Triradical Thermochemistry from Collision-Induced Dissociation Threshold Energy Measurements. The Heat of Formation of 1,3,5-Trimethylenebenzene

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Abstract: A method for measuring the heats of formation of triradicals using energy-resolved collision-induced dissociation (CID) of chloro-substituted biradical negative ions is described. This method is applied to the determination of the heat of formation of 1,3,5-trimethylenebenzene, which was generated by CID of the 5-chloromethyl-*m*-xylylene ion. The measured CID threshold energy for chloride loss (0.83 ± 0.07 eV) is combined with the electron affinity of the 5-chloromethyl-*m*-xylylene biradical (1.120 ± 0.059 eV) to give a heat of formation of the triradical of 111.0 ± 4.1 kcal/mol that agrees with the bond additivity value of 109.3 ± 2.1 kcal/mol. The measured heat of formation indicates a third C−H bond dissociation energy (BDE) in 1,3,5-trimethylbenzene of 88.2 ± 5.0 kcal/mol, indistinguishable from the C−H BDE in toluene or the first or second C−H BDEs in *m*-xylene. The results are in agreement with the predictions made on the basis of simple qualitative and high-level molecular orbital theories that predict negligible interaction between the unpaired electrons in the high-spin triradical.

Recent approaches to the design and construction of magnetic organic compounds (organoferromagnets) have utilized high-spin biradicals and triradicals as ferromagnetic coupling units for building larger structures that have many unpaired electrons.[1−11] Polyradical molecules with average spin quantum numbers as large as $S = 10$ and $S = 40$ have been built by using biradical and triradical building blocks, respectively.[9,10,12] These approaches are successful because the underlying polyradicals have high-spin ground states, and the singlet−triplet (ΔE_{S-T}) and the quartet−doublet (ΔE_{Q-D}) energy splittings for such biradical and triradical coupling units are sufficiently large so that small perturbations do not change the state ordering.[3,13−19]

Organic biradicals and triradicals are defined as species that contain two or three weakly interacting electrons, respectively, in nearly degenerate nonbonding molecular orbitals (NBMOs).[20] If these NBMOs are nondisjoint, which means that they span common atoms in the molecule, the molecule is predicted to be high-spin in its ground-state electronic configuration.[21,22]This has been experimentally confirmed for the non-Kekulé type biradicals such as *m*-xylylene **1**,[23] and trimethylenemethane **2**,[24] where the ground states were determined by spectroscopic studies to be triplets, and the singlet−triplet energy splittings (ΔE_{S-T}) were measured to be 10 and 15 kcal/mol, respectively.[25,26]

The ground-state configurations of polyradicals can also be probed by using thermochemistry. For example, the heats of formation of biradical species such as *m*-xylylene **1**,[27] trimethylenemethane **2**,[26] 1,3-bis-methylenecyclobutane **3**,[28] the three benzyne isomers **4a**−**c**,[29] and the three (α,n)-dehydrotoluene isomers **5a**−**c**[30] have been measured and used to derive the bond dissociation energies (BDEs) required for formation of these

