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GENERATION, THERMOCHEMISTRY, AND CHEMISTRY OF CARBENE ANION RADICALS AND RELATED SPECIES*

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CONTENTS

1. INTRODUCTION

In 1976, it occurred to the author that several types of potentially interesting 'unknown' divalent and monovalent reactive intermediates would be possible by sequentially stripping $R\cdot$, R^+, or R^- from saturated organic molecules (Scheme 1). The tri-, di-, and monovalent members of a vertical series are also related to one another by simple redox steps. For the present concern, we will ignore the carbocations (R_3C^+), carbanions (R_3C^-), free radicals ($R_3C\cdot$), and carbenes (R_2C) as being well established species with reasonably understood and predictable chemistry. Of the five remaining types of reactive intermediates whose thermodynamic properties and chemistry were essentially unknown, four are charged ($R_2C^\pm$ and $RC^\pm$) and one is neutral (RC). Three of the charged species will have doublet ground states, while the carbyne negative ions (RC^-) offer the intriguing prospect of a singlet–triplet multiplicity problem. We named these four charged, carbon-centered species *hypovalent ion radicals* (HIR)[1] with the expectation that various other atom-centered HIR species would also become available and fit into this general classification.

To generate the carbon-centered HIR species, diazo compounds and diazirenes appeared reason-

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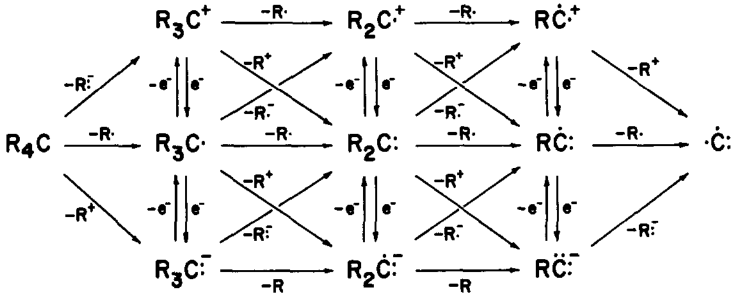
* Dedicated to Arthur G. Anderson on his 70th birthday and retirement from the University of Washington.



Scheme 1.

able as starting materials with the potential loss of N_2 as the source of two vacant valence sites. Therefore, oxidation and reduction of a diazo compound could potentially generate the corresponding carbene cation or anion radical, $R_2C^{\pm}$, *if* the excess energy deposited in the $R_2CN_2^{\pm}$ species exceeded the binding energy of the N_2 molecule. This approach would be especially useful in the gas phase where third body collisional stabilization of the diazoalkane anion or cation radicals depends on the pressure of a bath gas. However, the approach might not operate in the condensed phase where collisional stabilization within the solvent cage is probable. In this latter case, the presence of charge stabilizing structural features in the molecule to allow for loss of N_2 would have to be evaluated.

Jugelt, Pragst and coworkers[2–8] reported that in solution, diazo compounds with a number of structural variations could be oxidized electrochemically to the corresponding diazo cation radicals. The $R_2CN_2^{+\cdot}$ species were reported to have sufficient lifetimes (by cyclic voltammetry and rotating Pt disk electrode) to participate in free radical chain reactions. While suggestions of the presence of another reactive intermediate were made, no unambiguous evidence for their involvement was given. Elofson *et al.*,[9] suggested the formation of $H_2C^{+\cdot}$ in the electrochemical oxidation of $CH_2{=}N_2$ in the presence of pyridine which formed the methylpyridinium ion. These and other early results were reviewed by Fry.[10]

Recently, Parker and Bethell[11] demonstrated that electrochemical oxidation of $Ph_2C{=}N_2$ and the related diazoalkanes derived from dibenzo[*a*,*e*]cycloheptatriene and dibenzo[*a*,*d*]cyclohepta-1,4-diene do yield the corresponding carbene cation radicals by a first-order decomposition of the respective diazoalkane cation radicals (Eqn 1) with $\Delta H^{\dagger} \approx 16$ kcal mol^{-1} and $\Delta S^{\dagger} \approx 0$ e.u. With CH_3OH as solvent, the major products were $Ar_2C(OCH_3)_2$, $Ar_2C{=}O$, and Ar_2CHOCH_3. The related oxidation of 9-diazofluorene ($Fl{=}N_2$) did not give the corresponding carbene cation radical.[12]

$$Ar_2C{=}N_2 - e^- \rightarrow Ar_2CN_2^{+\cdot} \rightarrow Ar_2C^{+\cdot} + N_2 \qquad (1)$$

The report by Webster[13] in 1966 suggesting that the intermediate formed in the electrochemical or mild chemical reduction of diazotetracyanocyclopentadiene was tetracyanocyclopentadienylidene anion radical (Eqn 2) was important in this area of hypovalent anion radicals. However, only a few reactions of the carbene anion radical were reported. This idea received support from the conclusions of Sargent *et al.*,[14,15] that the reductions of *gem*-dihalides also proceeded via carbene anion radicals as intermediates. While these latter conclusions are suspect, we are without the further arguments of Professor Sargent due to his untimely death. Kauffman and Hage[16] reported that reduction of $Ph_2C{=}N_2$ by sodium in ether produced $Ph_2\dot{C}{-}N{=}N^-Na^+$ rather than loss of N_2 to yield $Ph_2C^{-\cdot}$. However, these authors showed that the chemical reduction of PhN_3 gave products consistent with $PhN^{-\cdot}$ being the reactive intermediate.[16]

$$(NC)_4\text{-}c\text{-}C_5{=}N_2 + e^- \rightarrow (NC)_4\text{-}c\text{-}C_5^{-\cdot} + N_2 \qquad (2)$$

Based on this background, we decided to begin our studies of HIR species with the generation of carbene anion radicals and related species. We expected a low probability of molecular rearrangement in the structures of these doublet negative ion species since all bonding MOs are occupied. However, high reactivity was expected for these intermediates where they might react as bases, nucleophiles, and free radicals. The author was fortunate to convince his colleague Dale Hawley to examine the electrochemical reduction of selected diazo compounds. Section 2 will deal with the results obtained from the condensed-phase studies while Section 3 will summarize the gas-phase results.

2. CONDENSED-PHASE RESULTS

The reports that electrochemical reduction of $Ph_2C{=}N_2$[17] and 9-diazofluorene ($Fl{=}N_2$)[18,19] yielded the corresponding carbene anion radicals as the major reactive intermediates were challenged by Bethell, Parker and coworkers[20–25] based on their results of detailed kinetic studies. To solve this controversy, Hawley *et al.*,[26] developed triple-potential-step chronoamperametry (TPSCA) and applied this new electrochemical technique to the reductions of $Ph_2C{=}N_2$ and $Fl{=}N_2$. The results completely supported the proposal of Bethell and Parker that the corresponding diazo anion radicals were the intermediates while the carbene anion radicals did not appear to be involved. This report was followed by a paper by Cheng and Hawley[27] outlining the electrochemical formation and decomposition of $Ph_2CN_2^{-\cdot}$ and $Ph_2CN_2^{2-}$.

