PERKIN 2

Synthesis, properties and reactivity of the phenylcarbene anion in the gas phase†

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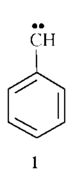
Received (in Cambridge, UK) 20th July 1999, Accepted 28th September 1999

The gas-phase synthesis and characterization of phenylcarbene anion, $PhCH^{\bullet -}$ ($\mathbf{1}^{\bullet -}$), are reported. This archetypal arylcarbene radical anion is produced in isomerically-pure form by dissociative electron ionization of phenyldiazirine in a flowing afterglow–triple quadrupole instrument. The structure and purity of $PhCH^{\bullet -}$ are established by authentication of its oximate derivative, $PhCHNO^-$, by collision induced dissociation (CID). *Ab initio* calculations indicate a $^2A''$ ground state for $\mathbf{1}^{\bullet -}$, with a π-radical/σ-anion electronic configuration, which is 11–12 kcal mol^{-1} lower in energy than the π-anion/σ-radical $^2A'$ state. Reactions of $PhCH^{\bullet -}$ with a series of small molecules are described that reveal its strong base and nucleophilic character. $PhCH^{\bullet -}$ abstracts a sulfur-atom from CS_2 and OCS, N-atom from N_2O, and H-atom from $(CH_3)_2NH$, propene and $(CH_3)_2S$. Nucleophilic displacement of Cl^- from CH_3Cl by $\mathbf{1}^{\bullet -}$ occurs at 41% of the collision rate; more than forty times faster than for the benzyl anion. $PhCH^{\bullet -}$ exchanges both the carbene hydrogen and a hydrogen in the phenyl ring upon reaction with ND_3 or D_2O, which is consistent with theoretical predictions that indicate similar energies for $PhCH^{\bullet -}$ and α,*n*-didehydrotoluene anion isomers. Acid–base bracketing and Cooks' kinetic method were used to determine the proton affinity and electron binding energy of $PhCH^{\bullet -}$ to be 392.0 ± 2.1 kcal mol^{-1} and 27.8 ± 0.7 kcal mol^{-1}, respectively. These quantities were used to derive the heat of formation of phenylcarbene. The value obtained, 103.8 ± 2.2 kcal mol^{-1}, is in excellent agreement with that recently measured by energy-resolved collision-induced dissociation (102.8 ± 3.5 kcal mol^{-1}: J. C. Poutsma, J. J. Nash, J. A. Paulino and R. R. Squires, *J. Am. Chem. Soc.*, 1997, **119**, 4686).

Introduction

Considerable effort has been dedicated over the years to investigate the physical properties, reactivity, and electronic structure of aryl carbenes.[1] These species elicit interest in a variety of ways, such as serving as important photoaffinity labeling reagents[2] and exhibiting complex structural rearrangements.[3–5] Further, aryl carbenes are key substrates for laser flash photolysis studies of carbene reaction kinetics,[6] and recent work in this area has led to the observation of kinetically stable aryl carbenes.[7] The archetype, phenylcarbene (**1**), has a long and storied history. Observation of **1** by electron paramagnetic resonance spectroscopy established the triplet as the ground state.[8] From the ratio of the zero-field splitting parameters, *D*/*E*, a carbene bond angle of 155° was estimated.[9] In addition, phenylcarbene has been characterized by infrared and UV–visible spectroscopy,[10] and by fluorescence spectroscopy.[11] Experimental evidence for the rearrangement of phenylcarbene to a ring-expanded intermediate has been obtained;[12] *ab initio* calculations have aided in the identification of this intermediate as cycloheptatetraene.[13] The bimolecular chemistry of phenylcarbene proceeds almost exclusively from the singlet state, regardless of the method of carbene generation.[14] This suggests a rapid spin-state equilibrium and hence a small singlet–triplet splitting. In fact, recent high-level *ab initio*[13] and density functional[15] calculations predict this energy difference to be 3–5 kcal mol^{-1}. No experimental measurements of the singlet–triplet splitting for phenylcarbene have been reported.



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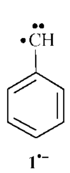

$\mathbf{1}^{\bullet -}$

One of the best experimental techniques for determining singlet–triplet energy gaps (ΔE_{ST}) of carbenes and biradicals is negative ion photoelectron spectroscopy (NIPES).[16] This experiment requires an intense beam of the negative ion corresponding to the reactive molecule of interest. The appropriate ion is mass-selected, the ion beam is crossed with a fixed-frequency laser, and the kinetic energies of the photodetached electrons are measured. The difference between the measured electron affinities for the singlet and triplet states of the neutral photodetachment product gives the singlet–triplet gap. The NIPES technique can provide accurate measurements of ΔE_{ST}, often with uncertainties less than ±0.01 eV. This method has been employed to determine ΔE_{ST} for several different carbenes and biradicals, including CH_2,[17] halocarbenes,[18] vinylidene,[19] the benzynes[20] and trimethylenemethane.[21] Some of these measurements were made possible by the ability to generate the desired negative ion through $H_2^{+\bullet}$ abstraction from a neutral precursor by atomic oxygen anion, $O^{\bullet -}$. Because of the fundamental importance of ΔE_{ST} for phenylcarbene, generation of the radical anion of phenylcarbene ($\mathbf{1}^{\bullet -}$) by this simple synthetic approach would be desirable. However, the reaction of

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† Listings of geometries (in GAUSSIAN94 archive format) obtained from (U)B3LYP/6-31+(d), (U)BPW91/6-31+G(d) and CAS(9,8)/3-21G calculations, total electronic energies, zero-point energies and 298 K temperature corrections (derived from (U)B3LYP/6-31+G(d), BPW91/6-31+G(d) or CAS(9,8)/3-21G harmonic frequencies, unscaled), for phenylcarbene anion and related species, together with a listing of gas phase proton affinity bracketing results for $PhCH^{\bullet -}$, are available as supplementary data. For direct electronic access see http://www.rsc.org/suppdata/p2/1999/2249, otherwise available from BLDSC (SUPPL. NO. 57653, pp. 10) or the RSC Library. See Instructions for Authors available *via* the RSC web page (http:www.rsc.org/authors).

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§ We wish to dedicate this paper, completed after Bob's death, to the memory of Bob, whose enthusiasm and love of chemistry continue to inspire us in our scientific endeavors.

$O^{\bullet -}$ with toluene cannot be employed. Deuterium-labeling studies indicate that $H_2^{\bullet +}$ abstraction occurs from both the methyl group and the ring, which results in a mixture of isomeric $C_7H_6^{\bullet -}$ anions.[22] Indeed, the α,n-didehydrotoluene anions ($n = 2$–4) are calculated to be quite close in energy to $\mathbf{1}^{\bullet -}$ (*vide infra*). Thus, a different method of generation of $\mathbf{1}^{\bullet -}$ is needed, as are reliable means for establishing its isomeric purity.

Carbene radical anions are not unprecedented species.[23] McDonald and co-workers have generated many carbene radical anions by dissociative electron attachment to diazo compounds.[24] Grabowski and co-workers and Nibbering and co-workers have characterized a variety of different carbene radical anions formed from $O^{\bullet -}$ reactions.[25–28] The formation and reactivity of the simplest carbene radical anion, $CH_2^{\bullet -}$, have been reported.[29] McDonald and Gung investigated the thermochemistry and reactivity of diphenylcarbene radical anion ($Ph_2C^{\bullet -}$) formed by dissociative electron ionization of Ph_2CN_2.[24d] They measured the proton affinity of $Ph_2C^{\bullet -}$ and derived a value for $\Delta H_f(Ph_2C^{\bullet -})$. The related species, phenylnitrene radical anion ($PhN^{\bullet -}$), is easily generated by electron ionization of PhN_3. The synthesis, proton affinity, heat of formation, and ion–molecule reactions of $PhN^{\bullet -}$ have been examined,[30] and the electron affinity of phenylnitrene has been determined by photoelectron[31] and photodetachment spectroscopy.[32] However, the analogous synthetic approach to phenylcarbene anion, *i.e.*, dissociative electron ionization of phenyldiazomethane, is not useful since it produces mainly the undissociated phenyldiazomethane molecular anion.[24]

In this paper, we describe the generation of isomerically-pure gaseous phenylcarbene radical anion, $\mathbf{1}^{\bullet -}$, and the characterization of its reactivity with a series of neutral molecules. The electron affinity of phenylcarbene is determined by the Cooks' kinetic method, and the proton affinity of $PhCH^{\bullet -}$ is measured by acid–base bracketing techniques. From these two quantities, the heat of formation of phenylcarbene is derived and shown to be in excellent agreement with a previous value obtained in our laboratory by energy-resolved collision-induced dissociation.[33] *Ab initio* calculations of the structure, state energies, conformational properties and thermochemistry of phenylcarbene anion are described and compared with the experimental results.

Experimental

The gas-phase experiments were performed at room temperature (298 ± 2 K) in a flowing afterglow–triple quadrupole instrument described in detail elsewhere.[34] In this instrument, helium buffer gas is maintained in the 1 m × 7.3 cm flow reactor at 0.4 Torr, with a flow rate of 200 STP $cm^3\ s^{-1}$ and flow velocity of 9400 $cm\ s^{-1}$. Primary ions are generated by electron ionization (EI) of neutral molecules introduced near the electron emission source located at the upstream end of the flow tube. These ions are swept down the flow reactor by the helium buffer gas, and allowed to react with gaseous neutral compounds introduced *via* leak valves. The product ions are cooled to ambient temperature by up to 10^5 collisions with the buffer gas. Negative ions in the flowing plasma are extracted through a 0.5 mm orifice and focused into a triple quadrupole mass analyzer for single-stage or tandem mass spectrometric analysis. Hydroxide ion is formed by ionization of a N_2O–CH_4 mixture, and F^- is produced by dissociative EI of NF_3.