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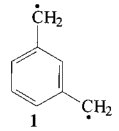
biradicals.[31] For both high-spin and low-spin biradicals, measured BDEs reflect the ground-state electronic configuration of the molecules and the degree of interaction between the unpaired electrons. For example, the C−H bond dissociation energies in the phenyl radical (i.e., the second C−H BDEs in benzene) in the *ortho*, *meta*, and *para* positions to form the singlet benzynes **4a**−**c** have recently been measured to be lower than that in benzene by 36.0 ± 3.1, 20.7 ± 3.2, and 4.8 ± 3.0 kcal/mol, respectively.[29,32] The difference between the first and second bond dissociation enthalpies in benzene reflects 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*).[32] In contrast, the measured BDEs for the formation of the *triplet* benzynes are all about 113 kcal/mol,[32] the same as that in benzene, indicating little interaction between the two unpaired electrons. Similarly, the triplet ground states of *m*-xylylene and trimethylenemethane have been confirmed from measurements of their heats of formation.[26,33] Both biradicals have heats of formation that agree with those predicted by using bond additivity methods that assume little or no interaction between the two unpaired electrons, such that the second BDE is essentially the same as the first. In certain cases, the heats of formation of triplet biradicals do not equal bond additivity values. An example that illustrates this is the biradical 1,3-bismethylenecyclobutane, **3**. Hill and Squires[28] have measured a heat of formation for **3** that is 16 kcal/mol higher than the value predicted by bond additivity. However, this discrepancy is explained by the fact that **3**, unlike the radical from which it is derived, is not stabilized by electron delocalization because that would involve a nonfavorable, cyclobutadiene-like configuration.[34]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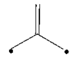
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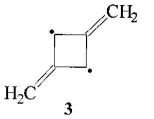
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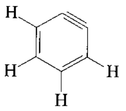
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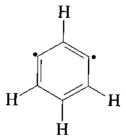
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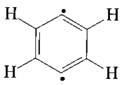
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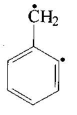
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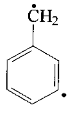
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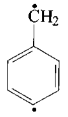
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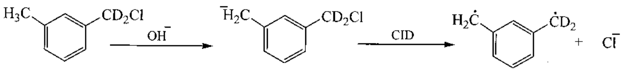
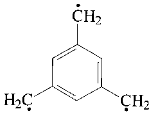
The heats of formation of many of the biradicals described above were determined by using energy-resolved collision-induced dissociation (CID) threshold measurements with α,*ω*-halo-substituted carbanions.[29] For example, we recently reported the determination of the heat of formation of *m*-xylylene[27] from the threshold energy for chloride loss from the 3-(chloromethyl)-benzyl anion as shown in Scheme 1. The measured activation energy for halide loss is combined with auxiliary thermochemical data for the reactant and product ions according to a simple thermochemical cycle to derive the heat of formation of the neutral diradical. The heat of formation of *m*-xylylene obtained from this approach is in good agreement with the value obtained by combining the electron affinity of *m*-xylylene with the proton affinity of the *m*-xylylene anion.[27]

Scheme 1



In this paper, we extend the CID approach to the determination of the thermochemical properties of triradicals, and report the first measurement of the heat of formation of a triradical species, 1,3,5-trimethylenebenzene, **6**. Triradical **6** was chosen as the first system because both qualitative theory[21,22] and high-level molecular orbital calculations[18,19] predict it to have a high-spin ground-state such that its heat of formation should be very close to that predicted by bond additivity. Therefore, determination of the heat of formation of **6** would serve as a test of the CID approach for measuring the thermochemical properties of triradicals.


6

Kenmitz et al.[19] have recently provided a detailed description of the electronic structure of **6**. The nonbonding molecular orbitals (NBMOs) of this non-Kekulé, odd-alternate hydrocarbon, shown in Figure 1, have atoms in common, and thus are nondisjoint. Therefore, the Coulombic repulsion between the three electrons that occupy the NBMOs will be minimized when the electrons each occupy a different MO and all have parallel spins ($S = {}^3/_2$).[19] The qualitative prediction of a high-spin ground state[21,22] has been confirmed by multireference configuration interaction (MR−CI) calculations[18,19] that predict D_{3h} quartet ground state for 6 ($^4A_1''$) with a quartet−doublet energy splitting (ΔE_{D-Q}) of 14 kcal/mol.[19]

Triradical **6** can be generated in the gas phase by CID of the chloromethyl substituted *m*-xylylene ion, **7**$^-$, as shown in eq 1. Ion **7**$^-$ is synthesized in the gas phase by using the reaction of

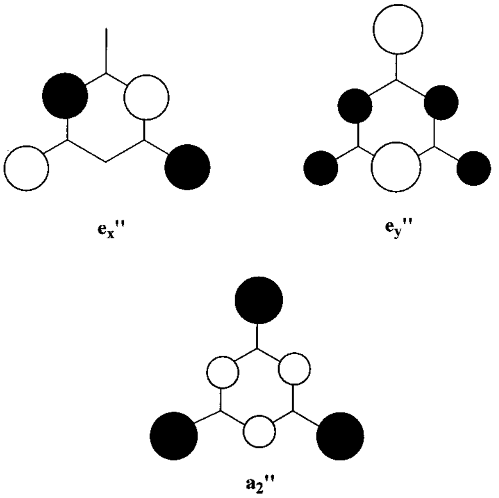


Figure 1. Schematic representation of the *π* NBMOs of 1,3,5-trimethylenebenzene, **6** (D_{3h}).