Kinetics were used to obtain the first unequivocal evidence for the formation of a carbene anion radical in the condensed phase.[26,28] Electrochemical reduction of $(EtO_2C)_2C{=}N_2$ (**1**) in DMF at 222 K afforded a relatively stable diazoalkane anion radical **2** which decomposed on the time scale of the experiment. The first-order or pseudo-first-order decomposition of **2** ($-d[\mathbf{2}]/dt = k[\mathbf{2}]$) gave the enolate anion $(EtO_2C)_2CH^-$ as the observed product. Further studies established that this decomposition pathway involved the intramolecular loss of N_2 giving the carbene anion radical $(EtO_2C)_2C^{-\cdot}$ (**3**) (Eqn 3).[28] The rate constant in aprotic media (DMF and CH_3CN) for the loss of N_2 from **2** was determined to be $8 \pm 2\ s^{-1}$ at 235 K. In the presence of an excess of electroinactive H^+ donors (benzoic acid, guanidinium perchlorate, or $(CF_3)_2CHOH$), the coulometric *n* value of 2 was determined. Dissociation of electrogenerated **2** in the presence of H^+ donors followed the first-order rate law $-d[\mathbf{2}]/dt = 2k[\mathbf{2}]$, where the rate constant was the same as that in the aprotic media and the product was $(EtO_2)_2CH_2$.

$$\underset{\mathbf{1}}{(EtO_2C)_2C{=}N_2} + e^- \longrightarrow \underset{\mathbf{2}}{(EtO_2C)_2CN_2^{-\cdot}} \xrightarrow[-N_2]{k} \underset{\mathbf{3}}{(EtO_2C)_2C^{-\cdot}} \longrightarrow (EtO_2C)_2CH^- \tag{3}$$

To account for these factors, the authors proposed that the short-lived carbene anion radical **3** reacted in the absence of a H^+ donor by H-atom abstraction from the solvent–electrolyte system (SH) to yield $(EtO_2C)_2CH^-$ (Eqn 4). However, with added H^+ donors, it was concluded that rapid protonation of **3** occurred to yield the additional electroactive species $(EtO_2C)_2CH\cdot$ followed by electron transfer and protonation according to Eqns 5–7. The consumption of a second molecule of **2** and the regeneration of **1** (Eqn 6) accounted for the factor of 2 in the rate equation when **3** was formed in the presence of an acid HA capable of protonating **3**. This was the first study to make use of selective protonation of the $R_2C^{-\cdot}$ in the presence of the $R_2CN_2^{-\cdot}$ precursor.

$$\mathbf{3} + SH \rightarrow (EtO_2C)_2CH^- + \cdot S \tag{4}$$

$$\mathbf{3} + HA \rightarrow (EtO_2C)_2CH\cdot + A^- \tag{5}$$

$$(EtO_2)_2CH\cdot + \mathbf{2} \rightarrow (EtO_2C)_2CH^- + \mathbf{1} \tag{6}$$

$$(EtO_2C)_2CH^- + HA \rightarrow (EtO_2C)_2CH_2 + A^- \tag{7}$$

In a related paper, van Galen and Hawley[29] described the electroreduction of 2-diaza-5,5-dimethyl-1,3-cyclohexanedione (**4**) in $CH_3(CH_2)_2CN$. While added potential H-atom donors (1,4-cyclohexadiene, Ph_2CH_2, and $PhNH_2$) had no effect on the rate constant ($k = 1.0 \pm 0.1$ s^{-1} at 189 K on Pt) for loss of N_2 from the electrogenerated diazo anion radical, addition of $(EtO_2C)_2CH_2$ as a H^+ donor caused the coulometric n value to change from 1 (in the aprotic medium) to 2. The proposed mechanism was analogous to that given above for the reduction of **1** with the loss of N_2 from the diazoalkane anion radical yielding the carbene anion radical being rate limiting. The subsequent reactions of the carbene anion radical derived from **4** were analogous to those given in Eqns 4–6. Activation parameters were determined for the loss of N_2 from $\mathbf{4}^{-\cdot}$ ($E_a = 8.6$ kcal mol^{-1}, $A = 1 \times 10^{10}$ s^{-1}, and $\Delta S^{\dagger} = -12.9$ cal mol^{-1} K^{-1}) and $(EtO_2C)_2CN_2^{-\cdot}$ ($E_a = 9.8$ kcal mol^{-1}, $A = 2 \times 10^{10}$ s^{-1}, and $\Delta S^{\dagger} = -12$ cal mol^{-1} K^{-1}) in $CH_3(CH_2)_2CN$.

Bethell and Parker reported their independent studies on the electroreduction of **1**[30] and $Ph(PhCO)C{=}N_2$ (**5**)[30,31] in aprotic solvents. The rate constants for loss of N_2 from the diazo anion radicals **2** and $Ph(PhCO)CN_2^{-\cdot}$ (**6**) forming the corresponding carbene anion radicals **3** and $Ph(PhCO)C^{-\cdot}$ (**7**) were 407 and 125 s^{-1}, respectively, in DMF at 273.2 K with an increase in these rate constants measured in CH_3CN as the solvent. The activation parameters in DMF for loss of N_2 from **2** ($\Delta H^{\dagger} = 10.6$ kcal mol^{-1}, $\Delta S^{\dagger} = -7.4$ cal mol^{-1} K^{-1}) and **6** ($\Delta H^{\dagger} = 11.5$ kcal mol^{-1}, $\Delta S^{\dagger} = -6.4$ cal mol^{-1} K^{-1}) were determined; those for **2** are in reasonable agreement with those reported by van Galen and Hawley.[29] Protonation of $Ph(PhCO)C^{-\cdot}$ was reported not to afford an electroactive radical. This is unusual since protonation of the carbene anion radicals derived from the diazo compounds **1** and **4** showed an increase in the coulometric n value from 1 to 2 in the presence of H^+ donors.[28,29]

In their study of the reduction of diazo compound **5**, Bethell and Parker[30] noted a pronounced increase in the rate constant for loss of N_2 from **6** in CH_3CN by added water (1700 s^{-1} at 273.2 K). The authors suggested that this increase in the rate constant was due to formation of a hydrogen bonded complex **6**··HOH; it is interesting that in the reduction of diazo compound **4**, the presence of added CH_3OH had no effect on the rate constant for loss of N_2 from $4^{-\cdot}$.[29] With added PhOH, the rate of disappearance of **6** was reported to be dramatically increased (no data given) "accompanied by a sharp increase in the chronoamperometric current consistent with direct proton transfer to **6** and an overall two-electron process".

Bethell and Parker[32] observed that $Ph_4\text{-}c\text{-}C_5H_4^{-\cdot}$ was generated by reduction of the corresponding diazoalkane. These authors suggested in this paper that the formation of a carbene anion radical from the corresponding diazoalkane anion radical was related to the pK_a of the carbon acid, e.g. tetraphenylcyclopentadiene. This approach means that the major stabilization of the carbene anion radical by delocalization is the doubly occupied nonbonded MO at the hypovalent center.

