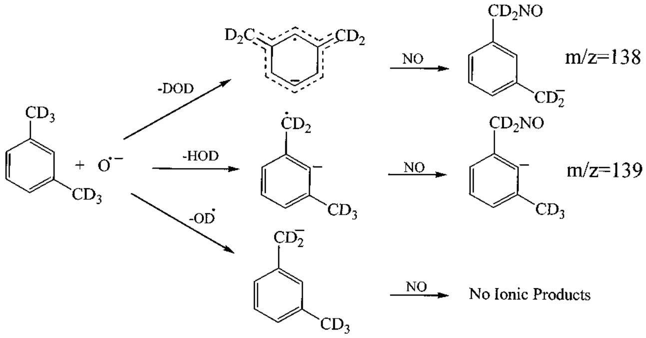
Figure 1. Mass spectrum of the products of the reaction of *m*-xylylene-d_6 with atomic oxygen ion from *m*/*z* 100 − 115.

the reaction of $O^{•-}$ with *m*-xylene is **1**$^-$, with the rest corresponding to unspecified 3-methyl-α,*n*-dehydrotoluene ions resulting from ring abstraction. The small (<2%) signal of *m*/*z* 107 observed in the spectrum is a result of less than complete deuterium labeling in the *m*-xylene-d_6 and/or H/D exchange with adventitious water in the flowing afterglow (vide infra).

Reactivity and Characterization. The products of the reaction of *m*-xylene with $O^{•-}$ can also be investigated using ion/molecule reactions. We have examined the reactivity of the ions with standard reagents to determine their structures. For example, given that the *m*-xylylene and 3-methyl-α,*n*-dehydrotoluene ions have radical character, they might be expected to undergo radical reactions. Similarly, **1**$^-$ is expected to undergo reactions similar to those of the 3-methylbenzyl anion, whereas the α,*n*-dehydrotoluene ions are expected to exhibit phenyl anion-like reactivity.[35] Therefore, reactivity studies, especially when carried out on labeled systems, can be used to characterize the products of eq 3.

The first reaction examined was that with nitric oxide. Nitric oxide has been shown to react with closed-shell ions by addition followed by electron detachment,[36] such that no ionic products are observed, whereas adducts[36] and other products[37,38] have been observed with open-shell ions. Therefore, we might expect adduct formation with the *m*-xylylene and α,*n*-dehydrotoluene ions but not with the 3-methylbenzyl anion. In agreement with this expectation, both the *m*/*z* 104 and 105 ions formed from unlabeled *m*-xylene react away completely when NO is added to the flowing afterglow, but the only product observed at low NO flows is an adduct ion at *m*/*z* 134. This result verifies that only the open-shell M-2H ions give ionic products with nitric oxide. In addition, at higher flows of NO, a second NO molecule adds to the *m*/*z* 104 ion, but the adduct of *m*/*z* 105 is not observed.

Scheme 2



This result is further illustrated by the reactions of the ions derived from the labeled *m*-xylenes as shown in Scheme 2. For example, with *m*-xylene-d_6, only the ions that result from HD^+ or D_2^+ transfer form adducts with nitric oxide, in a ratio that reflects the relative abundances of the reactant ions, whereas the NO adduct of the $[M-D]^-$ ion is not observed at all. This result indicates that the **1**$^-$ and the 3-methyl-α,*n*-dehydrotoluene ions form adducts with NO at comparable rates. For the *m*-xylene-d_3 system, both the *m*/*z* 106 and 107 ions form adducts with NO. However, whereas the ratio of the *m*/*z* 107 to 106 ions is 0.78, the ratio of the corresponding adduct ions is 0.19. This result reflects the fact that the *m*/*z* 107 signal consists of a mixture of 3-methyl-α,*n*-dehydrotoluene ion resulting from H_2^+ transfer and the 3-methylbenzyl anion resulting from transfer of D^+. The ratio of the adduct ions indicates that 70% of the open-shell ions is the *m*-xylylene ion, in agreement with the amount estimated from the reaction of $O^{•-}$ with *m*-xylene-d_6.

Like most organic anions,[39] the ions derived from *m*-xylene undergo addition with CO_2 to form carboxylate ions, and the reactivity of the carboxylates reflects the ion structure. The carboxylates of the open-shell ions have radical sites and therefore undergo addition with NO, but the carboxylated 3-methylbenzyl anion does not react with nitric oxide. In this case, the reactions of the ions obtained from *m*-xylene-d_3 indicate that 70% of the open-shell ions have the *m*-xylylene structure.