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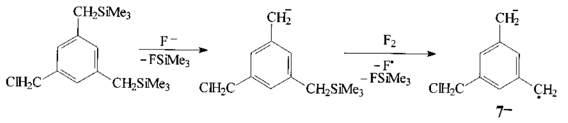
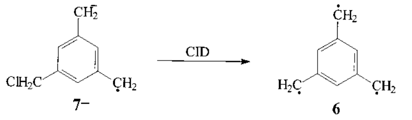
Scheme 2

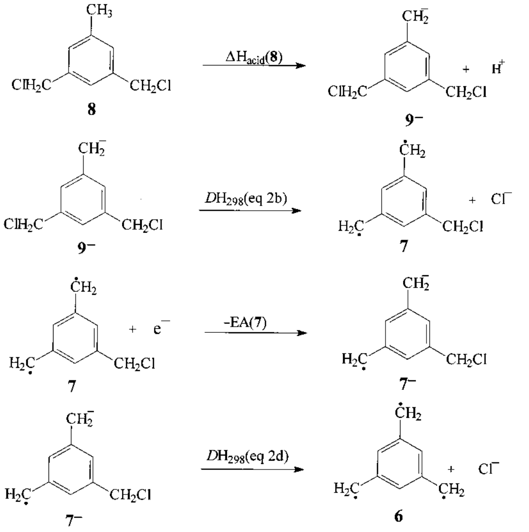


trimethylsilyl-substituted benzyl anions with F_2 (the "Squires" reaction),[35] as shown in Scheme 2. Regiospecific synthesis can



(1)

be carried out because the positions of the two trimethylsilyl groups determine the positions of charged and odd-spin sites in the radical anion product.[36] The thermochemical measurements used to determine the heat of formation of **6** are shown in eq 2 and include the determination of two CID threshold energies, a gas-phase acidity, and an electron affinity. To be considered useful, it is important that the measured heat of formation of the triradical have reasonable error limits. The expected uncertainty in the final value can be estimated by recognizing that steps 2a and 2b constitute a measurement of the heat of formation of 5-chloromethyl-*m*-xylylene, **7**, whereas step 2c gives the heat of formation of the chloro-substituted precursor ion **7**$^-$, which upon CID in step 2d, leads to the heat of formation of **6**. Biradical heats of formation determined by using these types of procedures generally have uncertainties of about ±3 kcal/mol.[28,37] Given that uncertainties in electron affinities and CID threshold measurements are about 1−2 and 2−2.5 kcal/mol, respectively, we anticipate an uncertainty of only about ±4 kcal/mol in the heat of formation of the triradical.



(2a)

(2b)

(2c)

(2d)

In this work we describe the measurements of the thermodynamic quantities needed to obtain the heat of formation of the triradical 1,3,5-trimethylenebenzene **6**, $\Delta H_{f,298}$(**6**). We describe the synthesis of the ions needed to make each measurement, the thermodynamic quantity obtained from each measurement, and the significance of each result in determining $\Delta H_{f,298}$(**6**). We also derive the second and the third C−H bond dissociation energies in 1,3,5-trimethylbenzene, and discuss these quantities in light of the electronic structure of the triradical.

Experimental Section

All the gas-phase experiments described in this paper were carried out in a flowing afterglow-triple quadrupole instrument described elsewhere.[38,39]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 ion, F^-, is produced by electron ionization (EI) of NF_3 in the upstream end of the flow tube. 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. The ions in the flow tube, thermalized to ambient temperature by ca. 10^5 collisions with the helium buffer gas, are extracted from the flow tube through a 1 mm orifice in a nosecone and are then focused into an EXTREL triple quadrupole analyzer.

Collision-induced dissociation (CID) studies are carried out by selecting the ions 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 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 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.[39] 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-maximum of 0.5−1.5 eV (laboratory frame).

Energy-resolved cross sections are fit using the assumed model shown in eq 3,[40−42]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 that reflects the energy deposition function for the collision between the ion and the target,[43] and σ_o is a scaling factor.

$$\sigma(E) = \sigma_0 \sum_i \left[\frac{g_i P_D(E, E_i, \tau)(E + E_i - E_T)^n}{E} \right] \tag{3}$$

Modeling is carried out by minimizing the deviation between the model function and the steeply rising portion of the appearance curve just above threshold, ignoring the low-energy "tail" that is attributed to collisions of ions outside of the collision cell. 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 RRKM theory, to account for potential kinetic shifts that result from slow dissociation on the instrumental time scale (τ = ca. 30 μs). The dissociation reactions are assumed to have loose, product-like transition states that correspond to the "phase-space limit"