Thus, the conclusions from the groups of Hawley and of Bethell and Parker are converging as the reductions of more diazoalkanes are examined. The observation of rate acceleration by water in the loss of N_2 from **6** places an even more severe requirement on the purity of the solvent/electrolyte systems and on the diazo compounds used in these studies. At a minimum, reaction conditions must be sought to reduce the rates of the reactions of the diazo anion radicals with their environment other than N_2 loss. If such are found, "a much wider range of carbene anion radical structures will be accessible than thought hitherto."[30] However, it will be difficult to selectively determine specific chemical reactions of these hypovalent reactive intermediates in the condensed phase, e.g. attempts to capture **3** with added electroinactive carbonyl containing molecules have not proven successful.[33]

3. GAS-PHASE STUDIES

Because of the expected high reactivity for these HIR species and the literature given in the Introduction, it appeared that it would be difficult to ascertain exactly what was occurring and which intermediates were involved from studies in the condensed phase. The gas phase should offer the best environment for generating and determining the chemistry and thermochemistry of carbene anion radicals and related hypovalent species. Of the three major gas-phase methods used for determining the reactions of ions with neutral molecules (high pressure mass spectrometry,[34] ion cyclotron resonance spectrometry (ICR),[35,36] and the flowing afterglow (FA) apparatus[37,38]), most of the studies with carbene anion radicals have been done in FAs.

3.1. *Operation of the flowing afterglow apparatus*

A diagram of the Kansas State University FA is shown in Fig. 1. Since the FA has been previously described,[39,40] a brief outline of the experiments will suffice here. We first establish and maintain a constant fast flow of helium as the buffer gas by introducing helium via the two inlets in the upstream end of the 1.5 m long flow tube and exhaust it with a Roots blower-mechanical pumping system; our usual operating conditions are $P_{He} = 0.5$ torr and $\bar{v} = 80$ m s^{-1} at 298 K. The electron gun is turned on and the neutral precursor to the carbene or nitrene anion radical can then be added via inlet 1. The method of adding these precursors at inlet 1 varied from introduction of a dilute (with helium) gas mixture from a 5-L bulb (c-$C_5H_4{=}N_2$, $(CF_3)_2C{=}N_2$, PhN_3), to an inverted L-shaped finger containing the pure neutral precursor ($EtO_2CCH{=}N_2$, $PhCH{=}N_2$, $Ph_2C{=}N_2$, $Fl{=}N_2$, PhN_3), to a flow-through reservoir where the vapors of the solid or liquid, pure neutral precursor were swept into the flow tube with a constant, but adjustable, small flow of helium ($Ph_2C{=}N_2$ and $Fl{=}N_2$).

With PhN_3 and most diazo compounds, attachment of thermal energy electrons occurs dissociatively ($-N_2$) giving the corresponding nitrene ($PhN^{-\cdot}$) or carbene anion radical ($R_2C^{-\cdot}$).[41] To check that all electrons [free and from Penning ionization by He(2^3S) atoms[42]] were consumed early in the upstream end of the flow tube (this is essential for kinetic measurements), SF_6 was added via inlet 4. If electrons are present, the ion signal at m/z 146 ($SF_6^{-\cdot}$) is observed. If this occurs, the flow of the precursor is increased until the $SF_6^{-\cdot}$ signal is no longer observed.

The initially formed excited $PhN^{-\cdot}$ and $R_2C^{-\cdot}$ species were cooled to their vibrational ground states by numerous collisions with the helium buffer gas in the 70 cm distance between inlet 1 and the ion/molecule neutral inlet located about half-way down the flow tube. Addition of the neutral substrate via this inlet initiates the desired ion/molecule reaction in the final 65 cm of the flow tube.

The fast helium flow is sampled through orifices in two nose cones into a differentially pumped compartment ($\approx 10^{-7}$ torr) containing the quadrupole mass filter and electron multiplier which

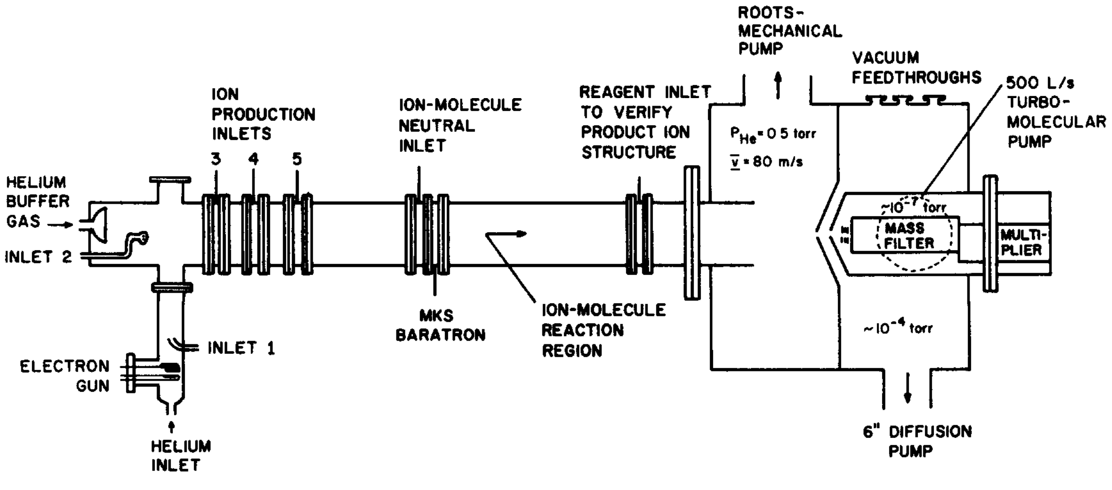


Fig. 1. Schematic diagram of the KSU flowing afterglow apparatus with a modular flow tube. Reprinted with permission from McDonald, R. N.; Chowdhury, A. K. *J. Am. Chem. Soc.* **107**, 4123 (1985). Copyright 1985 American Chemical Society.

continuously monitor the ion composition of flow. Although the neutral products from the ion/molecule reactions are not directly observed, their structures are assumed based on thermochemistry and mass balance.

Kinetics of the bimolecular ion/molecule reactions are determined under pseudo-first-order conditions where the concentration of the added neutral substrates [N] ($>10^{11}$ molecules cm^{-3}) is in large excess over that of the ion concentration ($<10^{8}$ ions cm^{-3}). The 65 cm reaction distance, which is directly related to the reaction time, is held constant, but [N] is varied. At each new [N] added to the flow, averages of 8–10 negative ion spectra are obtained (to improve signal-to-noise) and computer integration yields the ion signal intensities for the starting and product ions. From a series of such measurements at different [N], a plot of log (ion signal intensities) vs increasing [N] is generated and the slope of the linear decay of the starting ion is transformed into the bimolecular ion/molecule reaction rate constant by equations already given.[39] In the FA, rate constants can be measured for reactions that occur on every collision ($\approx 10^{-9}$ cm^{3} molecule^{-1} s^{-1}) with the lower limit being reactions that occur in one out of every 10^{4} collisions. The formation of the negative ion products was also monitored in these experiments.