Kinetics measurements were performed by the variable neutral flow method using a pair of fixed-position reagent gas inlets.[34] The estimated uncertainty in the measured rate coefficients is ±20%. Product ion yields for ion–molecule reactions were estimated from observed or extrapolated ion signal ratios obtained with low concentrations of added neutral reagent.

For collision-induced dissociation (CID) experiments, ions mass-selected in the first quadrupole undergo collisions with argon target gas in the rf-only, gas-tight central quadrupole (Q2). The axial kinetic energy of the ions in Q2 is determined by the quadrupole rod offset voltage, which can be varied from 0–200 V. The ionic fragments are extracted with an electrostatic lens into the third quadrupole for mass analysis, and detected with a conversion dynode/electron multiplier operated in pulse-counting mode. When examining reactions of mass-selected ions with reactive gases in Q2, the quadrupole offset voltage is kept as low as possible so as to minimize contributions from CID and endothermic ion–molecule reactions.

For determination of the electron affinity of phenylcarbene, CID of the adduct formed upon reaction of $\mathbf{1}^{\bullet -}$ with SO_2 was carried out at a collision energy of 30 eV (lab) and an argon target pressure of 0.200 mTorr. The given fragment ion yield ratios, $I[R^-]/I[SO_2^{\bullet -}]$, comprise the average of at least 20 individual intensity measurements for each fragment. Error propagation in calculating the ion intensity yield ratios and in obtaining the EA calibration equation was estimated in accordance with standard procedures.[35]

Materials

Phenyldiazomethane (**2**) was obtained by thermolysis of the sodium salt of the tosylhydrazone of benzaldehyde under reduced pressure.[36] Phenyldiazirine (**3**) was synthesized by oxidative cleavage of 2,4,6-triphenyl-1,3,5-triazabicyclo[3.1.0]-hexane using *tert*-butyl hypochlorite, according to the procedure reported by McMahon *et al.*[10] *syn*-Benzaldehyde oxime and cycloheptatriene were purchased from Aldrich and used without further purification. Gas purities were as follows: He (99.995%), Ar (99.955%), N_2O (99.5%), $^{\bullet}NO$ (99%), $^{\bullet}NO_2$ (99.5%), SO_2 (99.98%), O_2 (99%), CO_2 (99.5%), OCS (97.5%), NF_3 (98%) and CH_4 (99%), NH_3 (anhydrous, 99.5%), ND_3 (99% d_3), propene (99%), CH_2ClF (99%). All other reagents were obtained from commercial sources and used as supplied except for degassing of liquid samples prior to use.

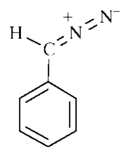
Computational details

Optimized geometries and total energies for phenylcarbene anion and related species were obtained from B3LYP[37] and BPW91[38] calculations in conjunction with a 6-31+G(d) basis set, *i.e.*, B3LYP/6-31+G(d) and BPW91/6-31+G(d). Harmonic vibrational frequencies were computed from analytically evaluated gradients and were used for estimating zero-point energy and temperature corrections without scaling. Charge and spin distributions were determined for selected species with use of the Natural Population Analysis (NPA) method of Weinhold.[39] For the $^2A''$ and $^2A'$ states of $\mathbf{1}^{\bullet -}$, CASSCF calculations were carried out with a 3-21G basis set for geometry optimization, and with a 6-31+G(d) basis set for energies. The active space consisted of the seven π orbitals and the carbene σ orbital, *i.e.*, CASSCF(9,8). Harmonic vibrational frequencies for the $^2A''$ and $^2A'$ states were computed at the CASSCF(9,8)/3-21G level and used without scaling. The optimized geometries, total energies, zero-point energies, and temperature corrections for all molecules and ions considered in this work are provided in Table S1 of the Supplementary Material.† All calculations were carried out with the GAUSSIAN94 suite of programs.[40]

Results and discussion

Synthesis of phenylcarbene radical anion

A common synthetic route to carbenes is extrusion of molecular nitrogen upon thermolysis or irradiation of diazo compounds. Accordingly, a rational approach for the generation of phenylcarbene radical anion ($\mathbf{1}^{\bullet -}$) is dissociative electron attachment to phenyldiazomethane (**2**) in an electron ionization (EI) source. Others have attempted this route to $\mathbf{1}^{\bullet -}$ unsuccessfully.[24] We tried variations on the EI approach, with minor



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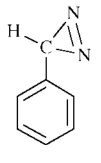

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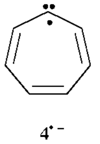
success. Simple EI ionization under flowing afterglow conditions produces nearly exclusively the molecular anion of phenyldiazomethane (*m/z* 118, $\mathbf{2}^{\bullet-}$). Use of a DC discharge source[41] results in low yields of an ion with *m/z* 90 that is likely to be $\mathbf{1}^{\bullet-}$. However, the harsh ionization conditions produce many other fragment ions that would complicate the subsequent characterization of $\mathbf{1}^{\bullet-}$. Other ionization conditions with **2** were tried, however, the yield of $\mathbf{1}^{\bullet-}$ relative to $\mathbf{2}^{\bullet-}$ never exceeded 10%.

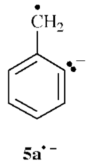
Alternative precursors to carbenes are diazirines. Electron ionization of phenyldiazirine (**3**) proved to be a much better method for generating phenylcarbene radical anion than EI ionization of **2**. This is not surprising: the higher LUMO energy of **3** relative to that of **2** and the relief of ring strain in the diazirine molecular anion ($\mathbf{3}^{\bullet-}$) provide a greater driving force for dissociation of $\mathbf{3}^{\bullet-}$ by loss of N_2, yielding $\mathbf{1}^{\bullet-}$. High yields of $C_7H_6^{\bullet-}$ ions (*m/z* 90) are formed upon EI of **3**, along with lesser amounts of ions with *m/z* 89 ($C_6H_5C^-$; phenylcarbyne anion[42]), *m/z* 91 ($C_6H_5CH_2^-$; benzyl anion), *m/z* 117 ($C_6H_5CN_2^-$; deprotonated phenyldiazirine), and an unidentified ion with *m/z* 119. Under optimized conditions of ion source voltage and flow rate of **3**, hundreds of thousands of counts s^{-1} of $\mathbf{1}^{\bullet-}$ are produced, in yields exceeding ten times those of any other ions. The ion yield is sufficient for characterization of the structure and reactivity of this $C_7H_6^{\bullet-}$ radical anion.

Structure analysis

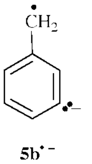
Mechanistically, phenylcarbene radical anion ($\mathbf{1}^{\bullet-}$) is the species most likely to be generated from ionization of phenyldiazirine. However, several different $C_7H_6^{\bullet-}$ structural isomers must be considered, especially those that can be formed by rearrangement of $\mathbf{1}^{\bullet-}$. It has been established that neutral singlet phenylcarbene ($^1A'$ **1**) rearranges to bicyclo[4.1.0]hepta-2,4,6-triene with a barrier of about 15 kcal mol^{-1} and then to cycloheptatetraene, with an overall exothermicity of *ca.* −15 kcal mol^{-1}.[13] The corresponding rearrangement by $\mathbf{1}^{\bullet-}$ should have a significantly higher barrier because the *p*-orbital at the exocyclic carbon is singly occupied and significant antibonding character would be present in the transition state. Moreover, the rearrangement intermediate, the molecular anion of bicyclo-[4.1.0]hepta-2,4,6-triene, is probably unbound with respect to electron detachment. B3LYP/6-31+G(d) calculations find the cycloheptatetraene molecular anion ($\mathbf{4}^{\bullet-}$) to be a stable species with a puckered, asymmetric (C_1) structure and an electron binding energy of 5.4 kcal mol^{-1}. While neutral cycloheptatetraene is lower in energy than phenylcarbene,[13] the radical anion $\mathbf{4}^{\bullet-}$ is calculated to lie 13.4 kcal mol^{-1} higher in energy than phenylcarbene anion $\mathbf{1}^{\bullet-}$ due to the significantly greater electron affinity of phenylcarbene compared to cycloheptatetraene (*vide infra*). The α,*n*-didehydrotoluene radical anions ($\mathbf{5a}^{\bullet-}$–$\mathbf{5c}^{\bullet-}$: $n = 2, 3, 4$) are calculated to be nearly isoenergetic with $\mathbf{1}^{\bullet-}$, all with energies within 1 kcal mol^{-1}. In principle, $\mathbf{5a}^{\bullet-}$–$\mathbf{5c}^{\bullet-}$ could be formed from $\mathbf{1}^{\bullet-}$ by acid-catalyzed rearrangement of a proton from a ring position to the exocyclic carbon, if a suitable Brønsted acid is present in the flow tube.