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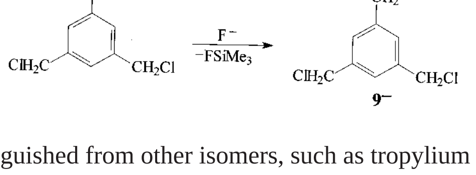
and are calculated using the approach described by Rodgers et al.[44] Physical parameters for the reactants and products, including vibrational frequencies, rotational constants, and polarizabilities, are calculated at the Becke3LYP/6-31+G* level of theory.[45] Vibrational frequencies are scaled by 0.965 to account for anharmonicities. Dissociation energies obtained from the fitting procedures correspond to the 0 K energies, and are converted to the 298 K bond dissociation enthalpies, DH_{298}, using the integrated heat capacities for the reactants and products obtained from the scaled, calculated frequencies. All analysis is carried out using the CRUNCH program developed by Armentrout and co-workers.[40−42,44]

Materials. 1,3,5-Tris(chloromethyl)benzene was prepared by treating 1,3,5-tris(bromomethyl)benzene with 15 equiv of LiCl in DMF at room temperature for 5 h.[46] Hexane was added to the reaction flask and the mixture was washed with water to remove DMF, dried, and the solvent was completely removed. The product was crystallized from petroleum ether. The 1,3,5-tris(bromomethyl)benzene was prepared by refluxing overnight 1 equiv of freshly distilled 1,3,5-trimethylbenzene with 3.2 equiv of *N*-bromosuccinimide and 0.04 mol % benzoylperoxide in CCl_4 under a 300-W incandescent lamp.[47] The solution was filtered and CCl_4 was removed under vacuum. Hexane was then added and the solution was washed with $NaHCO_3$ and dried with $MgSO_4$. Purification was achieved using silica gel column chromatography with hexane as eluent. Substantial amounts of mono- and bis-brominated 1,3,5-trimethylbenzene were isolated and subjected to a second treatment of NBS as described above. The mono- and bis-trimethylsilyl compounds were prepared by adding 1 equiv of 1,3,5-tris(chloromethyl)benzene to a refluxing THF solution containing 1 or 2 equiv of Mg turnings and trimethylsilyl chloride, and refluxing the mixture for 5 h. The products were purified by column chromatography with hexane as eluent. Deuterium-labeled α-chloro-1,3,5-trimethylbenzene ($(CH_3)_2C_6H_3CD_2$-Cl) was prepared by the reduction of methyl 3,5-dimethylbenzoate with lithium aluminum deuteride,[48] followed by chlorination with $SOCl_2$.[49] All other reagents were obtained from commercial sources and were used as supplied. Gas purities were as follows: He (99.995%), CH_4 (99%), F_2 (5% in He), NF_3 (99%).

Results and Discussion

The heat of formation of triradical **6** has been determined using the thermochemical cycle shown in eq 2. This cycle requires three major measurements, each of which will be discussed in detail: (1) the heat of formation of the biradical 5-chloromethyl-*m*-xylylene **7**, (2) the EA of **7**, and (3) the CID threshold energy measurement of chloride loss from ion $\mathbf{7}^-$.

The Heat of Formation of 5-Chloromethyl-*m*-xylylene, 7. Determination of the heat of formation of 5-chloromethyl-*m*-xylylene, **7**, requires measurement of the gas-phase acidity of **8** at the methyl site (eq 2a) and the chloride binding enthalpy of ion $\mathbf{9}^-$ (eq 2b). We first describe the measurement of the chloride binding energy from a CID threshold measurement, and then discuss the gas-phase acidity.



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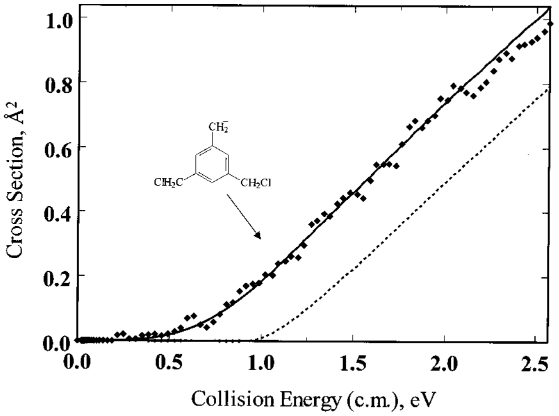

Figure 2. Cross sections for Cl^- formation upon collision-induced dissociation of $\mathbf{9}^-$ with Ar target as a function of translational energy in the center-of-mass frame. The solid line is the model appearance curve calculated using eq 3, and the broken line represents the unconvoluted function.