3.2. *Generation of carbene anion radicals and* $PhN^{-\cdot}$

The structural variations of the carbene anion radicals which have been generated to date in the gas phase range from the parent $H_2C^{-\cdot}$[43,44] and the unsaturated $H_2C{=}C^{-\cdot}$[45–47] to the structurally more complex $Ph_2C^{-\cdot}$[48] and $Fl^{-\cdot}$ (where Fl = 9-fluorenylidene).[49] The methods used to generate these species are shown in Eqns 8–11.

$$CH_4 + e^- \longrightarrow C^-,\ CH_2^-,\ C_2^-,\ \text{and}\ C_2H^- \xrightarrow{\text{SIFT}} CH_2^{-\cdot} \qquad (8)$$

$$C_2H_4 + O^{-\cdot} \longrightarrow H_2C{=}C^{-\cdot} + H_2O \qquad (9)$$

$$R_2C{=}N_2 + e^- \longrightarrow R_2C^{-\cdot} + N_2 \qquad (10)$$

$$(R_2C = CF_3(H)C^{50},\ (CF_3)_2C^{51},\ c\text{-}C_5H_4^{39},\ Ph_2C^{48},\ Fl^{49})$$

$$PhN_3 + e^- \longrightarrow PhN^{-\cdot} + N_2 \qquad (11)$$

DePuy *et al.*,[44] generated the mixture of C_1 and C_2 negative ions shown in Eqn 8 by electron impact on CH_4. When this mixture was separated by a quadrupole mass filter tuned to *m/z* 14, only the $CH_2^{-\cdot}$ ions emerge which were injected into a second, downstream FA (Selected Ion Flow Tube) for further study.

The interesting H_2^+ transfer reaction between C_2H_4 and $O^{-\cdot}$ was first observed by Lindinger *et al.*,[45] with characterization of the product as $H_2C{=}C^{-\cdot}$ by Dawson and Nibbering.[46,52] Reaction 9 occurs because of the large H-atom affinity of $O^{-\cdot}$ (110.8 kcal mol^{-1})[53] and proton affinity of HO^- (390.8 ± 0.4 kcal mol^{-1}).[54]

The dissociative attachment of thermal or near-thermal energy electrons by diazo compounds is illustrated with the five examples in Eqn 10. This process appeared to be general until we observed that $PhCH{=}N_2$ and $EtO_2CCH{=}N_2$ formed their parent diazo anion radicals on electron attachment; these examples will be discussed in Section 3.5. Since the diazo and azido structures are isoelectronic, we hoped that organic azides would also dissociatively attach thermal energy electrons to produce the corresponding nitrene anion radicals. This proved to be correct with PhN_3[55] as shown in Eqn 11, but failed with *tert*-BuOC(=O)N_3 which exclusively formed N_3^-.[49]

3.3. *Proton affinities and heats of formation of carbene anion radicals and* $PhN^{-\cdot}$

In the studies of these hypovalent species, it was considered important to first establish their proton affinities (PA). If the ΔH_f° of the product free radical was known or could be calculated, the ΔH_f° of the HIR species could be calculated with the relationship in Eqn 12 illustrated with the cyclopentadienylidene anion radical ($c\text{-}C_5H_4^{-\cdot}$). In these calculations, we use $\Delta H_f^\circ(H^+) = 367.2$ kcal mol^{-1} based on the stationary electron convention. With ΔH_f°(HIR), the ΔH_{rx} for the reactions of the HIR species with neutral molecules can be calculated.

$$c\text{-}C_5H_4^{-\cdot} + H^+ \rightarrow c\text{-}C_5H_5\cdot$$

$$\Delta H_f^\circ(c\text{-}C_5H_4^{-\cdot}) = \Delta H_f^\circ(c\text{-}C_5H_5\cdot) - \Delta H_f^\circ(H^+) + \mathrm{PA}(c\text{-}C_5H_4^{-\cdot}) \qquad (12)$$

In FA experiments, PAs of negative ions are usually measured by the bracketing method. In this method, the ion/molecule reactions of the negative ion with several neutral, potential H^+ donor substrates, HA, of known gas-phase acidity[54] are examined. In those reactions where H^+ transfer is not observed ($k_{\mathrm{total}} < 10^{-13}$ cm^3 molecule^{-1} s^{-1}), H^+ transfer is assumed to be endothermic. It is important that if reactions other than H^+ transfer occur with the HA neutral that they do not obscure the possibility of a slower, competitive H^+ transfer channel. The PA bracketing data for $c\text{-}C_5H_4^{-\cdot}$ are given in Table 1. From these data, PA($c\text{-}C_5H_4^{-\cdot}$) = 377±2 kcal mol^{-1} which is only slightly less basic than CH_3O^-, but considerably more basic than the carbanion $c\text{-}C_5H_5^-$. Using $\Delta H_f^\circ(c\text{-}C_5H_5\cdot) = 60.9 \pm 1.2$ kcal mol^{-1}[56] and $\Delta H_f^\circ(H^+) = 367.2$ kcal mol^{-1},[53] ΔH_f° ($c\text{-}C_5H_4^{-\cdot}$) = 70.7 kcal mol^{-1} was calculated. The PAs and ΔH_f°s of the carbene anion radicals and $PhN^{-\cdot}$, and the PAs of the corresponding carbanions and $PhNH^-$ are given in Table 2.

The data in Table 2 are interesting in that they allow us to see the effects of substituents on the intrinsic basicity, PA, of the carbene anion radical relative to those same substituent effects on the PA of the corresponding carbanion. $H_2C^{-\cdot}$ is a weaker Bronsted base than is H_3C^- by 9 kcal mol^{-1}. Replacement of a hydrogen in $H_2C^{-\cdot}$ by CN or CF_3 groups, or both hydrogens by CF_3 groups yield carbene anion radicals with the same PAs, within the error limits, as those of the corresponding carbanions. Therefore, the base weakening effects of these groups are *about 25% smaller* in the carbene anion radicals than in the related carbanions. Incorporation of the hypovalent center into a cyclopentadiene ring ($c\text{-}C_5H_4^{-\cdot}$ and $Fl^{-\cdot}$) *increases* the base strength of the carbene anion radical by about 20 kcal mol^{-1} over that of the carbanions $c\text{-}C_5H_5^-$ and FlH^-, respectively. A similar effect is seen in comparing the PAs of $Ph_2C^{-\cdot}$ and Ph_2CH^- where the carbene anion radical is the *stronger* base by 15 kcal mol^{-1}.

The three factors involved in these substituent effects are the differences in (a) the R—C$^-$—R bond angles in the carbene anion radical and the carbanion, (b) the bond strengths of the new C—H bonds generated by protonation of $R_2C^{-\cdot}$ vs R_2CH^-, and (c) the electron affinities (EA) of the ground state (triplet or singlet) carbene R_2C and the radical $R_2HC\cdot$. The H—C—H bond angle in $H_2C^{-\cdot}$ was calculated to be 102±3°[62] while the H—C—H bond angle in planar CH_3^- is 120°. Assuming that the hypovalent center retains this geometry in $Ph_2C^{-\cdot}$, the phenyl rings would be forced to rotate much further from planarity than exists in Ph_2CH^- thus decreasing their ability to delocalize the electron pair in $Ph_2C^{-\cdot}$; this is a base strengthening effect in the HIR anion. Molecular distortion from this small bond angle at C_1 in $c\text{-}C_5H_4^{-\cdot}$ and $Fl^{-\cdot}$ would be expected to occur, but would undoubtedly increase the energy of the HIR species leading to an increase in their basicities.