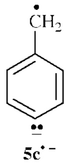
$\mathbf{4}^{\bullet-}$



$\mathbf{5a}^{\bullet-}$



$\mathbf{5b}^{\bullet-}$

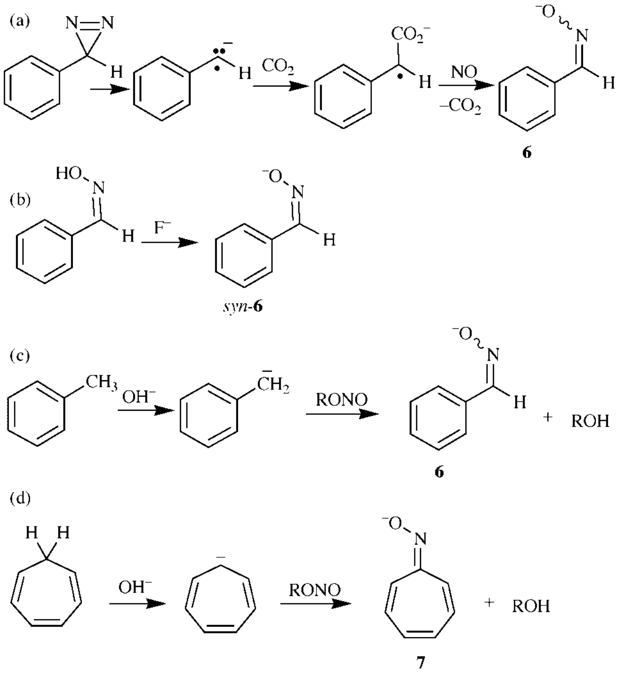


$\mathbf{5c}^{\bullet-}$

The structure of the $C_7H_6^{\bullet-}$ ion generated from phenyldiazirine was confirmed to be phenylcarbene radical anion by chemical derivatization combined with CID. The $C_7H_6^{\bullet-}$ ion itself does not yield any detectable fragments upon low-energy CID (E_{coll}[lab] = 20 or 30 eV). We hypothesized that carbene radical anions, $RCH^{\bullet-}$, should yield oximate ions, $RCHNO^-$, upon addition of nitric oxide, ${}^{\bullet}NO$. These products could serve as useful derivatives for structural characterization since authentic oximate ions are readily generated in the gas phase by independent syntheses. Addition of ${}^{\bullet}NO$ results in fast depletion of $C_7H_6^{\bullet-}$, but the major reaction channel appears to be associative electron detachment [eqn. (1)], as only traces (<3%)

$$C_6H_7^{\bullet-} + {}^{\bullet}NO \longrightarrow C_6H_7NO + e^- \qquad (1)$$

of an adduct ion, $C_7H_6NO^-$, are observed. No product ions incorporating two ${}^{\bullet}NO$ molecules are detected. In contrast, α,3-didehydrotoluene radical anion, $\mathbf{5b}^{\bullet-}$, readily adds two ${}^{\bullet}NO$ molecules.[43] The α,2- and α,4-isomers are expected to react similarly. Therefore, we conclude that the $C_7H_6^{\bullet-}$ ions generated by dissociative electron ionization of phenyldiazirine do not have the didehydrotoluene radical anion structures $\mathbf{5a}^{\bullet-}$–$\mathbf{5c}^{\bullet-}$.



Scheme 1

In order to generate the oximate derivative of $\mathbf{1}^{\bullet-}$, a "neutral-switching" reaction sequence was employed. Addition of CO_2 to $C_7H_6^{\bullet-}$ yields a distonic carboxylate radical anion, $C_6H_7CO_2^{\bullet-}$, and subsequent reaction of this species with ${}^{\bullet}NO$ forms exclusively an anion of the constitution $C_7H_6NO^-$ [Scheme 1(a)]. An analogous group transfer reaction has been observed in the reaction of ${}^{\bullet}NO$ with the acetate radical, ${}^{\bullet}CH_2CO_2^-$.[44] Collision-induced dissociation of $C_7H_6NO^-$ (**6**) at a collision energy of E_{coll}[lab] = 20 eV yields OH^- as the major fragment; at E_{coll}[lab] = 30 eV the ionic fragments are OH^-, CNO^-, $C_6H_5^-$ (formed with nearly equal intensities) and a trace of $C_6H_4CN^-$. These results are presented in Table 1. Authentic *syn*-**6** was generated by deprotonation of *syn*-benzaldehyde oxime using F^- [Scheme 1(b)]. This ion gives mainly OH^- upon CID at E_{coll}[lab] = 20 eV. At E_{coll}[lab] = 30 eV, the fragments are OH^-, CNO^-, $C_6H_5^-$, and a trace of $C_6H_4CN^-$. The relative yield of OH^- from authentic *syn*-**6** is much larger than that

Table 1 Collision-induced dissociation (CID) fragments of $C_7H_6NO^-$ ions[a]

	20 eV (lab)		30 eV (lab)	
$C_7H_6NO^-$	CID products	Rel. intensity	CID products	Rel. intensity
6, from $C_6H_5CH^{\bullet-}$	OH^- (*m/z* 17)	100	OH^- (*m/z* 17)	86
	$C_7H_4N^-$ (*m/z* 102)	11	CNO^- (*m/z* 42)	93
			$C_6H_5^-$ (*m/z* 77)	100
			$C_7H_4N^-$ (*m/z* 102)	<10
syn-**6**, from *syn*-PhCHNOH	OH^- (*m/z* 17)	100	OH^- (*m/z* 17)	100
	$C_6H_5^-$ (*m/z* 77)	6	CNO^- (*m/z* 42)	36
	$C_7H_4N^-$ (*m/z* 102)	13	$C_6H_5^-$ (*m/z* 77)	23
			$C_7H_4N^-$ (*m/z* 102)	7
6, from $PhCH_2^-$ + ^{i}amyl nitrite	OH^- (*m/z* 17)	100	OH^- (*m/z* 17)	100
	CNO^- (*m/z* 42)	3	CNO^- (*m/z* 42)	54
	$C_6H_5^-$ (*m/z* 77)	4	$C_6H_5^-$ (*m/z* 77)	50
	$C_7H_4N^-$ (*m/z* 102)	13	$C_7H_4N^-$ (*m/z* 102)	12
6, from cycloheptatrienide + ^{i}amyl nitrite			OH^- (*m/z* 17)	22
			CN^- (*m/z* 26)	33
			CNO^- (*m/z* 42)	100
			$C_4H_4N^-$ (*m/z* 66)	<20
			$C_6H_5O^-$ (*m/z* 93)	<20
			$C_7H_5N^-$ (*m/z* 103)	<20

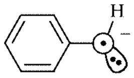
[a] Argon target at pressures of 6–7 × 10^{-5} Torr. See text for discussion of synthesis of $C_7H_6NO^-$ ions.

from **6** generated by the stepwise sequence starting with $\mathbf{1}^{\bullet-}$. It is likely that oximate **6** derived from $\mathbf{1}^{\bullet-}$ is a mixture of *syn* and *anti* isomers. Therefore, a synthetic method that produces a mixture of *syn* and *anti* oximates was sought. DePuy *et al.* reported that many carbanions react with alkyl nitrites (RONO) to form oximate anions.[45] Accordingly, reaction of isoamyl nitrite with benzyl anion affords benzaldehyde oximate **6**, presumably as a mixture of *syn*- and *anti*-isomers [Scheme 1(c)]. CID of this ion at E_{coll}[lab] = 20 eV results in predominantly OH^-; at E_{coll}[lab] = 30 eV the fragments are OH^-, CNO^-, $C_6H_5^-$ and $C_6H_4CN^-$. The relative intensities of CNO^- and $C_6H_5^-$ (54% and 50%) are intermediate between the fragment intensities obtained for the oximate derived from $\mathbf{1}^{\bullet-}$ (CNO: 93% and C_6H_5: 100%) and for the pure *syn*-oximate ion (CNO: 36% and C_6H_5: 23%). This intermediacy indicates that a significant amount of the *anti*-isomer is present in oximate **6** derived from $\mathbf{1}^{\bullet-}$.

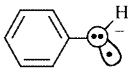
Cycloheptatrienone oximate (**7**) would be the derivative obtained if the $C_7H_6^{\bullet-}$ species is the rearranged isomer, cycloheptatetraene molecular anion ($\mathbf{4}^{\bullet-}$). Authentic cycloheptatrienone oximate was generated by deprotonation of cycloheptatriene with OH^- followed by reaction of the resulting $C_7H_7^-$ ion with isoamyl nitrite [Scheme 1(d)]. The 30 eV (lab) CID spectrum obtained from **7** is qualitatively different from those described above for **6**. The common fragments are OH^-, CN^-, and CNO^-; however, $C_6H_5^-$ is absent from the CID spectrum of **7**. Other fragment ions not observed in the CID spectra of **6** include: $C_4H_4N^-$ (*m/z* 66), $C_6H_5O^-$ (*m/z* 93) and $C_7H_5N^-$ (*m/z* 103). Taken as a whole, the results from CID of the $C_7H_6NO^-$ species formed by the different methods outlined in Scheme 1 provide conclusive evidence that the structure of $C_7H_6^{\bullet-}$ generated from phenyldiazirine is phenylcarbene radical anion $\mathbf{1}^{\bullet-}$.