The 3,5-bis(chloromethyl)benzyl anion, $\mathbf{9}^-$, is generated by fluoride-induced desilylation as shown in eq 4. Ion $\mathbf{9}^-$ can be distinguished from other isomers, such as tropylium ion, by the reaction with nitrous oxide. Benzyl anions, including $\mathbf{9}^-$, react with N_2O by the addition and loss of H_2O,[50] while alternate ion isomers, such as tropylium anion, do not undergo this reaction.[51] Collision-induced dissociation of the mass-selected $\mathbf{9}^-$ ion gives chloride as the only ionic fragment, consistent with formation of biradical **7** as the corresponding neutral. The cross-sections as a function of center-of-mass collision energy for dissociation of ion $\mathbf{9}^-$ are shown in Figure 2. Average values of DH_{298} (eq 2b) and *n* obtained by modeling the cross sections for the dissociation of ion $\mathbf{9}^-$ are listed at the bottom of Table 1. The chloride binding enthalpy (298 K) for ion $\mathbf{9}^-$ obtained from replicate measurements is 0.98 ± 0.08 eV, where the uncertainty includes the standard deviation of the values obtained from replicate measurements, a 0.15 eV (lab) uncertainty in the absolute energy scale, and a 0.01 eV contribution due to uncertainty in the choice of the transition state.[52] The measured chloride binding enthalpy for ion $\mathbf{9}^-$ is ca. 3 kcal/mol higher than that obtained previously for the 3-(chloromethyl)benzyl ion shown in Scheme 1,[27] which agrees with the expectation that an extra electron withdrawing group (the chloromethyl group in ion $\mathbf{9}^-$) stabilizes the ion with respect to the neutral biradical. Determination of the heat of formation of **7** also requires the gas-phase acidity of the α,α′-dichloro-1,3,5-trimethylbenzene, **8**, in the nonsubstituted methyl position. As we previously described,[27] standard approaches for determining gas-phase acidities, such as equilibrium measurements and bracketing,[53] are not applicable for the present system because the methyl position is not the most acidic site in the molecule. However, an accurate value for the acidity of the methyl group can likely be obtained indirectly using the relationship shown in eq 5,[53] where DH_{298}(R−H) is the homolytic C−H bond dissociation enthalpy, EA(R) is the electron affinity of radical

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Table 1. Supplemental and Derived Thermochemical Data[a]

parameter	value	reference
298 K Enthalpies of Formation		
1,3,5-trimethylbenzene	-3.8 ± 0.3	88
α,α′-dichloro-1,3,5-trimethylbenzene, **8**	-19.2 ± 1.0	bond additivity (78)
5-(chloromethyl)-*m*-xylene, **11**	-11.2 ± 1.0	bond additivity (78)
HCl	-22.1	80
5-methyl-*m*-xylylene, **10**	74.9 ± 3.3	this work
5-chloromethyl-*m*-xylylene, **7**	63.3 ± 3.1	this work
1,3,5-trimethylenebenzene, **6**	111.0 ± 4.1	this work
Gas-Phase Acidities		
HCl	333.4 ± 0.1	81
Electron Affinities		
3,5-bis(chloromethyl)benzyl radical, **9**	31.4 ± 1.8	this work
5-chloromethyl-*m*-xylylene, **7**	25.8 ± 1.4	this work
Chloride Dissociation Energies		
DH_{298}(3,5-$(CH_2)_2C_6H_3CH_2Cl$), $\mathbf{7}^-$	19.1 ± 1.6	this work
n^b	1.4 ± 0.1	
DH_{298}(3-CH_2,5-$CH_2ClC_6H_3CH_2Cl$), $\mathbf{9}^-$	22.6 ± 1.8	this work
n^b	1.5 ± 0.1	
CH Bond Dissociation Energies		
$DH_{298}(C_6H_5CH_2-H)$	89.8 ± 0.6	82
DH_{298}(3-$CH_2C_6H_4CH_2-H$)	90.7 ± 2.9	27
DH_{298}(3,5-$(CH_2)_2C_6H_3CH_2-H$)	88.2 ± 5.0	this work

[a] Values in kcal/mol. [b] Exponent in eq 3.