Table 1. Data for bracketing Pa($c\text{-}C_5H_4^-$).[a]

Ion+ROH		Was RO$^-$ observed?	$\Delta H_{\mathrm{acid}}^\circ$(ROH), kcal mol^{-1}[b]
$c\text{-}C_5H_4^{-\cdot} + CH_3OH$	→	No	379.2±2
$c\text{-}C_5H_4^- + C_2H_5OH$	→	Yes	376.1±2
$c\text{-}C_5H_4^- + n\text{-}C_3H_7OH$	→	Yes	374.7±2
$c\text{-}C_5H_4^- + tert\text{-}C_4H_9OH$	→	Yes	373.3±2

[a] Reference 39.
[b] Reference 54.

Table 2. PAs and ΔH_f°s of hypovalent anion radicals, and PAs of the corresponding carbanions and $PhNH^-$

Hypovalent species	PA(HIR), kcal mol^{-1}	ΔH_f°(HIR), kcal mol^{-1}	PA(R_2CH^-),[m] kcal mol^{-1}
H_2C^{-} [a]	407.4±0.9	77.8±0.6	416.6±1
$NCCH^{-\cdot}$ [b]	374±3	66.8±4	372.2±2
$CF_3CH^{-\cdot}$ [c]	377.2±2	−113.6±2	375±3[n]
$(CF_3)_2C^{-\cdot}$ [d]	365.0±2	−282.2±4	364.0±2[d]
$H_2C{=}C^{-}$ [e]	382.9[f]	89[g]	408±3[o]
c-$C_5H_4^{-\cdot}$ [h]	377.0±2	70.7±3.2	356.1±2
Ph_2C^{-} [i]	380.0±2	81.8±2	364.5±4
Fl^{-} [j]	≈370	[l]	353.3±2
PhN^{-} [k]	372.0	60.0±2	367.1±2[p]

[a] Reference 43.
[b] Reference 47.
[c] Reference 50.
[d] Reference 51.
[e] Reference 57.
[f] Calculated at the MP2/4-31+G level.
[g] Calculated using $\Delta H_f^\circ(H_2C{=}CH\cdot) = 71.5$ kcal mol^{-1}.[58] This $\Delta H_f^\circ(H_2C{=}C^{-\cdot})$ is in excellent agreement with that calculated from the estimated $\Delta H_f^\circ(H_2C{=}C{:}) = 98$ kcal mol^{-1} [57] and the measured $EA(H_2C{=}C{:}) = 10.8 \pm 4.6$ kcal mol^{-1}.[59]
[h] Reference 39.
[i] Reference 48.
[j] Reference 49.
[k] Reference 55.
[l] $\Delta H_f^\circ(FlH_2)$ is unknown.
[m] Reference 54.
[n] Reference 60.
[o] Reference 61.
[p] PA($PhNH^-$).

Factors (b) and (c) are derived from the thermochemical cycle for describing the gas-phase acidities of HA molecules [$\Delta H^\circ_{acid}(HA) = PA(A^-)$].[54]

$$HA \rightarrow A\cdot + \cdot H \quad \Delta H^\circ_{298} = D^\circ(H{-}A)$$

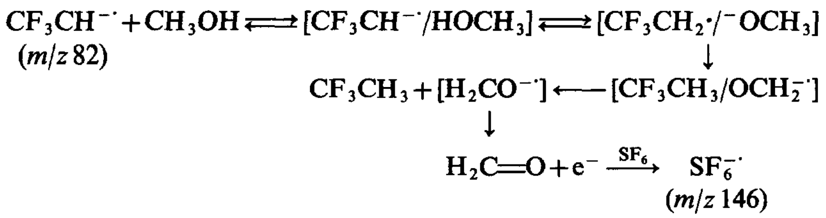
$$\underline{A\cdot + \cdot H \rightarrow A^- + H^+} \quad \Delta H^\circ_{298} \approx \Delta H^\circ_0 = IP(H) - EA(A)$$

$$HA \rightarrow A^- + H^+ \quad \Delta H^\circ_{298} = \Delta H^\circ_{acid}$$

$$\Delta H^\circ_{acid}(HA) = PA(A^-) \approx D^\circ(H{-}A) + IP(H) - EA(A)$$

The importance of the strengths of the new CH bonds produced when $R_2C^{-\cdot}$ and R_2CH^- is shown in the c-$C_5H_4^{-\cdot}$/c-$C_5H_5^-$ pair where $D^\circ(c\text{-}C_5H_4^{\cdot}{-}H) > 100$ kcal mol^{-1} [63] is expected for a C(sp^2)—H bond while $D^\circ(c\text{-}C_5H_5{-}H) = 81.2 \pm 1.2$ kcal mol^{-1} [56] which yields PA(c-$C_5H_4^{-\cdot}$) > PA(c-$C_5H_5^-$). A similar argument probably applies to the $Fl^{-\cdot}$/FlH^- pair.

The larger PA of H_3C^- compared to that of $H_2C^{-\cdot}$ is due to the significant difference in the electron affinities of the neutrals ($EA(CH_3) - EA(CH_2) \approx -13$ kcal mol^{-1}) while the product D°(C—H)s are in the opposite direction ($D^\circ(H_3C{-}H) - D^\circ(H_2C^{\cdot}{-}H) \approx -4$ kcal mol^{-1});[43] $\Delta PA = (PA(H_3C^-) - PA(H_2C^{-\cdot})) = \Delta D^\circ - \Delta EA = 9$ kcal mol^{-1}. The necessary thermodynamic data have been reported for the $PhN^{-\cdot}$/$PhNH^-$ pair. The PA($PhN^{-\cdot}$) > PA($PhNH^-$) relationship is due primarily to the lower EA of the hypovalent negative ion (EA(PhN) = 33.7±0.3 kcal mol^{-1} and EA(PhNH) = 39.3±0.7 kcal mol^{-1} [64]) with similar NH bond dissociation energies



Scheme 2

($D°(PhN^{\cdot}{-}H) = 92.1 \pm 2.3$ kcal mol^{-1} and $D°(PhNH{-}H) = 92.8 \pm 2.6$ kcal mol^{-1} [64]) in the products of protonation. Unfortunately, the EAs of the other carbenes have not been determined. The above data and analysis indicate that the suggestion by Bethell and Parker[32] for the condensed-phase decomposition of diazoalkane anion radicals to carbene anion radicals being related to the pK_a of the corresponding carbon acid is qualitative at best.