Electronic structure

The lowest-energy valence electronic configuration for planar phenylcarbene radical anion has seven electrons in the benzylic π system and double-occupancy of the carbene σ orbital ($\pi^7\sigma^2$), giving the $^2A''$ ground state. Thus, $\mathbf{1}^{\bullet-}$ may be thought of as a α-deprotonated benzyl radical; isoelectronic with phenylaminyl radical, $PhNH^{\bullet}$.[46] B3LYP/6-31+G(d) calculations give a CCH angle of 107° about the carbene carbon in $^2A''$ $\mathbf{1}^{\bullet-}$, and an exocyclic CC bond distance of 1.427 Å. For comparison, the corresponding angles and distances in the $^3A''$ state of phenylcarbene (**1**) and the benzyl radical are 135°, 1.396 Å, 121.2°, and 1.409 Å, respectively. Natural population analysis (NPA) with use of the B3LYP/6-31+G(d) wave functions gives a total odd-spin and negative charge at the exocyclic carbon of 0.583 and −0.596, respectively.



$\tilde{\mathbf{X}}$ $^2A''$



$\tilde{\mathbf{a}}$ $^2A'$

The benzylic anion/σ-radical configuration ($\pi^8\sigma^1$) corresponds to the $\tilde{a}^2$ A′ excited state. Attempts to locate this state at the B3LYP/6-31+G(d) level were unsuccessful, as the trial wave functions consistently collapsed to the $^2A''$ configuration during SCF optimization, regardless of the initial geometry. This was not a problem with the "pure" DFT methods such as BPW91 and, of course, with multiconfigurational (CASSCF) calculations in which the electronic state is constrained. BPW91/6-31+G(d) calculations locate the $^2A'$ state 11.1 kcal mol^{-1} higher in energy than the $^2A''$ state, whereas CASSCF(9,8)/6-31+G(d)//CASSCF(9,8)/3-21G calculations give an energy difference of 12.3 kcal mol^{-1}. The CCH angle and exocyclic CC bond distance in $^2A'$ are predicted to be 135.8° (BPW91), 131° (CAS), 1.378 Å (BPW91), and 1.367 Å (CAS), respectively. Natural population analysis with use of the BPW91/6-31+G(d) wave functions for the ã $^2A'$ state gives a total odd-spin and negative charge at the exocyclic carbon of 1.028 and −0.405, respectively.

The $^2A''$ and $^2A'$ states are mixed by rotation of the carbene carbon. Rotation of the CH group in $^2A''$ $\mathbf{1}^{\bullet-}$ to a 90° orientation with respect to the ring raises the energy by 5.8 kcal mol^{-1} (ν = 424i cm^{-1}, B3LYP/6-31+G(d)), and leads to an opening of the CCH angle to 116°. For comparison, the B3LYP/6-31+G(d) rotational barriers in $^3A''$ phenylcarbene, benzyl radical and benzyl anion are 3.4, 12.9, and 25.0 kcal mol^{-1}, respectively. Inversion of the CH group in $^2A''$ through a second-order C_{2v} transition structure with a $\pi^8\sigma^1$ valence electron configuration (the $^2B_2$ state, ν = 768i; 712i cm^{-1}) is computed to have a 15 kcal mol^{-1} barrier, whereas the rotation–inversion barrier for $^3A''$ phenylcarbene through a second-order saddle point (the $^3A_2$ state, ν = 461i; 769i cm^{-1}) is only 4.1 kcal mol^{-1}. The substantially greater barrier for the carbene anion arises from the large energy penalty associated with the electronic promotion that occurs from the sp hybridized a′ orbital in the ground state of the anion to the (pure p) b_1 orbital in the lowest energy C_{2v} transition structure.

Thus, the calculations indicate that addition of an electron to phenylcarbene leads to a "stiffening" of the potentials for motion (rotation and inversion) of the exocyclic CH group with respect to the phenyl ring. Nevertheless, like neutral phenylcarbene, phenylcarbene anion $\mathbf{1}^{\bullet -}$ is still quite fluxional with respect to rotation of the carbene carbon.

Ion–molecule reactions

The reactions of $\mathbf{1}^{\bullet -}$ were examined with a series of small molecules that are frequently employed for structural analysis of organic anions.[47–49] Interpretation of the reactivity of organic ions in the flow reactor can be complicated by the presence of background reagent gases and isobaric product ion impurities. Therefore, many of the reactions described below were also performed with mass-selected $\mathbf{1}^{\bullet -}$ in Q2 of the triple quadrupole analyzer.

Termolecular association yielding a distonic carboxylate radical anion occurs exclusively upon reaction of $\mathbf{1}^{\bullet -}$ with CO_2 (Scheme 1), as is true for most carbanions.[50] Ion $\mathbf{1}^{\bullet -}$ reacts with OCS and CS_2 predominantly by sulfur-atom abstraction, producing thiobenzaldehyde molecular ion [eqn. (2)]. For OCS,

$$\begin{aligned} C_6H_5CH^{\bullet -} + XCS &\longrightarrow [C_6H_5CHS]^{\bullet -} + CX \qquad (2)\\ &\longrightarrow [C_6H_5CHCOS]^{\bullet -}\\ X = O, S & \end{aligned}$$

91% of the product ions result from S-atom abstraction and 9% from addition, while reaction with CS_2 results in S-atom abstraction (98%) and adduct (2%). Preference for S-atom abstraction is usually indicative of a strongly basic carbanion,[51] but it can also indicate reaction at the radical site of a distonic radical anion.[52] The reactivity of OCS towards $\mathbf{1}^{\bullet -}$ differs from that of diphenylcarbene radical anion ($Ph_2C^{\bullet -}$), which gives mainly the adduct (85%).[24] This is consistent with a significantly higher basicity for $\mathbf{1}^{\bullet -}$ (*vide infra*) relative to $Ph_2C^{\bullet -}$ [ΔH_{acid} ($Ph_2CH^{\bullet}$) = 380 ± 2.0 kcal mol^{-1}],[24] and the larger size of $Ph_2C^{\bullet -}$, which facilitates termolecular association.

Ion $\mathbf{1}^{\bullet -}$ reacts with N_2O primarily by N-atom abstraction to give $C_6H_5CHN^-$ (*m*/*z* 104) [eqn. (3a)]. This process has precedent in the reaction of vinylidene radical anion ($CH_2{=}C^{\bullet -}$) with N_2O, which produces CH_2CN^-.[53] Deprotonated phenyldiazomethane ($C_6H_5CN_2^-$, *m*/*z* 117) is also produced as a minor product [eqn. (3b)]. Both reactions are consistent with attack of the carbene carbon on the terminal nitrogen of N_2O.

$$\begin{aligned} C_6H_5CH^{\bullet -} + N_2O &\longrightarrow C_6H_5CHN^- + {}^{\bullet}NO \qquad (3a)\\ &\longrightarrow C_6H_5CN_2^- + HO^{\bullet} \qquad (3b) \end{aligned}$$

Phenylcarbene radical anion reacts with molecular oxygen by multiple pathways [eqn. (4)]. The $\mathbf{1}^{\bullet -}$ signal is depleted entirely. The observed products are $C_6H_5^-$ (phenide, *m*/*z* 77), $C_6H_5O^-$ (phenoxide, *m*/*z* 93), $C_6H_5CO_2^-$ (benzoate, *m*/*z* 121) and $O^{\bullet -}$ (*m*/*z* 16), but the major reaction pathway is associative detachment [eqn. (4a)]. Phenoxide (*m*/*z* 93) appears to be both a primary and a secondary product of this reaction; at higher O_2 flows, the phenide signal decreases in intensity as the phenoxide signal increases.

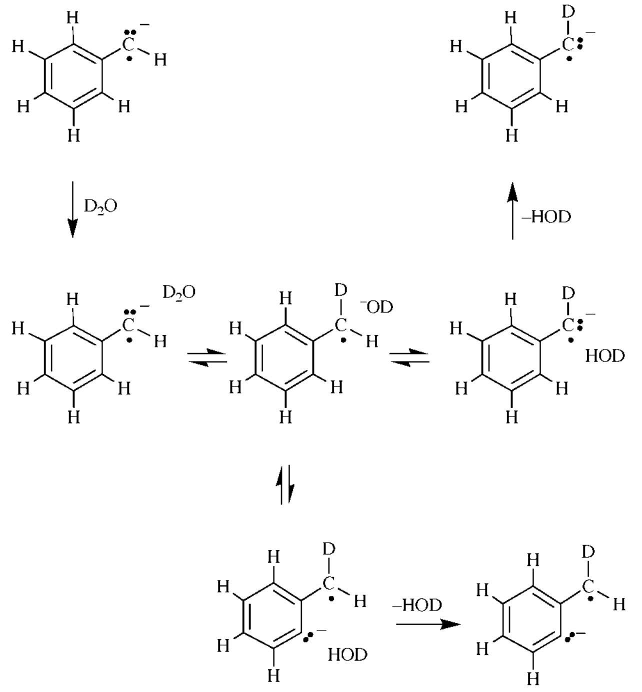
$$\begin{aligned} C_6H_5CH^{\bullet -} + O_2 &\longrightarrow e^- + [C_7H_6O_2] \qquad (4a)\\ &\longrightarrow C_6H_5^- + [HCO_2]^{\bullet} \qquad (4b)\\ &\longrightarrow C_6H_5O^- + [HCO]^{\bullet} \qquad (4c)\\ &\longrightarrow C_6H_5CO_2^- + H^{\bullet} \qquad (4d)\\ &\longrightarrow O^{\bullet -} + C_6H_5CH{=}O \qquad (4e) \end{aligned}$$

These reactions represent different degrees of oxidation of the exocyclic carbon in $C_6H_5CH^{\bullet -}$. All of these pathways except for associative detachment have precedent in the reaction of $Ph_2C^{\bullet -}$ with O_2.[24c] However, a significant amount of O_2 adduct is generated from $Ph_2C^{\bullet -}$, whereas no adduct is observed in the reaction of $C_6H_5CH^{\bullet -}$ with O_2.