Reaction of the ions with CS_2 also shows that a mixture of open-shell ions is formed. By utilizing *m*-xylene-d_6, we are able to distinguish the reactivity of the *m*-xylylene ion (*m*/*z* 108) from that of the 3-methyl-α,*n*-dehydrotoluene ion (*m*/*z* 109). The *m*/*z* 108 ion is found to react exclusively by CS_2 addition, consistent with what is expected for a benzylic ion. On the other hand, the *m*/*z* 109 ion reacts by both CS_2 addition and by S atom abstraction. We interpret this to mean that the dehydrotoluene ion is much more basic than the *m*-xylylene,[40−43] suggesting that the dehydrotoluene is a phenyl-like anion with

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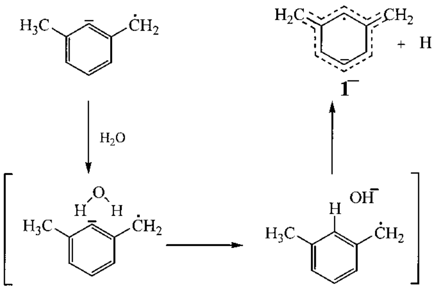
Scheme 3



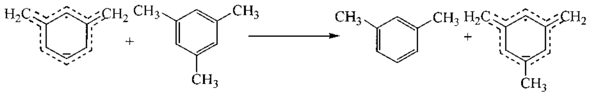
a benzylic radical. This electronic structure is consistent with what is expected given that the EA of a phenyl radical is ~0.1 eV higher than that of benzyl.[44]

The M-2H ions formed in the reaction of $O^{\bullet -}$ with unlabeled *m*-xylene react with CS_2 by addition and by S atom abstraction. The sulfur atom abstraction pathway indicates that the dehydrotoluene ion is formed in the reaction and the *m*/*z* 104 signal is likely a mixture of isomers. However, we have found that the dehydrotoluenes rearrange to **1**⁻ in the presence of weak acids. For example, although there is no apparent reaction between the *m*/*z* 104 ion and water, the reactivity of the ion changes in that it no longer gives a sulfur atom abstraction product with CS_2. We attribute this to water-catalyzed isomerization of the dehydrotoluene ions to the *m*-xylylene ion.[16] The mechanism for the isomerization is likely similar to that proposed for H/D exchange of carbanions,[45−47] as shown in Scheme 3. Most importantly, the results with CS_2 indicate that the dehydrotoluene can be removed from the reaction mixture by the addition of water. Therefore, it is possible to examine the reactivity of the pure *m*-xylylene ion without having to use deuterium-labeled reagents.

Acid/Base Reactions. Given that the EA of **1** has been measured,[15] the enthalpy of formation can be determined if the proton affinity of the ion (i.e., the gas-phase acidity of 3-methylbenzyl radical) is known. In light of this possibility, we have carried out reactions of the ion with acids to bracket the gas-phase acidity. For these experiments, we used the M-2H ion (*m*/*z* 104) derived from unlabeled *m*-xylene. The ions are first allowed to react with water introduced directly downstream from the electron gun to isomerize the dehydrotoluene component to **1**⁻, as already described. Acids are added ~50 cm farther downstream to allow the reaction with water to occur to completion.

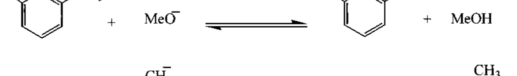
The *m*/*z* 104 ion prepared in this fashion does not appear to react with fluorobenzene ($\Delta G_{\text{acid}} = 379.1 \pm 2.0$ kcal/mol).[48,49] Reaction is observed with methanol, toluene, cumene, and ethanol ($\Delta G_{\text{acid}} = 375.2 \pm 0.2$, 374.9 ± 0.2, 372.9 ± 2.0, and 371.7 ± 1.1 kcal/mol, respectively).[50−53] Moreover, for the reagents with which reaction occurs, we also observe the formation of the conjugate base anion, suggesting that proton transfer has occurred. However, all the reagents that appear to react with the *m*-xylylene anion are also found in control experiments to undergo proton transfer with the 3-methylbenzyl anion. Therefore, given that *m*/*z* 105 is always formed along with the *m*-xylylene ion, we are not able to unequivocally assign the formation of the conjugate base anion to deprotonation by **1**⁻. From these results, we conclude that the acid/base properties of 3-methylbenzyl radical are similar to those of *m*-xylene (vide infra). This conclusion is supported by the measured rates of the reactions. The kinetics plots of signal versus reagent flow[26] are reasonably linear, as would be expected if each ion were undergoing simple proton transfer. For the acids with which reaction is observed, we find that the **1**⁻ ion reacts at rates similar to those for the reaction of the 3-methylbenzyl anion, *m*/*z* 105, suggesting comparable thermodynamic driving forces for the two reactions.