The reactions of $CF_3CH^{-\cdot}$, $(CF_3)_2C^{-\cdot}$, and $Ph_2C^{-\cdot}$ with alcohols containing $C_\alpha H$ bonds produced rapid decays of the ion signal of the hypovalent negative ion, but considerably less product RO^- ions than predicted from mass balance. This problem was most obvious in the reaction of $CF_3CH^{-\cdot}$ with CH_3OH where the fast decay of $CF_3CH^{-\cdot}$ had a bimolecular rate constant of 5×10^{-10} cm^3 molecule^{-1} s^{-1}, *but no product ions were observed.* The problem of the missing product ions was solved when we added a mixture of CH_3OH and SF_6. Although SF_6 did not react with $CF_3CH^{-\cdot}$, the introduction of a mixture of CH_3OH and SF_6 to the helium flow containing $CF_3CH^{-\cdot}$ produced $SF_6^{-\cdot}$ at m/z 146 and the magnitude of this ion signal was dependent upon the amount of CH_3OH added. The reaction sequence that we believe is involved is shown in Scheme 2. The overall process is H_2^{+} transfer from the alcohol molecule to the carbene anion radical. The detachment of the electron from $H_2CO^{-\cdot}$ is expected since $H_2C{=}O$ has a negative EA (-0.86 eV).[65]

Other evidence in support of this scheme is the observation of a small amount of the ketyl anion radical $(CF_3)_2CO^{-\cdot}$ (m/z 166) from the reaction of $CF_3CH^{-\cdot}$ with $(CF_3)_2CHOH$[50] (Eqn 13) where H^+ transfer is 28.8 kcal mol^{-1} exothermic. While the EA of $(CF_3)_2C{=}O$ has not been reported, the ketone readily attaches a thermal energy electron to yield the ketyl anion radical, and $(CF_3)_2CO^{-\cdot}$ was a minor product of electron transfer in the reaction of $PhN^{-\cdot}$ (EA = 1.46 ± 0.02 eV)[64,66] with the ketone.[67]

$$\underset{(m/z\ 82)}{CF_3CH^{-\cdot}} + (CF_3)_2CHOH \xrightarrow{0.94} \underset{(m/z\ 167)}{(CF_3)_2CHO^-} + CF_3CH_2\cdot \tag{13a}$$

$$\xrightarrow{0.06} \underset{(m/z\ 166)}{(CF_3)_2CO^{-\cdot}} + CF_3CH_3 \tag{13b}$$

In a related reaction between $(CF_3)_2C^{-\cdot}$ with CH_3SH, the minor product ion at m/z 46 was believed to be $H_2CS^{-\cdot}$ [68] formed by H_2^{+} transfer (Eqn 14c);[51] the ^{34}S isotope was clearly seen in the product ions of Eqns 14b and 14c. Observation of the products of H^+ and of H-atom transfer in reaction 14 suggested that both of these product ions could arise from the same complex $[(CF_3)_2CH\cdot/^-SCH_3]$ where $EA((CF_3)_2CH\cdot) \approx (EA(CH_3S\cdot) = 1.88$ eV).[69] In the related reaction of $CF_3CH^{-\cdot}$ with CH_3SH, the ion at m/z 46 was 20% of the product ions (Eqn 15).[50]

$$\underset{(m/z\ 150)}{(CF_3)_2C^{-\cdot}} + CH_3SH \xrightarrow{0.83} \underset{(m/z\ 151)}{(CF_3)_2CH^-} + CH_3S\cdot \tag{14a}$$

$$\xrightarrow{0.11} \underset{(m/z\,47)}{CH_3S^-} + (CF_3)_2CH^{\bullet} \tag{14b}$$

$$\xrightarrow{0.06} \underset{(m/z\,46)}{H_2CS^{-\bullet}} + (CF_3)_2CH_2 \tag{14c}$$

$$\underset{(m/z\,182)}{CF_3CH^{-\bullet}} + CH_3SH \xrightarrow{0.80} \underset{(m/z\,47)}{CH_3S^-} + CF_3CH_2^{\bullet} \tag{15a}$$

$$\xrightarrow{0.20} \underset{(m/z\,46)}{H_2CS^{-\bullet}} + CF_3CH_3 \tag{15b}$$

The above evidence leads us to favor proton transfer preceding H-atom transfer shown in Scheme 2 in these $H_2^{+\bullet}$ transfer reactions. The sequence of these steps requires that the complex formed by exothermic H^+ transfer be sufficiently long lived to allow for some H-atom transfer prior to separation to the reaction product ion and neutral. For those reactions where H^+ transfer would be endothermic, this endothermic step can occur within the collision complex $[R_2C^{-\bullet}/HOR']$. This is possible because such collision complexes are formed with 10–20 kcal mol^{-1} of excess energy due to the ion-dipole and ion-induced dipole forces with even larger excess energies possible due to hydrogen bonding. However, the components of the H^+ transfer complex $[R_2CH^{\bullet}/^{-}OR']$ cannot separate since that would be an overall endothermic reaction. Therefore, the only forward reaction available for this latter complex is H-atom transfer if this leads to an overall exothermic reaction. This latter case is demonstrated in the $H_2^{+\bullet}$ transfer reaction between $CF_3CH^{-\bullet}$ with CH_3OH in Scheme 2.

3.4. *Nucleophilicity of carbene anion radicals and* $PhN^{-\bullet}$

The investigations of the nucleophilic reactivity of carbene anion radicals and $PhN^{-\bullet}$ are divided into two catagories, (a) S_N2 reactions with methyl derivatives and (b) additions to carbonyl group containing molecules.

3.4.1. S_N2 *Reactions.* Brauman[70] and Bohme[71] and their coworkers established a kinetic nucleophilicity order for gas-phase negative ions in their reactions with methyl halides and certain other derivatives. These and other results led Brauman and his group[72,73] to model these S_N2 reactions with a double-minimum on the potential energy surface. The first and second minima were the collision complex $[Nuc^-/CH_3X]$ and the complex of methyl group exchange $[Nuc{—}CH_3/X^-]$, respectively, which were separated by the standard transition state $[Nuc^{\delta-}\cdot\cdot CH_3\cdot\cdot X^{\delta-}]$. Theoretical calculations have supported this double-minimum potential surface[74,75] and have led to the conclusion that a similar surface also describes S_N2 reactions in dipolar aprotic solvents, e.g. DMF.[75]

Since these hypovalent negative ions are novel structures, it was, therefore, of interest to determine where the carbene anion radicals and $PhN^{-\bullet}$ fit into the relative S_N2 kinetic order defined by Bohme.[71] The CH_3X molecules used were X = Cl, Br, and O_2CCF_3 in their order of increasing reactivity with nucleophilic anions. The reactivity data are given in Table 3. For those hypovalent species where rate constants are available for the reactions with CH_3Cl and CH_3Br, we conclude that $CF_3CH^{-\bullet}$, c-$C_5H_4^{-\bullet}$, $Ph_2C^{-\bullet}$, and $Fl^{-\bullet}$ are of medium nucleophilicity while $PhN^{-\bullet}$ is of low nucleophilicity in S_N2 reactions.