Phenylcarbene radical anion reacts with methyl chloride by displacement of Cl^- with a measured rate coefficient of 8.4×10^{-10} cm^3 s^{-1}, corresponding to a reaction efficiency (k_{obs}/k_{coll})[54] of 41%. For comparison, benzyl anion ($C_6H_5CH_2^-$) reacts with CH_3Cl with a rate coefficient of 1.8×10^{-11} cm^3 s^{-1} corresponding to an efficiency of 0.9%. Other experimental[26a] studies have shown that halomethylene radical anions ($CHX^{\bullet -}$) react with methyl halides by nucleophilic substitution more slowly than their closed-shell counterparts (CH_2X^-). The reactivity difference in these cases has been attributed[55] to a greater degree of charge transfer in the reactant complex for [CH_2X^-/CH_3X] relative to [$CHX^{\bullet -}/CH_3X$], which correlates with the electron-binding energies of the reactant ions (the electron affinities of $CH_2X^{\bullet}$ are lower than those of CHX). In contrast, $C_6H_5CH^{\bullet -}$ reacts with CH_3Cl more than forty times faster than does $C_6H_5CH_2^-$, even though its electron-binding energy is greater (27.8 kcal mol^{-1} *versus* 21.0 kcal mol^{-1}, *vide infra*). The difference can be understood in terms of the exceptionally low reactivity of the benzyl anion, which is caused by the delocalization of its frontier π molecular orbital.[56]

Phenylcarbene radical anion exhibits hydrogen-atom abstraction with suitable donors. In general, H-atom abstractions by radical anions in the gas phase are slow processes that do not compete effectively with other reactions such as proton transfer.[57] Thus, in order to observe these reactions the neutral reagent must be chosen such that alternative reaction pathways are slow or non-existent. Ion $\mathbf{1}^{\bullet -}$ readily abstracts a hydrogen atom from $(CH_3)_2NH$, propene and $(CH_3)_2S$, which have C–H bond dissociation enthalpies of 87 ± 2, 88.8 ± 0.4 and 96.6 ± 1.0 kcal mol^{-1}, respectively.[58–60] Molecules with stronger C–H or N–H bonds, such as benzene ($DH[C_6H_5\text{–}H] = 113.5 \pm 0.5$ kcal mol^{-1})[61] and NH_3 ($DH[NH_2\text{–}H] = 108.2 \pm 0.3$ kcal mol), do not exhibit H-atom transfer to $\mathbf{1}^{\bullet -}$. Therefore, the hydrogen atom affinity of $\mathbf{1}^{\bullet -}$, $DH[C_6H_5CH^-\text{–}H]$, is at least 96.6 kcal mol^{-1}. The mechanism for overall H-atom transfer is likely to be a two-step process in which proton transfer from the donor RH to $\mathbf{1}^{\bullet -}$ occurs within the ion–molecule complex followed by electron transfer from the incipient R^- to $C_6H_5CH_2^{\bullet}$.

Phenylcarbene radical anion $\mathbf{1}^{\bullet -}$ undergoes up to two H/D exchanges[49] with ND_3 and D_2O, and it abstracts D^+ from CH_3OD. These results indicate a basicity for $\mathbf{1}^{\bullet -}$ between that of OD^- and CH_3O^-, which is verified in the next section. Reversible deuteron/proton transfer to the exocyclic carbon of $\mathbf{1}^{\bullet -}$ by ND_3 or D_2O leads to exchange of the α-hydrogen *via* a benzyl radical intermediate (Scheme 2). B3LYP/6-31+G(d) calculations indicate that the acidities of the *o*-, *m*-, and *p*-hydrogens of benzyl radical are within 5 kcal mol^{-1} of those of the α-hydrogens. Therefore, exchange of ring hydrogens can also occur within a long-lived ion–molecule complex of $\mathbf{1}^{\bullet -}$ and either D_2O or ND_3. Nevertheless, the occurrence of only two H/D exchanges indicates that the secondary steps are inefficient compared to dissociation of the complex.[62] Given the degree of H/D exchange and the predicted similarities of the energies of $\mathbf{1}^{\bullet -}$, $\mathbf{5a}^{\bullet -}$, $\mathbf{5b}^{\bullet -}$ and $\mathbf{5c}^{\bullet -}$, it is likely that reactions between $\mathbf{1}^{\bullet -}$ and ND_3 or D_2O produce an isomeric mixture of partially-exchanged[63] phenylcarbene and didehydrotoluene radical anions. This is confirmed by the fact that the H/D-exchanged $C_7H_{6-n}D_n^{\bullet -}$ ($n = 1, 2$) ions react by addition of two ${}^{\bullet}NO$ molecules—a characteristic reaction of didehydrotoluene radical anions.[43] Furthermore, when termolecular addition of CO_2 to $\mathbf{1}^{\bullet -}$ is effected, the resulting carboxylate (*m*/*z* 134) undergoes a unique switching reaction with NO_2 to form deprotonated



Scheme 2

α-nitrotoluene (*m*/*z* 136) as the exclusive product. When the H/D-exchanged $C_7H_{6-n}D_n^{\bullet -}$ (n = 1,2) ions react with CO_2, the resulting carboxylates are mass selected and allowed to react with NO_2 in the second quadrupole. The ion population no longer reacts with NO_2 exclusively by switching, but also reacts by addition of NO_2 and subsequent fragmentation which is another reaction characteristic of didehydrotoluene radical anions. Indeed, it is clear that an isomeric mixture of partially-exchanged phenylcarbene and didehydrotoluene radical anions is produced.

Thermochemistry

The gas-phase basicity of $\mathbf{1}^{\bullet -}$ (equivalently, the gas-phase acidity of benzyl radical) was determined by the bracketing technique.[64] Neutral molecules with known gas-phase acidities[60] were allowed to react with $\mathbf{1}^{\bullet -}$, and the occurrence or non-occurrence of proton transfer was monitored. A summary table of the bracketing results for 11 different reference acids spanning a 20 kcal mol⁻¹ range in ΔG_{acid} is provided in the Supplementary Material.† No proton transfer was observed from the weak acids NH_3, benzene, $(CH_3)_2NH$, CH_3SCH_3 and naphthalene. Proton transfer proceeds to a significant extent with the stronger acids furan, pyridine, CH_2FCl and CH_3OH, while slow proton transfer is observed from propene and H_2O. From these results $\Delta G_{acid}(PhCH_2^{\bullet})$ is assigned to be 383.8 ± 2.0 kcal mol⁻¹.

The enthalpy of acid dissociation for benzyl radical, $\Delta H_{acid}(PhCH_2^{\bullet})$, can be obtained from $\Delta G_{acid}(PhCH_2^{\bullet})$ using the relation $\Delta H_{acid} = \Delta G_{acid} + T\Delta S_{acid}$.[64] The entropy term, ΔS_{acid}, is estimated from $\Delta S_{acid} = S(H^+) + \Delta S_{rot}$, where $S(H^+)$ is the standard entropy of a proton (26.0 cal mol⁻¹ K⁻¹),[65] and ΔS_{rot} is the change in rotational entropy upon acid dissociation. The rotational symmetry number for benzyl radical decreases from 2 to 1 upon deprotonation, thereby contributing $R \ln (2/1) = 1.4$ cal mol⁻¹ K⁻¹ to ΔS_{rot}. Accordingly, $\Delta S_{acid}(PhCH_2^{\bullet}) = 27.4$ cal mol⁻¹ K⁻¹, and $T\Delta S_{acid} = 8.2$ kcal mol⁻¹ at 298 K. In this manner, $\Delta H_{acid}(PhCH_2^{\bullet})$ (and the proton affinity of $\mathbf{1}^{\bullet -}$) is determined to be 392.0 ± 2.1 kcal mol⁻¹. At the B3LYP/6-31+G(d) level of theory, $\Delta H_{acid}(PhCH_2^{\bullet})$ is predicted to be 395.9 kcal mol⁻¹ based on the computed enthalpy change for isodesmic reaction [eqn. (5)] and the experimental value for $\Delta H_{acid}(CH_3^{\bullet})$.[60]

Table 2 Fragment ion yield ratios, $r = I[R^-]/I[SO_2^{\bullet -}]$, from collision-induced dissociation of $RSO_2^{\bullet -}$ ions and electron affinities of the reference neutral compounds, R

Compound (R)	EA(R)/eV[a]	*r*
Benzyl radical	0.912 ± 0.006	0.122 ± 0.001
m-Xylylene biradical	0.919 ± 0.008	0.186 ± 0.005
Phenyl radical	1.096 ± 0.006	2.780 ± 0.028
m-Chlorobenzyl radical	1.272 ± 0.008	7.274 ± 0.199
m-Bromobenzyl radical	1.307 ± 0.008	13.004 ± 0.460
Phenylcarbene	*1.207 ± 0.030*	*5.494 ± 0.840*

[a] Reference 70.

$$(^2B_1)PhCH_2^{\bullet} + (^2B_1)CH_2^{\bullet -} \longrightarrow (^2A'')PhCH^{\bullet -} + (^2A_2'')CH_3^{\bullet} \quad (5)$$