One reagent that gives a product attributable to reaction with *m*-xylylene ion is 1,3,5-trimethylbenzene (mesitylene), which reacts by H_2^+ transfer to give, presumably, a methyl-substituted *m*-xylylene ion (eq 7). Although H_2^+ transfer has been proposed previously to occur in the reaction between *o*-benzyne ion and methanol,[54] this is the first instance in which H_2^+ transfer has been observed between an organic ion and organic reagent to form an open-shell ion.[55]

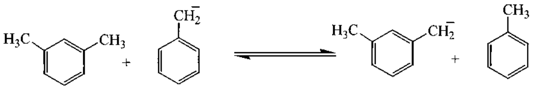


(7)

Enthalpy of Formation of *m*-Xylylene. The goal of the bracketing experiments just described was to determine the gas-phase acidity of 3-methylbenzyl radical so that the enthalpy of formation could be determined using eq 1. Although we are not able to assign the acidity of 3-methylbenzyl radical directly, we estimate from the reactivity studies that it is indistinguishable from that of *m*-xylene. The acidity of *m*-xylene was determined in this work from the proton-transfer equilibrium data for the reaction shown in eq 8a. The average pseudo-first-order rate constant, k_f, for the forward reaction obtained from replicate measurements is $(1.7 \pm 0.6) \times 10^{-10}$ mol/s. Similarly, the rate constant for the reverse reaction, k_r, is $(1.6 \pm 0.5) \times 10^{-10}$ mol/s, which means ΔG(eq 8a) $= -0.06 \pm 0.65$ kcal/mol, where the uncertainty is conservatively assigned to allow for up to a factor of 3 error in the measured equilibrium constant. Our value of ΔG(eq 8a) is in good agreement with that obtained by Caldwell and Bartmess for this reaction.[56,57]



(8a)



(8b)

Neumark and co-workers[50] have derived $\Delta G_{\text{acid}}(CH_3OH) =$

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[44] Gunion, R. F.; Gilles, M. K.; Polak, M. L.; Lineberger, W. C. *Int. J. Mass Spectrom. Ion Processes* **1992**, *117*, 601.

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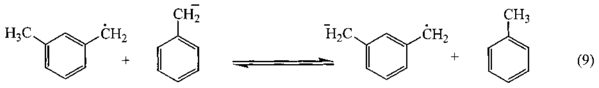
375.2 ± 1.1 kcal/mol using the homolytic O−H BDE[58,59] and the EA of the methoxy radical. Combining this value with ΔG(eq 8a) gives ΔG_{acid}(*m*-xylene) = 375.1 ± 1.3 kcal/mol. The quantity ΔH_{acid}(*m*-xylene) can be determined using $\Delta H = \Delta G + T\Delta S$, where the entropy term was calculated using eq 8b. Ellison and co-workers[51] have reported the ΔS_{acid}(toluene) = 24.7 ± 1.6 cal/mol K. The entropy change for the reaction in eq 8b is calculated to be 1.29 cal/mol K, using frequencies calculated at the B3LYP/6-31+G* level of theory,[60] which gives ΔS_{acid}(*m*-xylene) = 26.0 ± 2.0 cal/mol K, and ΔH_{acid}(*m*-xylene) = 382.8 ± 1.6 kcal/mol.

On the basis of the reactivity of the *m*-xylylene negative ion, ΔG_{acid}(3-methylbenzyl) is 375.1 ± 2.0 kcal/mol. Again, the quantity ΔH_{acid}(3-methylbenzyl) is calculated using $\Delta H = \Delta G + T\Delta S$. The entropy of deprotonation for 3-methylbenzyl radical was determined by calculating the entropy change for the proton-transfer reaction shown in eq 9, which has $\Delta S = -0.03$ eu at the B3LYP/6-31+G* level of theory.



Therefore, ΔS_{acid}(3-methylbenzyl) is predicted to be the same as ΔS_{acid}(toluene) = 24.7 ± 1.6 cal/mol K, which gives ΔH_{acid}(3-methylbenzyl) = 382.5 ± 2.1 kcal/mol. Combining this acidity with the EA of *m*-xylylene (0.919 ± 0.008 eV)[15] and the ionization potential (IP) of hydrogen atom according to eq 1 gives BDE(3-$CH_2C_6H_4CH_2$−H) = 90.1 ± 1.7 kcal/mol.[61] Similarly, the C−H BDE in *m*-xylene is calculated from the acidity and EA (0.905 ± 0.008 eV)[15] to be 90.1 ± 1.7 kcal/mol,[61] such that the second C−H bond in *m*-xylene is as strong as the first. This result is a consequence of the fact that the acidity and EA of 3-methylbenzyl radical are essentially the same as those for *m*-xylene and *m*-xylylene, respectively. From the BDEs and the enthalpy of formation of *m*-xylene (4.12 kcal/mol),[62] the enthalpy of formation of *m*-xylylene is calculated to be 80.1 ± 3.8 kcal/mol, where the uncertainty reflects the fact that both BDE values depend on the acidity of *m*-xylene.

Collision-Induced Dissociation Threshold Measurements. Wenthold and Squires[16,23] have shown that biradical enthalpies of formation can also be obtained using CID threshold energy measurements with halogen-substituted ions. Therefore, it is possible to obtain a second value for the enthalpy of formation of *m*-xylylene by measuring the dissociation energy for 3-(chloromethyl)benzyl anion, as shown in eq 10a. The enthalpy of formation of the biradical is calculated from the bond dissociation enthalpy, DH_{298}, using eq 11.