In the case of c-$C_5H_4^{-\bullet}$, the kinetic S_N2 nucleophilicity of the hypovalent negative ion can be compared with that of the corresponding carbanion c-$C_5H_5^-$. Whereas c-$C_5H_5^-$ did effect S_N2 displacement with CH_3Br at a slow rate ($k_{total} = 2.5 \times 10^{-12}$ cm^3 molecule^{-1} s^{-1}), no reaction was observed with CH_3Cl ($k_{total} < 10^{-13}$ cm^3 molecule^{-1} s^{-1}) even though the latter reaction is calculated to be 32 kcal mol^{-1} exothermic.[76] The explanation offered for this marked difference in the rate constants for the two reactions with CH_3Br ($k(c\text{-}C_5H_4^{-\bullet})/k(c\text{-}C_5H_5^-) \approx 50$) was that the thermo-

Table 3. Rate constants for the S_N2 reactions of carbene anion radicals and PhN^- with CH_3X molecules

Hypovalent species[a]	CH_3Cl[b]	CH_3Br[b]	$CH_3O_2CCF_3$[b]
H_2C^-	[c]		
$NCCH^-$ [d]			
$CF_3CH^{-\cdot}$	9.6×10^{-11}	5.1×10^{-10}	7.9×10^{-10}
$(CF_3)_2C^-$	$<10^{-13}$		
$c\text{-}C_5H_4^-$	$\approx10^{-13}$	1.1×10^{-10}	
$Ph_2C^{-\cdot}$	3.2×10^{-11}	3.9×10^{-10}	[e]
Fl^-	2.8×10^{-11}	2.2×10^{-10}	[e]
$PhN^{-\cdot}$	$<10^{-13}$	1.8×10^{-11}	not observed[f]

[a] References for these hypovalent negative ions are given in Table 2.

[b] Rate constants in the units of $cm^3\ molecule^{-1}\ s^{-1}$.

[c] Reference 44; Cl^- was the major product ion, but the rate constant was not given.

[d] Reference 47; $NCCH^{-\cdot}$ was reported to react with CH_3I as a nucleophile.

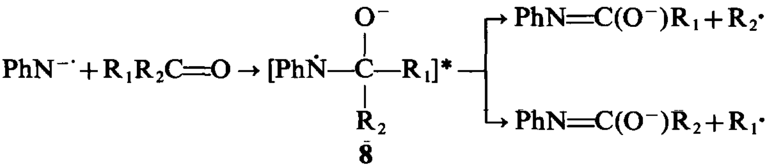
[e] This reaction occurred at or near the collision limit with the major product forming channels being carbonyl group addition followed by radical β-fragmentation; <10% involved S_N2 displacement at methyl forming $CF_3CO_2^-$.

[f] Reference 67; this fast reaction occurred exclusively by carbonyl group addition followed by radical β-fragmentation.

chemistry of the two reactions influenced the separate kinetic barriers. This is seen in the methyl cation affinities (MCA) of the two negative ions; $MCA(c\text{-}C_5H_4^{-\cdot}) = 279$ kcal mol^{-1} and $MCA(c\text{-}C_5H_5^-) = 258$ kcal mol^{-1}.[77] Thus, the CH_3^+ transfers in S_N2 displacement reactions are 21 kcal mol^{-1} *more exothermic* to the hypovalent negative ion $c\text{-}C_5H_4^{-\cdot}$ than to the carbanion $c\text{-}C_5H_5^-$.

3.4.2. *Additions to carbonyl groups.* When the gas-phase studies of ion-molecule reactions of hypovalent negative ions began, a common theme among investigators was that additions of anions to carbonyl groups forming tetrahedral adducts in the gas phase were not important product forming channels. A likely reason for this was the reversibility of such nucleophilic addition reactions which should be more important in the gas phase than in the condensed phase due to the reduced probability of excess energy removal from the addition adduct by collisional stabilization and the absence of other solvation effects. The results of the chloride ion/acyl chloride displacement reactions do not appear to require the tetrahedral adduct as an energy minimum.[80,81] However, two direct observations of such tetrahedral intermediate negative ions formed by adding anions to carbonyl centers have been reported in FA experiments.[82,83]

The structures of the hypovalent negative ions, e.g. $PhN^{-\cdot}$, suggested that they could be used to probe carbonyl addition reactions *if* the addition adduct **8** rapidly underwent radical β-fragmentation which would eliminate the retro-addition step (Eqn 16). A requirement for this approach to work was that the likely competing reactions of H^+ transfer and of S_N2 reactions with esters, must be minimized. $PhN^{-\cdot}$ appeared to be well suited to this task with a relatively low PA (Table 2) and a low kinetic S_N2 nucleophilicity (see Section 3.4.1).



$$PhN^{-\cdot} + R_1R_2C{=}O \rightarrow [Ph\dot{N}{-}C(O^-)(R_2){-}R_1]^* \rightarrow \begin{cases} PhN{=}C(O^-)R_1 + R_2^{\cdot} & (16a) \\ PhN{=}C(O^-)R_2 + R_1^{\cdot} & (16b) \end{cases}$$

8

The reactions of $PhN^{-\cdot}$ with the aldehydes RCHO where R = CH_3, C_2H_5, and $(CH_3)_3C$ demonstrated the value of this approach. To set the stage for these results, the reaction of CH_3CHO with the alkoxide anion $(CH_3)_3CO^-$ (PA = 373.3 ± 2 kcal mol^{-1} [54] which is approximately the PA of $PhN^{-\cdot}$) gave exclusively the enolate anion $H_2C{=}C(O^-)H$ at m/z 43 in a fast reaction that was exothermic by 6.9 kcal mol^{-1}.[49] In the reaction of CH_3CHO with $PhN^{-\cdot}$, only 10% H^+ transfer was observed while 90% of the product forming channels occurred by carbonyl addition followed by radical β-fragmentation (Eqn 17). The related reactions of C_2H_5CHO and $(CH_3)_3CCHO$ are shown in Eqns 18 and 19.[67]

Note that H^+ transfers from CH_3CHO and C_2H_5CHO to $PhN^{-\cdot}$ are minor product forming channels even though they are exothermic by 5.6 and 6.1 kcal mol^{-1}, respectively. It was suggested that the fragmentation channels a and b in Eqns 17–19 involve formation of excited addition adducts **8** where $R_1 = H$ and R_2 is the alkyl group. Although H-atom fragmentation exceeds CH_3 group fragmentation in Eqn 17, β-sission of the larger alkyl groups C_2H_5 and $C(CH_3)_3$ is the major product forming channel in Eqns 18 and 19, and the branching fractions follow the expected order for radical cleavage reactions.

$$\underset{(m/z\,91)}{PhN^{-\cdot}} + CH_3CHO \xrightarrow{0.31} \underset{(m/z\,120)}{PhN{=}C(O^-)H} + {\cdot}CH_3 \tag{17a}$$

$$\xrightarrow{0.59} \underset{(m/z\,134)}{PhN{=}C(O^-)CH_3} + {\cdot}H \tag{17b}$$

$$\xrightarrow{0.10} \underset{(m/z\,43)}{H_2C{=}C(O^-)H} + PhNH{\cdot} \tag{17c}$$

$$\underset{(m/z\,91)}{PhN^{-\cdot}} + C_2H_5CHO \xrightarrow{0.75} \underset{(m/z\,120)}{PhN{=}C(O^-)H} + {\cdot}C_2H_5 \tag{18a}$$