The electron binding energy of $\mathbf{1}^{\bullet -}$ (equivalently, the electron affinity of phenylcarbene) was measured with use of the kinetic method[66] in conjunction with the SO_2 procedure described previously.[52,67,68] Ion $\mathbf{1}^{\bullet -}$ reacts in the flow tube with SO_2 by termolecular addition, giving the sulfinate radical ion, $[C_6H_5CHSO_2]^{\bullet -}$, and to a lesser extent by associative electron detachment. Higher yields of $[C_6H_5CHSO_2]^{\bullet -}$ were achieved with use of the CO_2/SO_2 switching approach described by Grabowski[69] and used previously by us[67] in which CO_2 is first added to $\mathbf{1}^{\bullet -}$ forming $[C_6H_5CHCO_2]^{\bullet -}$, followed by reaction with SO_2. This produces $[C_6H_5CHSO_2]^{\bullet -} + CO_2$ and the adduct $[C_6H_5CH(CO_2)(SO_2)]^{\bullet -}$, in comparable amounts. Collision-induced dissociation of $[C_6H_5CHSO_2]^{\bullet -}$ yields $\mathbf{1}^{\bullet -}$, $SO_2^{\bullet -}$ and $SO^{\bullet -}$ as the only ionic products. The apparent CID onsets for formation of these ions are about 3.0, 3.8 and 2.2 eV (CM), respectively. The fragment ion yield ratio, $r = I[\mathbf{1}^{\bullet -}]/I[SO_2^{\bullet -}]$, resulting from CID of $[C_6H_5CHSO_2]^{\bullet -}$ at 6.2 eV (CM) with 0.200 mTorr argon target pressure was measured to be 5.494 ± 0.840, where the uncertainty is determined by the precision of replicate measurements.

In previous studies we have shown that for SO_2 and OCS adducts of carbanions, semilogarithmic relationships can be developed between the CID yield ratios, $I[R^-]/I[SO_2^{\bullet -}]$ and $I[R^-]/I[OCS^{\bullet -}]$, and the known electron affinities of the organic groups R.[52,67,68] Accordingly, a calibration relation for the $I[\mathbf{1}^{\bullet -}]/I[SO_2^{\bullet -}]$ ratio indicated above was constructed by measuring the yield ratios $I[R^-]/I[SO_2^{\bullet -}]$ obtained upon CID of RSO_2^- adducts for which the corresponding values of EA(R) are known. The calibrants comprise even- and odd-electron anions for which precise values of the electron affinities of the corresponding radicals and biradicals have been measured by negative ion photoelectron spectroscopy.[70] These reference species are listed in Table 2, along with their EAs and the measured yield ratios. We have shown previously that the presence of multiple fragmentation pathways is not detrimental to the accuracy of the electron binding energies obtained by the kinetic method, so long as the other pathways do not represent secondary fragmentations of the primary ions used for the ratio measurement.[68] The fragment ion $SO^{\bullet -}$ observed from CID of $[C_6H_5CHSO_2]^{\bullet -}$ can be ignored because its apparent onset is lower than that for $SO_2^{\bullet -}$ formation, *i.e.*, $SO^{\bullet -}$ cannot be a secondary fragmentation product of $SO_2^{\bullet -}$.

A plot of ln *r* ($r = I[R^-]/I[SO_2^{\bullet -}]$) *vs.* EA(R) is presented in Fig. 1. A weighted least squares analysis of the data results in the calibration relation eqn. (6).

$$EA(R) = (1.903 \pm 0.246 \text{ kcal mol}^{-1}) \ln r + (24.587 \pm 0.476 \text{ kcal mol}^{-1}) \quad (6)$$

Inserting the measured CID yield ratio for the SO_2 adduct of $\mathbf{1}^{\bullet -}$ into eqn. (6) gives an electron affinity for phenylcarbene of 27.8 ± 0.7 kcal mol⁻¹ (1.21 ± 0.03 eV), where the uncertainty is derived in the manner previously described.[44]

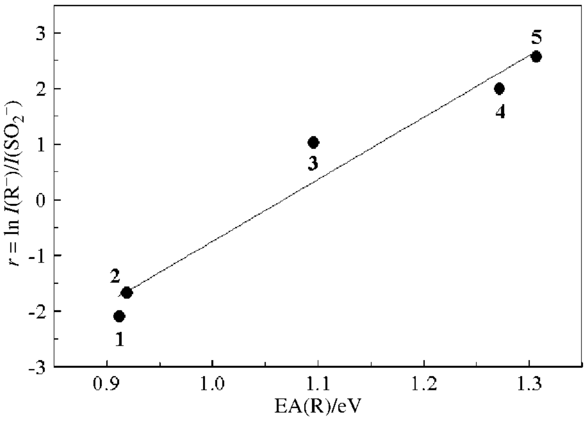


Fig. 1 Calibration plot for the determination of the electron affinity of phenylcarbene by the kinetic method: **1** = benzyl radical, **2** = *m*-xylylene biradical, **3** = phenyl radical, **4** = *m*-chlorobenzyl radical, **5** = *m*-bromobenzyl radical. See Table 2 for specific values of EA(R) and *r*.

Based on the B3LYP/6-31+G(d) energy difference for isodesmic reaction (7) and the experimental value[17] for EA(CH_2) =

$$({}^3A'')C_6H_5CH + ({}^2H_1)CH_2^{\bullet-} \longrightarrow ({}^2A'')C_6H_5CH^{\bullet-} + ({}^3B_1)CH_2 \quad (7)$$

15.1 ± 0.1 kcal mol^{-1}, the electron affinity of phenylcarbene is predicted to be 26.3 kcal mol^{-1}, in good agreement with the experimental result. The nearly two-fold increase in electron affinity in going from CH_2 to PhCH is entirely due to inductive, polarization and hyperconjugative effects of the phenyl group, as opposed to π charge delocalization, because the extra electron in ${}^2A''$ $PhCH^{\bullet-}$ is added to the σ orbital of the neutral carbene.

From the measured proton affinity and electron binding energy of $PhCH^{\bullet-}$, the heat of formation of phenylcarbene, $\Delta H_{f,298}$(PhCH), can be derived with use of eqn. (8).

$$\Delta H_{f,298}(PhCH) = \Delta H_{acid}(PhCH_2^{\bullet}) + \Delta H_{f,298}(PhCH_2^{\bullet}) + EA(PhCH) - \Delta H_{f,298}(H^+) \quad (8)$$

Using the literature quantities $\Delta H_{f,298}(PhCH_2^{\bullet})$ = 49.7 ± 0.6 kcal mol^{-1} [59] and $\Delta H_{f,298}(H^+)$ = 365.7 ± 0.01 kcal mol^{-1},[60] along with our experimental values for $\Delta H_{acid}(PhCH_2^{\bullet})$ = 392.0 ± 2.0 kcal mol^{-1} and EA(PhCH) = 27.8 ± 0.7 kcal mol^{-1}, we obtain a value for the absolute heat of formation of phenylcarbene of $\Delta H_{f,298}$(PhCH) = 103.8 ± 2.2 kcal mol^{-1}. This is in excellent agreement with the value recently determined by energy-resolved CID, $\Delta H_{f,298}$(PhCH) = 102.8 ± 3.5 kcal mol^{-1}.[33] From the new value for $\Delta H_{f,298}$(PhCH) and the heats of formation for benzyl radical and hydrogen, we calculate *DH*(PhCH–H) = 106.2 ± 2.3 kcal mol^{-1}.

Thus, we can conclude from these results that the 9.7 kcal mol^{-1} weaker acidity of $PhCH_2^{\bullet}$ compared to toluene (ΔH_{acid} [$PhCH_3$] = 382.3 ± 0.5 kcal mol^{-1})[59] results from a 16.4 kcal mol^{-1} greater CH bond strength in benzyl radical compared to toluene, *DH*($PhCH_2$–H) = 89.8 ± 0.6 kcal mol^{-1},[59] which is offset by the 6.8 kcal mol^{-1} greater electron affinity of phenylcarbene compared to benzyl radical (EA($PhCH_2$) = 21.0 ± 0.15 kcal mol^{-1}).

Conclusions

Isomerically-pure phenylcarbene anion ($PhCH^{\bullet-}$) has been generated in the gas phase by dissociative electron ionization (EI) of phenyldiazirine. The structure of the ion was identified by authentication of its oximate derivative $PhCHNO^-$. Density functional and CASSCF calculations indicate a ${}^2A''$ ground state for phenylcarbene anion, with a π-radical/σ-anion electronic configuration, whereas the π-anion/σ-radical ${}^2A'$ state is calculated to be 11–12 kcal mol^{-1} higher in energy. The reactivity of $PhCH^{\bullet-}$ is characteristic of a relatively strong base and nucleophile. Atom abstraction and condensation reactions with small molecules were observed that have precedents with other gaseous carbene radical anions. H/D exchange reactions indicate that $PhCH^{\bullet-}$ can undergo acid-catalyzed rearrangement to α,*n*-didehydrotoluene radical anion isomers; calculations indicate that phenylcarbene anion and all three didehydrotoluene radical anions are close in energy. Acid–base bracketing and Cooks' kinetic method were used to determine the proton affinity and electron binding energy of $PhCH^{\bullet-}$ to be 392.0 ± 2.1 kcal mol^{-1} and 27.8 ± 0.7 kcal mol^{-1}, respectively. These quantities were used to derive a value for the heat of formation of phenylcarbene of 103.8 ± 2.2 kcal mol^{-1}, in excellent agreement with the value determined from energy-resolved CID experiments.