The 3-(chloromethyl)benzyl anion can be generated by deprotonation of α-chloro-*m*-xylene using hydroxide. Although OH^- is capable of deprotonating both methyl sites in α-chloro-*m*-xylene, the use of deuterium-labeled reagent allows the 3-(chloromethyl)benzyl anion that results from proton transfer, **6**⁻, to be distinguished from α-chloro-3-methylbenzyl anion, **7**⁻, resulting from deuterium cation transfer, as shown in eq 10b.

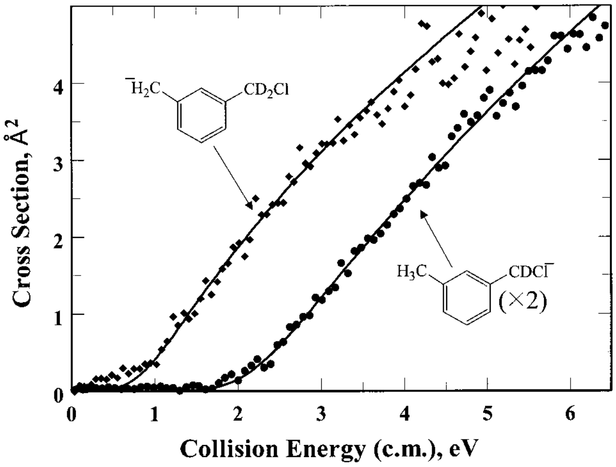
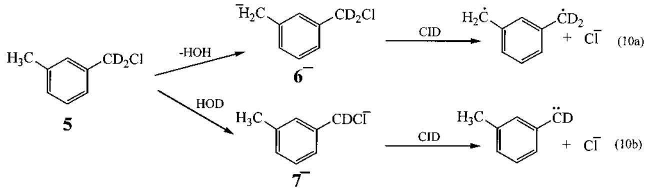
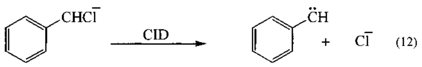


Figure 2. Cross sections for collision-induced dissociation of Cl⁻ from 3-(chloromethyl)benzyl and α-chloro-3-methylbenzyl anions as a function of translational energy in the center-of-mass frame. The solid lines are the model appearance curves calculated using eq 5.



$$\Delta H^\circ_{f,298}(C_8H_8) = DH_{298}(C_8H_8Cl) + \Delta H_{acid}(C_8H_9Cl) + \Delta H^\circ_{f,298}(C_8H_9Cl) - \Delta H_{acid}(HCl) - \Delta H^\circ_{f,298}(HCl) \quad (11)$$

The CID of the mass-selected **6**⁻ (*m/z* 141) gives chloride as the only ionic fragment. The cross sections as a function of center-of-mass collision energy are shown in Figure 2. Also shown in Figure 2 are the cross sections for dissociation of the α-chloro-3-methylbenzyl anion, **7**⁻ (*m/z* 140). Average values of DH_{298} and *n* obtained by modeling the cross sections for the dissociations of ions **6**⁻ and **7**⁻ are listed at the bottom of Table 1. The chloride binding enthalpies (298 K) of the 3-(chloromethyl)benzyl and α-chloro-3-methylbenzyl anions, obtained from replicate measurements, are 0.87 ± 0.07 and 1.70 ± 0.08 eV, respectively, where the uncertainty includes the deviation of the data, a 0.15 eV (lab) uncertainty in the absolute energy scale, and a contribution due to uncertainty in the choice of the transition state. Because of the low dissociation energy, the kinetic shift for the formation of *m*-xylylene from ion **6**⁻ is <0.01 eV. The threshold for the dissociation of **7**⁻ is similar to that reported previously by Poutsma and Squires (1.67 ± 0.10 eV)[63] for the dissociation of α-chlorobenzyl anion (eq 12).



Calculation of the enthalpy of formation of *m*-xylylene using eq 11 requires the gas-phase acidity of α-chloro-*m*-xylene in the nonchlorinated position. Standard approaches for determining gas-phase acidities, such as equilibrium measurements,[64] are not applicable in this case because the methyl position is not the most acidic site in the molecule. However, for the

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[59] Meot-Ner, M.; Sieck, L. W. *J. Phys. Chem.* **1986**, *90*, 6687.

[60] Entropies for vibrations are calculated from unscaled frequencies. Unsubstituted methyl groups are assumed to be hindered rotors with entropy contributions similar to that for the methyl group in toluene (ref 51).

[61] The small temperature correction term is ignored.

[62] Afeefy, H. Y.; Liebman, J. F.; Stein, S. E. Neutral Thermochemical Data. In *NIST Chemistry WebBook, NIST Standard Reference Database Number 69*, February 2000 ed.; Mallard, W. G., Linstrom, P. J., Eds.; National Institute of Standards and Technology: Gaithersburg, MD, 20899, 2000 (http://webbook.nist.gov).