9, and IE(H) is the ionization energy of hydrogen.[54]

$$DH_{298}(\mathrm{R-H}) = \mathrm{EA}(\mathrm{R}) + \Delta H_{\mathrm{acid}}(\mathrm{R-H}) - \mathrm{IE}(\mathrm{H}) \quad (5)$$

The advantage of this approach is that the electron affinity of the radical can be measured regiospecifically and therefore can be applied to the determination of the acidity of less thermodynamically favorable positions. A drawback of using eq 5 for determining the acidity is that it also requires the homolytic bond dissociation energy, *D*(R−H), which is generally not known. However, Kim et al.[55] have shown that remote halogen substitution does not significantly affect benzylic C−H BDEs, and that the C−H BDEs for a series of halogen-substituted toluenes are all about 89 ± 2 kcal/mol. Therefore, to determine the acidity of **8**, we have measured the electron affinity of **9** and assumed a BDE of 89 ± 2 kcal/mol.

The electron affinity of **9** has been determined by using the kinetic method developed by Cooks and co-workers.[56,57] This approach has been used successfully in the past for the measurement of electron affinities of both radicals[56,58,59] and biradicals,[27,28,37] and the accuracy of the method is demonstrated by systems such as *p*-benzyne and α-naphthyl radical, where kinetically determined electron affinities have recently been found to be in excellent agreement with values obtained spectroscopically.[32,59−62] The procedures for obtaining electron affinities using this approach have been described elsewhere.[27,37,58] The branching ratios for the collision-induced dissociation of SO_2 adducts of a series of substituted benzyl anions with known electron affinities are measured, and the semilog relationship between the branching ratios and the electron affinities is determined. In the simplest version of the kinetic method, the branching ratio for the SO_2 adduct of the unknown is measured and the electron affinity is determined from the calibration. In this work, we have used the calibration curve obtained by using benzyl radical calibrants (benzyl, *o*-, *m*-, and *p*-fluoro-, *p*-chloro- and *p*-bromobenzyl), as described previously.[27,55] The regression line reported in the previous work[27] has the form shown in eq 6, where $r = I(SO_2^-)/I(R^-)$, the ratio of the products obtained for CID of RSO_2^- at 4 eV (C.M.) and the EA is in kcal/mol.

$$\mathrm{EA}(\mathrm{R}) = 24.75 - 1.248 \ln r \quad (6)$$

The branching ratio for the dissociation of the SO_2 adduct of ion $\mathbf{9}^-$ was measured and found to be $r = (4.87 \pm 0.97) \times 10^{-3}$, implying an EA of 31.4 ± 1.8 kcal/mol (1.361 ± 0.077 eV) for radical **9**. Determination of electron affinities using the kinetic method requires certain assumptions that can lead to errors in the final values. For example, Ervin has shown recently that differences in dissociation energies for the different ions may lead to a 0.5−1.0 kcal/mol error into the measurement.[63] Similarly, we have used the branching ratio and calibration at a single energy, 4 eV, and different values could be obtained at different energies. The differences would result from differences in entropies for the competing dissociation channels.[64−67] To account for potential errors, we have determined how the measured EA is affected by changing the collision energy. For the present system, changing the collision energy by 2 eV results in a 1.4 kcal/mol change in the final electron affinity. Therefore, the final uncertainty assigned in the electron affinity of **9** includes a 0.25 kcal/mol due to uncertainty in the measured ratio, a 0.38 kcal/mol contribution due to statistical error in the calibration plot (the uncertainties of the EAs of the references are not significant), a 1 kcal/mol uncertainty to account for the potential differences in dissociation energies, as described by Ervin,[63] and a 1.4 kcal/mol component to account for potential errors due to choosing a single collision energy. The measured electron affinity of **9** is ca. 4 kcal/mol higher than the electron affinity of the 3-(chloromethyl)benzyl radical, reported previously,[27] similar to the difference between 3-(chloromethyl)benzyl radical and benzyl,[55,68] indicating that the effect of a *m*-chloromethyl substituent on the EA of benzyl is essentially additive. Using a homolytic C−H bond dissociation enthalpy for the methyl group in **8** of 89.0 ± 2.0 kcal/mol and an EA of 1.361 ± 0.077 eV for radical **9**, the gas-phase acidity of the methyl position in **8** is estimated to be 371.3 ± 2.7 kcal/mol, which means it is ca. 4 kcal/mol more acidic than the methyl position in α-chloro-*m*-xylene, previously reported to be 375.1 ± 2.3 kcal/mol,[27] consistent with the expected substituent effect.[69] The heat of formation of 5-chloromethyl-*m*-xylylene, **7**, obtained from the acidity of **8** and *DH* (eq 2b) and auxiliary thermochemical data (Table 1), is $\Delta H_{f,298}(\mathbf{7}) = 63.3 \pm 3.1$ kcal/