The yield of $1^{\bullet-}$ from EI of phenyldiazirine is sufficient for its characterization by negative ion photoelectron spectroscopy. Our estimate for EA(PhCH) is supported by reliable *ab initio* calculations and can aid in the identification of the triplet origin in the photoelectron spectrum. The calculations further suggest that the ã ${}^2A'$ excited state of $PhCH^{\bullet-}$ is too high in energy to be significantly populated at room temperature, and thus will not contribute to the photoelectron spectrum. However, the relatively small singlet–triplet splitting for phenylcarbene and the large difference in geometry about the exocyclic carbon between the anion and the neutral triplet carbene predicted by theory suggest that the spectrum is likely to be quite congested in the region of the singlet origin.

Acknowledgements

This work was supported by a grant and a Post-Doctoral Fellowship (R. A. S.) from the National Science Foundation.

References

1 (*a*) W. Kirmse, *Carbene Chemistry*, Academic Press, New York, 1971; (*b*) M. Jones and R. A. Moss, *Carbenes*, Wiley, New York, 1973; Vols. I and II; (*c*) M. Regitz, ed., *Methoden der Organischen Chemie*, Houben-Weyl, G. Thieme Verlag, Stuttgart, 1989, Vol. E19b.

2 (*a*) S. Fleming, *Tetrahedron*, 1995, **51**, 12479; (*b*) H. Bayley, *Photogenerated Reagents in Biochemistry and Molecular Biology*, Elsevier, Amsterdam, 1983.

3 (*a*) M. Jones, *Acc. Chem. Res.*, 1974, **7**, 415; (*b*) P. P. Gaspar, J.-P. Hsu, S. Chari and M. Jones, *Tetrahedron*, 1985, **41**, 1479.

4 (*a*) C. Wentrup, *Top. Curr. Chem.*, 1976, **62**, 173; (*b*) C. Wentrup, in *Reactive Intermediates*, R.A. Abramovitch, ed., Plenum, New York, 1980, Vol. 1, Chapter 4; (*c*) C. Wentrup, *Reactive Molecules*, Wiley-Interscience, New York, 1984, Chapter 4.

5 (*a*) W. M. Jones, *Acc. Chem. Res.*, 1977, **10**, 353; (*b*) W. M. Jones and U. H. Brinker, in *Pericyclic Reactions*, A. P. Marchand and R. E. Lehr, eds., Academic Press, New York, 1977, Vol. 1, Chapter 3; (*c*) W. M. Jones, in *Rearrangements in Ground and Excited States*, P. de Mayo, ed., Academic Press, New York, 1980, Vol. 1, Chapter 3.

6 M. S. Platz and V. M. Maloney, in *Kinetics and Spectroscopy of Carbenes and Biradicals*, M. S. Platz, ed., Plenum, New York, 1990, Chapter 8.

7 (*a*) H. Tomioka, T. Watanabe, K. Hirai, K. Furukawa, T. Takui and K. Itoh, *J. Am. Chem. Soc.*, 1995, **117**, 6376; (*b*) H. Tomioka, M. Hattori, K. Hirai and S. Murata, *J. Am. Chem. Soc.*, 1996, **118**, 8723.

8 (*a*) A. M. Trozzolo, R. W. Murray and E. Wasserman, *J. Am. Chem. Soc.*, 1962, **84**, 4990; (*b*) E. Wasserman, A. M. Trozzolo, W. A. Yager and R. W. Murray, *J. Chem. Phys.*, 1964, **40**, 2408.

9 J. Higuchi, *J. Chem. Phys.*, 1963, **39**, 1339.

10 R. J. McMahon, C. J. Abelt, O. L. Chapman, J. W. Johnson, C. L. Kreil, J.-P. LeRoux, A. M. Mooring and P. R. West, *J. Am. Chem. Soc.*, 1987, **109**, 2456.

11 K. W. Haider, M. S. Platz, A. Despres and E. Migirdicyan, *Chem. Phys. Lett.*, 1989, **164**, 443.

12 (*a*) R. C. Jones, A. B. Turner and W. M. Jones, *J. Am. Chem. Soc.*, 1969, **91**, 7754; (*b*) C. Wentrup and K. Wilczek, *Helv. Chim. Acta*, 1970, **53**, 1459; (*c*) P. Schissel, M. E. Kent, D. J. McAdoo and E. Hedaya, *J. Am. Chem. Soc.*, 1970, **92**, 2147.

13 (*a*) S. Matzinger, T. Bally, E. V. Patterson and R. J. McMahon, *J. Am. Chem. Soc.*, 1996, **118**, 1535; (*b*) M. W. Wong and C. Wentrup, *J. Org. Chem.*, 1996, **61**, 7022; (*c*) P. R. Schreiner, W. L. Karney, P. v. R. Schleyer, W. T. Borden, T. P. Hamilton and H. F. Schaefer, *J. Org. Chem.*, 1996, **61**, 7030.

14 T. G. Savino, K. Kanakarajan and M. S. Platz, *J. Org. Chem.*, 1986, **51**, 1305.

15 C. J. Cramer, F. J. Dulles and D. E. Falvey, *J. Am. Chem. Soc.*, 1994, **116**, 9787.

16 K. M. Ervin and W. C. Lineberger, in *Advances in Gas Phase Ion Chemistry*, N. G. Adams and L. M. Babcock, eds., JAI Press, Greenwich, CT, 1992, Vol. 1.

17 D. G. Leopold, K. K. Murray, A. E. S. Miller and W. C. Lineberger, *J. Chem. Phys.*, 1985, **83**, 4849.

18 (*a*) K. K. Murray, D. G. Leopold, T. M. Miller and W. C. Lineberger, *J. Chem. Phys.*, 1988, **89**, 5442; (*b*) M. K. Gilles, K. M. Ervin, J. Ho and W. C. Lineberger, *J. Phys. Chem.*, 1992, **96**, 1130.

19 K. M. Ervin and W. C. Lineberger, *J. Chem. Phys.*, 1989, **91**, 5974.

20 (*a*) P. G. Wenthold, R. R. Squires and W. C. Lineberger, *J. Am. Chem. Soc.*, 1998, **120**, 5279; (*b*) D. G. Leopold, A. E. S. Miller and W. C. Lineberger, *J. Am. Chem. Soc.*, 1986, **108**, 1379.

21 P. G. Wenthold, J. Hu, R. R. Squires and W. C. Lineberger, *J. Am. Chem. Soc.*, 1996, **118**, 475.

22 (*a*) K. Merrett, A. B. Young and A. G. Harrison, *Org. Mass Spectrom.*, 1994, **28**, 1124; (*b*) M. Annan and P. Vouros, *J. Am. Soc. Mass Spectrom.*, 1994, **5**, 367.

23 M. Born, S. Ingemann and N. M. M. Nibbering, *Mass Spectrom. Rev.*, 1997, **16**, 181.

24 (*a*) R. McDonald, *Tetrahedron*, 1989, **45**, 3993; (*b*) R. N. McDonald, A. K. Chowdhury and D. W. Setser, *J. Am. Chem. Soc.*, 1980, **102**, 6491; (*c*) R. N. McDonald, A. K. Chowdhury and W. D. McGhee, *J. Am. Chem. Soc.*, 1984, **106**, 4112; (*d*) R. N. McDonald and W. Y. Gung, *J. Am. Chem. Soc.*, 1987, **109**, 7328.

25 (*a*) J. Lee and J. J. Grabowski, *Chem. Rev.*, 1992, **92**, 1611; (*b*) J. J. Grabowski, in *Advances in Gas Phase Ion Chemistry*, N. G. Adams and L. M. Babcock, eds., JAI Press, London, 1992, vol. 1, pp. 43–81; (*c*) Y. Guo and J. J. Grabowski, *Int. J. Mass Spectrom. Ion Processes*, 1990, **97**, 253; (*d*) J. J. Grabowski and S. J. Melly, *Int. J. Mass Spectrom. Ion Processes*, 1987, **81**, 147.

26 (*a*) M. Born, S. Ingemann and N. M. M. Nibbering, *J. Chem. Soc., Perkin Trans. 2*, 1996, 2537; (*b*) M. Born, S. Ingemann and N. M. M. Nibbering, *J. Am. Chem. Soc.*, 1994, **116**, 7210.

27 (*a*) J. Kauw, M. Born, S. Ingemann and N. M. M. Nibbering, *Rapid Commun. Mass Spectrom.*, 1996, **10**, 1400; (*b*) H. E. K. Matimba, A. M. Crabbendam, S. Ingemann and N. M. M. Nibbering, *Int. J. Mass Spectrom. Ion Processes*, 1992, **114**, 85.

28 (*a*) J. H. J. Dawson, A. J. Noest and N. M. M. Nibbering, *Int. J. Mass Spectrom. Ion Phys.*, 1979, **30**, 189; (*b*) M. Born, S. Ingemann and N. M. M. Nibbering, *J. Am. Soc. Mass Spectrom.*, 1995, **6**, 71.

29 C. H. DePuy, S. E. Barlow, J. M. Van Doren, C. R. Roberts and V. M. Bierbaum, *J. Am. Chem. Soc.*, 1987, **109**, 4414.