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Table 1. Supplemental and Derived Thermochemical Data[a]

parameter		value	reference
		298 K enthalpies of formation	
m-xylene		4.12 ± 0.18	62
toluene		11.95 ± 0.15	62
HCl		−22.06 ± 0.02	62
1-(chloromethyl)-3-methylbenzene		−3.3 ± 1	bond additivity
m-xylylene, **1**			
from eq 1		80.1 ± 3.8	this work
from eq 11		81.2 ± 3.0	this work
average		80.8 ± 2.4	this work
		gas-phase acidities	
	ΔG_{acid}	ΔH_{acid}	
toluene	374.9 ± 0.2	383.2 ± 0.5	51
m-xylene	375.1 ± 1.3	382.8 ± 1.6	this work
3-methylbenzyl radical	375.1 ± 2.0	382.5 ± 2.1	this work
HCl		333.4 ± 0.1	57
		electron affinities	
benzyl		21.03 ± 0.14	44, 65
3-methylbenzyl		20.87 ± 0.14	15
m-xylylene, **1**		21.19 ± 0.18	15
3-(chloromethyl)benzyl, **6**		27.5 ± 1.2	this work
		chloride dissociation energies	
DH_{298}(3-$CH_2C_6H_4CD_2$−Cl^-)		20.1 ± 1.6	this work
n^b		1.6 ± 0.1	
DH_{298}(3-$CH_3C_6H_4CD$−Cl^-)		39.2 ± 1.8	this work
n^b		1.7 ± 0.1	

[a] Values in kcal/mol unless otherwise noted. [b] Exponent in eq 5.

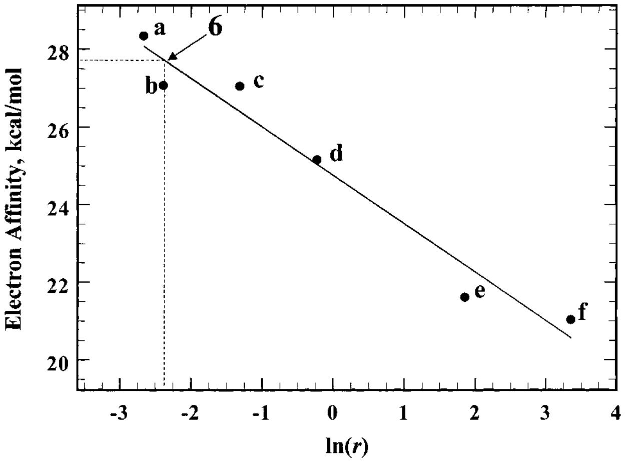

Figure 3. Plot of EA versus ln *r* for reference radicals, along with a linear fit to the data. The center of mass collision energy corresponds to 4.0 eV: (a) benzyl radical; (b) *p*-fluorobenzyl radical; (c) *o*-fluorobenzyl radical; (d) *m*-fluorobenzyl radical; (e) *p*-chlorobenzyl radical; and (f) *p*-bromobenzyl radical. The result for the 3-(chloromethyl)benzyl radical, **6**, is also indicated on the plot.

unsubstituted methyl group, an accurate value for the acidity can likely be obtained indirectly using the familiar relationship shown in eq 13,[64] where DH_{298}(R−H) is the homolytic C−H bond dissociation enthalpy, EA(R) is the electron affinity of the 3-(chloromethyl)benzyl radical, **6**, and IP(H) is the ionization potential of hydrogen.

$$DH_{298}(\mathrm{R{-}H}) = \mathrm{EA(R)} + \Delta H_{\mathrm{acid}}(\mathrm{R{-}H}) - \mathrm{IP(H)} \quad (13)$$

The key to this approach is that Kim et al.[65] have shown that the homolytic bond dissociation enthalpies of halogen-substituted toluenes are all ~89 kcal/mol. Therefore, the gas-phase acidities of ring-substituted toluenes can be reliably estimated by assuming a bond dissociation enthalpy of 89 ± 2 kcal/mol and measuring the EA.

The EA of the 3-(chloromethyl)benzyl radical, **6**, can be determined using the kinetic method developed by Cooks and co-workers.[66,67] The procedures for obtaining EAs using this approach have been described elsewhere.[20,68,69] The branching ratios for the CID of SO_2 adducts of a series of substituted benzyl anions with known EAs are measured. A semilog relationship between the branching ratios and the EAs is assumed, and a calibration plot is constructed. In the simplest version of the kinetic method, the branching ratio for the SO_2 adduct of the unknown is measured and the EA is determined from the calibration. This approach has been utilized by Squires and co-workers for the determination of *m*- and *p*-benzyne,[68] 1,3-bis-methylenecyclobutane-2,4-diyl,[20] and cyclopropyl radical.[69] The calibration curve obtained at a center-of-mass collision energy of 4 eV using benzyl and the 2-fluoro-, 3-fluoro-, 4-fluoro-, 4-chloro-, and 4-bromobenzyl radicals[65] as calibrants is shown in Figure 3. The regression line in Figure 3 has the form shown in eq 14, where $r = I(SO_2^-)/I(R^-)$.