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mol. The difference between this heat of formation for biradical **7** and that of *m*-xylylene[27] (~17 kcal/mol) is similar to the difference between the heat of formation of 5-chloromethyl *m*-xylene and that of *m*-xylene (15.3 ± 1.2 kcal/mol). The fact that the measured heat of formation of biradical **7** is about the same as the bond additivity value indicates that chloromethyl substitution does not have a significant effect on the first and second BDEs of *m*-xylene.

The Electron Affinity of 5-(Chloromethyl)-*m*-xylylene, 7. The heat of formation of ion $\mathbf{7}^-$ can be calculated from the heat of formation and electron affinity of **7** (EA(**7**)). The electron affinity of **7** was determined by using the kinetic method, as described for **9** in the previous section. Ion $\mathbf{7}^-$ was synthesized in the gas phase as shown in Scheme 2. Reactivity studies using ion−molecule reactions similar to those used for the *m*-xylylene ion[27] were performed with ion $\mathbf{7}^-$ to structurally characterize it. For example, ion $\mathbf{7}^-$, like most organic carbanions, was found to react with CO_2 molecules by forming a carboxylate adduct[70] that undergoes addition with NO, indicating that the carboxylate adduct had an open-shell character.[35,71,72]Also, ion $\mathbf{7}^-$ was found to react with CS_2 exclusively by addition and no sulfur atom abstraction was observed, indicating that $\mathbf{7}^-$ does not isomerize to a more basic phenyl anion.[73−76]

The CID branching ratio for the SO_2 adduct of $\mathbf{7}^-$ was measured to be $r = 0.420 \pm 0.084$ at 4 eV (center-of-mass), which gives EA(**7**) = 25.8 ± 1.4 kcal/mol (1.120 ± 0.059 eV), where the uncertainty is calculated as described above, except that changing the collision energy by 2 eV only changes the measured electron affinity by 0.8 kcal/mol for this system. The measured EA of **7** is ca. 4 kcal/mol higher than that of *m*-xylylene,[25] the same as the difference between the EAs of the 3-(chloromethyl)benzyl radical and benzyl, as discussed in the previous section.

The Heat of Formation of 1,3,5-Trimethylenebenzene. Collision-induced dissociation of $\mathbf{7}^-$ over the energy range 0−4 eV (C.M.) leads to the formation of chloride ion as the only ionic product. The cross-sections as a function of center-of-mass collision energy for dissociation of ion $\mathbf{7}^-$ are shown in Figure 3. Average values of DH_{298} (eq 2d) and n obtained by modeling the cross sections for the dissociation of $\mathbf{7}^-$ are listed at the bottom of Table 1. The chloride binding enthalpy (298K) for $\mathbf{7}^-$ obtained from replicate measurements is 0.83 ± 0.07 eV. By comparison with previously reported results,[27,77] the neutral product of the reaction is assigned to be the triradical, formed by direct dissociation. Direct dissociation is dynamically and energetically favored over rearrangement processes, which would require tight transition states, and large energy barriers.[77] In fact, the low dissociation threshold measured for $\mathbf{7}^-$ indicates that if rearrangement were to occur, it must have a barrier lower than ca. 0.9 eV. Therefore, the low dissociation energy strongly suggests that $\mathbf{7}^-$ dissociates by simple dissociation to form the triradical **6**.