30 (*a*) R. N. McDonald and A. K. Chowdhury, *J. Am. Chem. Soc.*, 1980, **102**, 5118; (*b*) R. N. McDonald, A. K. Chowdhury and D. W. Setser, *J. Am. Chem. Soc.*, 1981, **103**, 6599; (*c*) R. N. McDonald and A. K. Chowdhury, *J. Phys. Chem.*, 1982, **86**, 3641; (*d*) R. N. McDonald and A. K. Chowdhury, *J. Am. Chem. Soc.*, 1983, **105**, 198.

31 M. J. Travers, D. C. Cowles, E. P. Clifford and G. B. Ellison, *J. Am. Chem. Soc.*, 1992, **114**, 8699.

32 (*a*) P. S. Drzaic and J. I. Brauman, *J. Am. Chem. Soc.*, 1984, **106**, 3443; (*b*) R. N. McDonald and S. J. Davidson, *J. Am. Chem. Soc.*, 1993, **115**, 10857.

33 J. C. Poutsma, J. J. Nash, J. A. Paulino and R. R. Squires, *J. Am. Chem. Soc.*, 1997, **119**, 4686.

34 (*a*) P. J. Marinelli, J. A. Paulino, L. S. Sunderlin, P. G. Wenthold, J. C. Poutsma and R. R. Squires, *Int. J. Mass Spectrom. Ion Processes*, 1994, **130**, 89; (*b*) S. T. Graul and R. R. Squires, *Mass Spectrom. Rev.*, 1988, **7**, 263.

35 P. R. Bevington, *Data Reduction and Error Analysis for the Physical Sciences*, McGraw-Hill, New York, 1969.

36 X. Creary, *Org. Synth.*, 1990, **Coll. Vol. VII**, 438.

37 (*a*) A. D. Becke, *J. Chem. Phys.*, 1988, **88**, 2547; (*b*) C. Lee, W. Yang and R. G. Parr, *Phys. Rev.*, 1988, **B37**, 785.

38 J. Perdew and Y. Wang, *Phys. Rev. B*, 1992, **45**, 13244.

39 F. Weinhold and J. E. Carpenter, *The Structure of Small Molecules and Ions*, Plenum Press, New York, 1988.

40 M. J. Frisch, G. W. Trucks, H. B. Schlegel, P. M. W. Gill, B. G. Johnson, M. A. Robb, J. R. Cheeseman, T. Keith, G. A. Petersson, J. A. Montgomery, K. Raghavachari, M. A. Al-Laham, V. G. Zakrzewski, J. V. Ortiz, J. B. Foresman, J. Cioslowski, B. B. Stefanov, A. Nanayakkara, M. Challacombe, C. Y. Peng, P. Y. Ayala, W. Chen, M. W. Wong, J. L. Andres, E. S. Replogle, B. Gomperts, R. L. Martin, D. J. Fox, J. S. Binkley, D. J. Defrees, J. Baker, J. P. Stewart, M. Head-Gordon, C. Gonzalez and J. A. Pople, GAUSSIAN94, ver. D.2, Gaussian, Inc., Pittsburgh, PA, 1995.

41 In these experiments, a potential of −1.5 to −2.0 kV was applied across the discharge wire, and 50–80 mTorr argon was added to the helium buffer gas. Phenyldiazomethane vapors were admitted to the ion source as close to the discharge as possible.

42 R. A. Seburg, B. T. Hill, R. A. Jesinger and R. R. Squires, *J. Am. Chem. Soc.*, 1999, **121**, 6310.

43 J. Hu and R. R. Squires, *J. Am. Chem. Soc.*, in preparation

44 P. G. Wenthold and R. R. Squires, *J. Am. Chem. Soc.*, 1994, **116**, 11890.

45 (*a*) G. K. King, M. M. Maricq, V. M. Bierbaum and C. H. DePuy, *J. Am. Chem. Soc.*, 1981, **103**, 7133; (*b*) A. J. Noest and N. M. M. Nibbering, *Adv. Mass Spectrom.*, 1980, **8A**, 227.

46 C. R. Kemnitz, W. L. Karney and W. T. Borden, *J. Am. Chem. Soc.*, 1998, **120**, 3499.

47 (*a*) R. J. Schmitt, V. M. Bierbaum and C. H. DePuy, *J. Am. Chem. Soc.*, 1979, **101**, 6443; (*b*) C. H. DePuy and V. M. Bierbaum, *Acc. Chem. Res.*, 1981, **14**, 146; (*c*) A. J. Andrist, C. H. DePuy and R. R. Squires, *J. Am. Chem. Soc.*, 1984, **106**, 845; (*d*) C. H. DePuy, *Org. Mass Spectrom.*, 1985, **20**, 556; (*e*) S. R. Kass, J. Filley, J. Van Doren and C. H. DePuy, *J. Am. Chem. Soc.*, 1986, **108**, 2849; (*f*) N. M. M. Nibbering, *Adv. Phys. Org. Chem.*, 1988, **24**, 1.

48 S. R. Kass, J. Filley, J. M. Van Doren and C. H. DePuy, *J. Am. Chem. Soc.*, 1986, **108**, 2849.

49 (*a*) J. H. Stewart, R. H. Shapiro, C. H. DePuy and V. M. Bierbaum, *J. Am.Chem. Soc.*, 1977, **99**, 7650; (*b*) C. H. DePuy, V. M. Bierbaum, G. K. King and R. H. Shapiro, *J. Am. Chem. Soc.*, 1978, **100**, 2921.

50 V. M. Bierbaum, C. H. DePuy and R. H. Shapiro, *J. Am. Chem. Soc.*, 1977, **99**, 5800.

51 (*a*) C. H. DePuy and V. M. Bierbaum, *Tetrahedron Lett.*, 1981, **22**, 5129; (*b*) C. H. DePuy, V. M. Bierbaum, M. S. Robinson, G. E. Davico and R. Gareyev, *Tetrahedron*, 1997, **53**, 9847.

52 B. T. Hill and R. R. Squires, *J. Chem. Soc.*, *Perkin Trans. 2*, 1998, 1027.

53 J. H. J. Dawson and N. M. M. Nibbering, *J. Am. Chem. Soc.*, 1978, **100**, 1928.

54 T. Su and W. J. Chesnavich, *J. Chem. Phys.*, 1982, **76**, 5183.

55 M. L. McKee, *J. Org. Chem.*, 1997, **62**, 7942.

56 G. G. Gatev, M. Zhong and J. I. Brauman, *J. Phys. Org. Chem.*, 1997, **10**, 531.

57 P. G. Wenthold, J. Hu and R. R. Squires, *J. Mass Spectrom.*, 1998, **179/180**, 173, and references therein.

58 T. J. Burkey, L. Castelhano, D. Griller and F. P. Lossing, *J. Am. Chem. Soc.*, 1983, **105**, 4701.

59 G. B. Ellison, G. E. Davico, V. M. Bierbaum and C. H. DePuy, *Int. J. Mass Spectrom. Ion Processes*, 1996, **156**, 109.

60 W. G. Mallard and P. J. Linstrom, eds., NIST Chemistry WebBook, NIST Standard Reference Database Number 69, March 1998, National Institute of Standards and Technology, Gaithersburg, MD 20899 (http://nist.webbook.gov).

61 G. Davico, V. M. Bierbaum, C. H. DePuy, G. B. Ellison and R. R. Squires, *J. Am. Chem. Soc.*, 1995, **117**, 2590.

62 R. R. Squires, C. H. DePuy and V. M. Bierbaum, *J. Am. Chem. Soc.*, 1981, **103**, 4256.

63 Isomerically pure didehydrotoluene anions also undergo partial H/D exchange with ND_3 and D_2O to give 3 and 2 H/D exchanges, respectively.[43]

64 J. E. Bartmess and R. T. McIver, in *Gas Phase Ion Chemistry*, Vol. 2, M. T. Bowers, ed., Academic Press, New York, NY, 1979, Chapter 11.

65 M. W. Chase, C. A. Davies, J. R. Downey, D. J. Frurip, R. A. McDonald and A. N. Syverud, *J. Chem. Ref. Data*, 1985, **14**, suppl. 1 (JANAF Tables).

66 R. G. Cooks, J. S. Patrick, T. Kotiaho and S. A. McLuckey, *Mass Spectrom. Rev.*, 1994, **13**, 287.

67 (*a*) P. G. Wenthold, J. Hu and R. R. Squires, *J. Am. Chem. Soc.*, 1996, **118**, 11865; (*b*) J. Hu and R. R. Squires, *J. Am. Chem. Soc.*, 1996, **118**, 5816.

68 R. A. Seburg and R. R. Squires, *Int. J. Mass Spectrom. Ion Processes*, 1997, **167/168**, 541.

69 Y. Guo and J. J. Grabowski, *J. Am. Chem. Soc.*, 1991, **113**, 5923.

70 (*a*) Benzyl and phenyl radicals: R. Gunion, M. K. Gilles, M. Polak and W. C. Lineberger, *Int. J. Mass Spectrom. Ion Processes*, 1992, **117**, 601; (*b*) *m*-xylylene biradical: P. G. Wenthold, J. Kim and W. C. Lineberger, *J. Am. Chem. Soc.*, 1997, **119**, 1354; (*c*) halobenzyl radicals: P. G. Wenthold, J. Kim and W. C. Lineberger, unpublished results.

Paper 9/05870B