$$\mathrm{EA(R)} = 24.75 - 1.248 * \ln r \quad (14)$$

From the CID branching ratio for the SO_2 adduct of $\mathbf{6}^-$, $r = 0.107$, and the EA of radical **6** is 1.194 ± 0.053 eV. As usual, certain assumptions are involved in this measurement. First, it is assumed that the effective temperature[70] for the dissociation of the SO_2 adduct of $\mathbf{6}^-$ is the same as those of the calibrant ions. As Ervin has shown,[71] this assumption may introduce an error of 0.5−1.0 kcal/mol into the measurement. In addition, the relationship in eq 15 assumes that the entropy for the dissociation of the SO_2 adduct of $\mathbf{6}^-$ is the same as the entropies for the dissociation of the calibrant cluster ions. To test this assumption, we carried out a theoretical study of the measurement of the EA of **6** using the kinetic method. Using energies and geometries calculated at the B3LYP/6-31+G* level of theory and RRKM theory, we find that the difference in ΔS, the entropy of activation, among the different cluster ions to be 0.77 cal/mol K. Although full details of this study will be provided elsewhere,[72] the results indicate that neglecting the entropy contribution may lead to an error of up to 0.5 kcal/mol (using an effective temperature of 628 K at 4 eV collision energy). Therefore, the uncertainty assigned to EA(**6**) includes a 0.5 kcal/mol component, to account for potential errors that can arise by neglecting the entropy differences, in addition to a 1 kcal/mol contribution due to the uncertainty in the effective temperature, a 0.25 kcal/mol contribution to account for uncertainty in the ratio measurements (which corresponds to a ±20% uncertainty in the relative ratios), and a 0.38 kcal/mol contribution due to the statistical error in the regression plot (the uncertainties in the EAs of the references are negligible). The branching ratio for the dissociation of the SO_2 adduct of ion $\mathbf{7}^-$ was also measured and found to be $r = 0.336$, implying an EA of 1.132 eV. However, as an α-substituted benzyl anion, $\mathbf{7}^-$ is structurally different from the ring-substituted anions used as calibrants. Therefore, the entropy for the dissociation of the SO_2 adduct of $\mathbf{7}^-$ is not expected to be the same as that for

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(65) Kim, J. B.; Wenthold, P. G.; Lineberger, W. C. *J. Phys. Chem. A* **1999**, *103*, 19833.

(66) Cooks, R. G.; Patrick, J. S.; Kotiaho, T.; McCluckey, S. A. *Mass Spectrom. Rev.* **1994**, *13*, 287.

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(71) Ervin, K. M. *Int. J. Mass Spectrom.* **2000**, *195/196*, 271.

(72) Liu, X.; Hammad, L.; Wenthold, P. G., manuscript in preparation.

dissociation of the calibration ions, leading to even larger errors than those already discussed. An accurate determination of the EA of **7**$^-$ using the kinetic method would require full entropy analysis.[73,74] These experiments are currently underway and will be reported elsewhere.[72]

Using a homolytic C−H bond dissociation of enthalpy for the unsubstituted position of α-chloro-*m*-xylene of 89.0 ± 2.0 kcal/mol and an EA of 1.194 ± 0.053 eV for the 3-(chloromethyl)benzyl radical, the gas-phase acidity of the unsubstituted methyl position in α-chloro-*m*-xylene is estimated to be 375.1 ± 2.3 kcal/mol. Therefore, this position is more acidic than toluene or *m*-xylene ($\Delta H_{\mathrm{acid}} = 382.3 \pm 0.6$[51] and 382.8 ± 1.6 kcal/mol, respectively) but not quite as acidic as *m*- or *p*-chlorotoluene ($\Delta H_{\mathrm{acid}} = 374 \pm 3$ kcal/mol),[23] in agreement with what is expected on the basis of substituent effects.[75] The enthalpy of formation of *m*-xylylene obtained from the gas-phase acidity, chloride binding energy, and the auxiliary data[62] listed in Table 1 is $\Delta H_{\mathrm{f,298}}$(*m*-xylylene) = 81.2 ± 3.0 kcal/mol, which agrees within error with the value estimated from the reactivity of the *m*-xylylene ion.