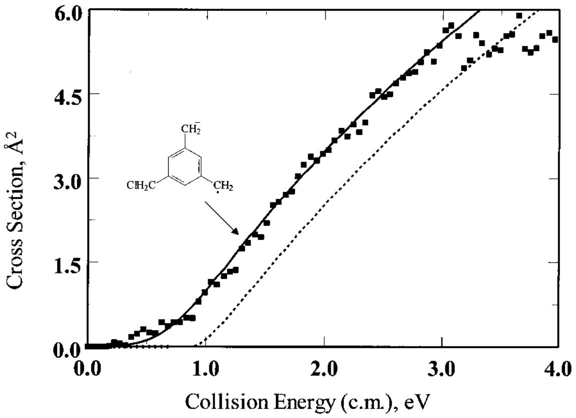
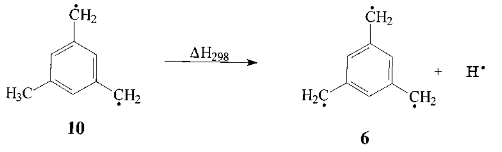


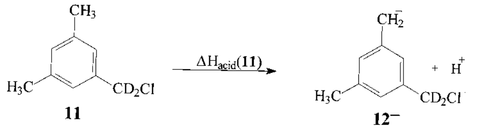
Figure 3. Cross sections for Cl^- formation upon collision-induced dissociation of $\mathbf{7}^-$ with Ar target as a function of translational energy in the center-of-mass frame. The solid line is the model appearance curve calculated using eq 3, and the broken line represents the unconvoluted function.

The heat of formation of 1,3,5-trimethylenebenzene, **6**, obtained from measuring ΔH_{acid}(**8**), *DH* (eq 2b), EA(**7**), *DH* (eq 2d), the heat of formation of **8**,[78,79]and the heat of formation[80] and gas-phase acidity[81] of HCl (Table 1), is $\Delta H_{f,298}(\mathbf{6}) = 111.0 \pm 4.1$ kcal/mol.

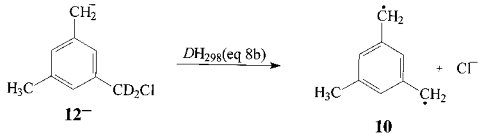
Comparison with Bond Additivity. A simple bond additivity estimate of the heat of formation of 1,3,5-trimethylenebenzene, **6**, calculated by using the heat of formation of 1,3,5-trimethylbenzene (Table 1) and the toluene $C_6H_5CH_2-H$ bond dissociation energy (BDE) (89.8 ± 0.6 kcal/mol)[82] three times gives $\Delta H_f(\mathbf{6}) = 109.3 \pm 2.1$ kcal/mol, indistinguishable from the value obtained in the present work. A more meaningful quantity that reflects on the electronic structure of the molecule is the third BDE in 1,3,5-trimethylbenzene, the enthalpy for the reaction in eq 7. However, calculation of the third BDE requires the heat of formation for 5-methyl-*m*-xylylene, **10**. We have determined this value experimentally by using an approach similar to that utilized to determine the heat of formation of **7**, as outlined in eq 8. From the measured acidity and chloride binding enthalpy,[83] the heat of formation of **10** is 74.9 ± 3.3 kcal/mol, which agrees with the value of 73.3 kcal/mol calculated by assuming that the difference in the heats of formation of **10** and *m*-xylylene is the same as for toluene and



(7)



(8a)



(8b)

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benzene. This gives a value of 88.2 ± 5.0 kcal/mol for the third C−H BDE in 1,3,5-trimethylbenzene, which is indistinguishable from the C−H BDE in toluene (89.8 ± 0.6 kcal/mol)[82] and the first and second C−H BDEs in *m*-xylene (90.1 ± 1.7 and 90.7 ± 2.9 kcal/mol, respectively),[27] indicating that there is negligible interaction between the unpaired electrons in the triradical, as expected on the basis of simple qualitative and more sophisticated ab initio[19] and density functional theory.[84]

Conclusion

The finding in this work that the heat of formation for 1,3,5-trimethylenebenzene is indistinguishable from that predicted by simple bond additivity and higher level molecular orbital theory establishes that the collision-induced dissociation approach used to determine thermochemical properties of carbenes,[77,85,86] carbynes,[8787−88] and biradicals[27,29,30] can also be applied to the study of even more reactive intermediates, including triradicals, without a significant loss of precision. Thus, the CID approach should continue to be useful for determining the energetics for decomposition of simple organic molecules, and for probing electron−electron interactions within open-shell reactive intermediates.

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Supporting Information Available: Figure 1S of the cross sections for collision-induced dissociation for Cl^- from **12**$^-$ as a function of center-of-mass collision energy and the details of the measurement of $\Delta H_{f,298}$(**10**) (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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