As part of this work, the acidity of the substituted position in α-chloro-*m*-xylene was determined using the bracketing approach. For example, we find that OH^- and CH_3O^- abstract both D^+ and H^+ from **5**, indicating that both methyl positions are more acidic than water or methanol ($\Delta G_{\mathrm{acid}}(H_2O) = 384.10 \pm 0.05$ kcal/mol, $\Delta G_{\mathrm{acid}}(CH_3OH) = 375.2 \pm 1.1$ kcal/mol).[50,64] The observation of H^+ transfer with these bases is consistent with the estimated gas-phase acidity at the nonchlorinated position already described. Reaction of **5** with the conjugate base anions of toluene ($\Delta G_{\mathrm{acid}} = 374.9 \pm 0.2$ kcal/mol),[51] ethanol (371.7 ± 1.1),[53] dichloromethane (369.0 ± 0.7),[76] *tert*-butyl alcohol (367.7 ± 2.1),[77] propionitrile (367.4 ± 2.0),[52] and dimethyl sulfoxide (366.4 ± 2.0)[52] results in transfer of D^+, leading to formation of **7**$^-$. Although deprotonation at the nonsubstituted methyl position to form **6**$^-$ is thermodynamically allowed for benzyl and ethoxide ions, it is likely much slower than that at the substituted site and is therefore not observed to an appreciable extent. Slow D^+ transfer is observed in the reaction of **5** with deprotonated methyl acetate ($\Delta G_{\mathrm{acid}} = 365.1 \pm 2.0$),[52] whereas neither H^+ nor D^+ transfer is observed in the reaction between **5** and the conjugate base anions of acetonitrile (365.2 ± 2.0),[52] benzyl alcohol (363.4 ± 2.0),[52] acetone (361.9 ± 2.0),[52] or weaker bases. From these results, we conclude that the acidity of **5** is between that of acetonitrile and dimethyl sulfoxide and assign $\Delta G_{\mathrm{acid}} = 365.5 \pm 2.0$ kcal/mol. The quantity $\Delta H_{\mathrm{acid}} = 373.8 \pm 2.1$ kcal/mol is calculated using $\Delta H = \Delta G + T\Delta S$, where $\Delta S = 28.0$ cal/mol K is calculated using the same procedure already described for *m*-xylene. Therefore, from the bracketing experiments we find that the gas-phase acidity value at the chlorinated position is slightly higher than that reported previously for benzyl chloride, 372.0 ± 2.0 kcal/mol.[78] The enthalpy of formation of 3-methylphenyl carbene is calculated from the bracketed acidity of the chlorinated position and the bond dissociation enthalpy in **7**$^-$ to be 98.3 ± 3.0 kcal/mol.

Although the neutral products are not detected, the enthalpies of formation determined from CID of **6**$^-$ and **7**$^-$ are assigned to *m*-xylylene and 3-methylphenylcarbene, respectively, on the basis of the following observations. First, the CID experiments with **7**$^-$ are similar to those reported previously by Poutsma and Squires for deprotonated benzyl chloride.[63] In that study, they ruled out formation of noncarbene products on the basis of dynamical and energy barrier arguments. For example, dissociation to form the carbene is kinetically favorable because it occurs by a simple bond cleavage through a loose transition state as opposed to a rearrangement through a tight transition state. Moreover, rearrangements to lower energy products are accompanied by high-energy barriers that would be manifested in the experiment. Therefore, the CID of **7**$^-$ is expected to give 3-methylphenylcarbene as the neutral product.

Similarly, the CID of **6**$^-$ should give *m*-xylylene. Again, direct dissociation is dynamically favored over a rearrangement process. Moreover, skeletal rearrangement will be accompanied by large barriers, in excess of that measured in the present experiment. In fact, the low dissociation threshold measured for **6**$^-$ indicates that if rearrangement were to occur, it must have a barrier lower than ∼0.9 eV. Therefore, the low dissociation energy strongly suggests that **6**$^-$ dissociates by simple dissociation to form *m*-xylylene.

Dissociation of the singlet benzyl anion to form the triplet biradical or carbene is formally spin-forbidden, and is therefore potentially slow on the experimental time scale. Wenthold et al.[23] have argued previously that dissociation of *o*- or *p*-chlorobenzyl anions to form dehydrotoluene biradicals suffers from a kinetic shift because of slow intersystem crossing (ISC). Given the biradical character of *m*-xylylene, it is important to recognize the possibility of a kinetic shift in this system as well. However, as discussed by Squires and co-workers,[23,63] slow ISC is expected only for those systems where the singlet state has a large degree of open-shell character. Intersystem crossing will be more favorable for systems such as carbenes where the lowest energy singlet states have closed-shell character because the accompanying change in orbital angular momentum compensates for the change in spin angular momentum of the electron.[79] Consequently, Poutsma and Squires did not see evidence for slow ISC in their studies of methylene, vinyl-, and phenylcarbene,[63] and we would not expect a kinetic shift in the dissociation of **7**$^-$. Moreover, the lowest energy singlet state of *m*-xylylene is the closed-shell, $^1A_1$ which is state, ∼10 kcal/mol lower in energy than the open-shell $^1B_2$ state.[15] Thus, ISC should be favorable for the dissociation of **6**$^-$. In previous studies, the possibility of a kinetic shift has been examined by utilizing bromo- and iodo- substituted ion precursors.[23,63] Unfortunately, we were unable to generate the 3-(bromomethyl)-benzyl anion by deprotonation of the deuterated bromo-*m*-xylene. Therefore, although the dissociation **6**$^-$ is not expected to suffer from a kinetic shift due to slow ISC, the possibility cannot be ruled out. If there is a kinetic shift, then the measured enthalpy of formation is formally an upper limit.

Thermochemical Results. A weighted average of the two measured enthalpies of formation gives $\Delta H_{\mathrm{f,298}}(\mathbf{1}) = 80.8 \pm 2.4$ kcal/mol. The final enthalpy of formation gives a second C−H bond dissociation energy in *m*-xylene of 90.7 ± 2.9 kcal/mol, only slightly higher than the first (90.1 ± 1.7 kcal/mol). The fact that the strength of the second C−H bond in 3-methylbenzyl radical is the same as that in *m*-xylene indicates

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(78) Most of the difference between the acidities of benzyl chloride and **5** is in the ΔS_{acid} term. Poutsma and Squires used ΔS_{acid}(benzyl chloride) = 24.3 cal/mol K. Recalculation of this quantity using the approach described in this work gives ΔS_{acid}(benzyl chloride) = 27.4 cal/mol K, and ΔH_{acid}(benzyl chloride) = 373.1 kcal/mol.

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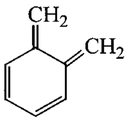
that the interaction between the two unpaired electrons is negligible, as expected for a triplet biradical.[24,25] Calculations at the CASSCF, CASPT2, and B3LYP levels of theory with 6-31G* basis sets predict that the second C−H bond in *m*-xylene should be weaker than the first by 2.5, 1.6, and 2.0 kcal/mol, respectively,[80] in reasonable agreement with the results obtained in this work.

For comparison, Hehre and co-workers[81] have determined the enthalpies of formation of *o*- and *p*-xylylene, **8** and **9**, respectively, by measuring their proton affinities. Both isomers were found to have an enthalpy of formation of 48 kcal/mol, significantly lower than that obtained for the *meta* isomer. The difference is because **8** and **9** have stable Kekule structures with singlet ground states, whereas **1** is a triplet, non-Kekule biradical. From their proton affinity measurements, Pollack et al.[81] were not able to determine the enthalpy of formation of **1**, but did provide a lower limit of 76 kcal/mol, in agreement with the results obtained here.



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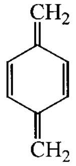

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The enthalpy of formation of 3-methylphenylcarbene is found in this work to be ∼18 kcal/mol higher than that of *m*-xylylene. The difference between the energies of these two isomers can be attributed to the benzylic delocalization of both electrons in *m*-xylylene, whereas one electron in 3-methylphenylcarbene is localized in an in-plane sp^2 orbital on the α carbon.[82−84] The enthalpy of formation of 3-methylphenylcarbene indicates that the α C−H bond dissociation energy in the 3-methylbenzyl radical is 108.3 ± 3.4 kcal/mol. This result is similar to the dissociation energy of the α C−H in benzyl radical reported by Poutsma and Squires.[63] Therefore, as expected, methyl substitution does not affect the stability of phenyl carbene.

Conclusions

Isotopic labeling and chemical reactivity studies indicate that the reaction of *m*-xylene with atomic oxygen ion proceeds by H_2^+ abstraction to form 75% *m*-xylylene radical anion and 25% unspecified ions corresponding to [α,ring] abstraction. Simple proton transfer is also observed. The open-shell anions generated in the reaction are characterized by their reaction with nitric oxide. Whereas the *m*-xylylene ion undergoes reactions characteristic of a benzylic ion, the M-2 ion resulting from α,ring abstraction shows phenyl anion-like reactivity.

The thermochemical properties of the 3-methylbenzyl radical are very similar to those for *m*-xylene, indicating that the *meta*-methylene substituent does not have a significantly different effect on the system than does a methyl substituent in the same position. The enthalpies of formation of *meta*-quinodimethane (*m*-xylylene, **1**) obtained by two different experimental approaches are in excellent agreement with each other, giving $\Delta H_{f,298}(\mathbf{1}) = 80.8 \pm 2.4$ kcal/mol. This value is consistent with what is predicted using a simple bond additivity approach and similar to what was found for trimethylenemethane[18,19] and the triplet benzynes.[17] The results indicate that *m*-xylylene can be thought of as a biradical with noninteracting radical centers.

Acknowledgment. This work was supported by the American Society for Mass Spectrometry and the Purdue Research Foundation. Thanks also go to the donors of the Petroleum Research Fund, as administered by the American Chemical Society, for partial support of this work. Special thanks go to Profs. Hilkka Kenttämaa, Weston Thatcher Borden, John Bartmess, Peter Armentrout, and Dr. David A. Hrovat for providing supporting information and helpful discussions. We also thank Rhonda Chyall and Great Lakes Chemical for the donation of some of the equipment used in this work.

JA002138N

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