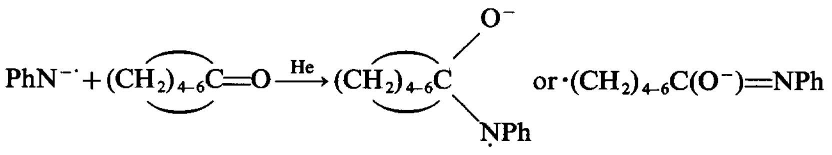
$$\xrightarrow{0.23} \underset{(m/z\,148)}{PhN{=}C(O^-)C_2H_5} + {\cdot}H \tag{18b}$$

$$\xrightarrow{0.02} \underset{(m/z\,57)}{CH_3CH{=}C(O^-)H} + PhNH{\cdot} \tag{18c}$$

$$\underset{(m/z\,91)}{PhN^{-\cdot}} + (CH_3)_3CCHO \xrightarrow{0.98} \underset{(m/z\,120)}{PhN{=}C(O^-)H} + {\cdot}C(CH_3)_3 \tag{19a}$$

$$\xrightarrow{0.02} \underset{(m/z\,176)}{PhN{=}C(O^-)C(CH_3)_3} + {\cdot}H \tag{19b}$$

In the reactions of $PhN^{-\cdot}$ with cyclic ketones (C_4 to C_7), the product ions from the reactions with cyclopentanone, cyclohexanone, and cycloheptanone were the total adducts (Eqn 20).[67] For observation of such adducts in gas-phase reactions, we assume termolecular collisional stabilization with the helium buffer gas is required to remove the excess energy in the adduct. The structures of these adduct product ions could be the cyclic adduct **9** formed by nucleophilic attack at the carbonyl center or the fragmented, ring-opened anion radical **10** shown in Eqn 20. The delocalization of the negative charge in **10** compared to **9** could be the driving force for the ring fragmentation.



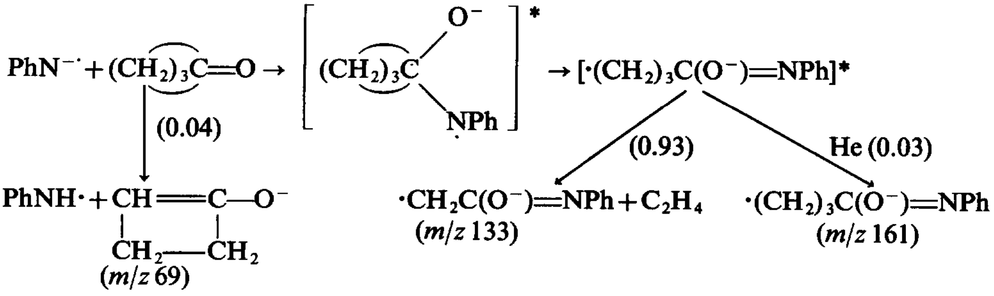
$$PhN^{-\cdot} + (CH_2)_{4\text{-}6}C{=}O \xrightarrow{He} (CH_2)_{4\text{-}6}C(O^-)(\dot{N}Ph) \quad \text{or} \; {\cdot}(CH_2)_{4\text{-}6}C(O^-){=}NPh \tag{20}$$

9 **10**

The answer to this question appears to be found in the results from the reaction of $PhN^{-\cdot}$ with cyclobutanone ($k_{total} = 6.6 \times 10^{-11}$ cm^3 molecule^{-1} s^{-1}) where the ion at *m/z* 133, the (adduct-C_2H_4)$^{-\cdot}$, was the major product along with small amounts of ions at *m/z* 69 and 161.[67] Our interpretation of how the three product ions (and their percentages) were formed in this reaction is shown in Scheme 3. The minor (4%) product anion at *m/z* 69 appears to be the enolate anion of cyclobutanone formed by H^+ transfer to $PhN^{-\cdot}$. The sequence of steps believed involved in the formation of the ion products at *m/z* 133 (93%) and 161 (3%) are nucleophilic addition of $PhN^{-\cdot}$ to the carbonyl center giving the cyclic adduct followed by radical β-fragmentation yielding the acyclic adduct. In this reaction, the acyclic adduct anion radical is more vibrationally excited than those representing **10** due to the release of the four-membered ring strain (E_s(cyclobutanone) = 22.6 kcal mol^{-1}).[79] While a small number of the excited acyclic adduct negative ions at *m/z* 161 are stabilized by collisions with the buffer gas, most of these excited acyclic adduct ions fragment with the loss of C_2H_4 to produce the major product ions at *m/z* 133. Using the reaction $CH_3CH_2CH_2\cdot \rightarrow \cdot CH_3 + C_2H_4$ to model this fragmentation, we calculate $\Delta H_{rx} = +25.8$ kcal mol^{-1} [84] for the loss of C_2H_4. These results and the mechanistic interpretation led to the suggestion that the structures of the adduct anion radical products formed in the reactions of $PhN^{-\cdot}$ with the C_5–C_7 cyclic ketones (Eqn 20) were the acyclic structures **10**. The reaction exothermicities in forming the anion radicals **10** from the three ketones must be less than the endothermicity required for the fragmentation of C_2H_4 in these cases.

With the above as background, a number of other reactions of $PhN^{-\cdot}$ with carbonyl containing molecules were examined. With several of these neutral substrates, H^+ transfer was found to be a competing reaction. Calculation of the bimolecular rate constants for the separate product forming channels from the measured product ion signal intensities can be in error due to some losses of the product ions in the reaction region of the FA primarily due to diffusion to the walls of the flow tube. Generally, this approach yields lower limits of the rate constants with their sum being *less* than k_{total} which is determined from loss of the starting ion. Therefore, we prefer to determine these rate constants by multiplying k_{total} by the branching fractions of the competitive product forming reaction channels. These branching fractions were determined at 8–10 different concentrations of the added neutral reactant (5–95% reaction) and at two different flow conditions ($P_{He} = 0.5$ torr, $v = 80$ m s^{-1} and $P_{He} = 1.0$ torr, $v = 42$ m s^{-1}), and found to be the same within our error limits of $\pm 4\%$ absolute. In this study, k_{total} was multiplied by the sum of the branching fractions for those channels yielding fragmented acylanilide anion products. This gave a series of rate constants $k^{C=O}$*s* for the neutral carbonyl-containing substrates reacting with $PhN^{-\cdot}$. When these $k^{C=O}$*s* were divided by $k^{C=O}$ for acetone, the series of $k_{rel}^{C=O}$*s* shown in Table 4 were generated.

Several interesting points emerge from considerations of the $k_{rel}^{C=O}$ values listed in Table 4: (a) a range of 7850 in $k_{rel}^{C=O}$ was observed; (b) the gas-phase relative reactivities of the carbonyl substrates with $PhN^{-\cdot}$ were those observed or expected for nucleophilic addition reactions with



Scheme 3.

Table 4. Relative rate constants for the carbonyl addition/fragmentation reactions of PhN^- with some carbonyl containing molecules

Neutral substrate	$k_{rel}^{C=O}$ [a]	ΔH_{rx},[b] kcal mol^{-1}
$(CH_3)_2C{=}O$	1	-19.0
$CH_3COC_2H_5$	4	-21.7
CF_3COCH_3	80	-22.4
$(CF_3)_2C{=}O$	83	-30.9
cyclobutanone	11	
CH_3CHO	12	-16.4
C_2H_5CHO	31	-18.4
$(CH_3)_3CCHO$	67	-23.7
HCO_2CH_3	0.2	-6.1
$CH_3CO_2CH_3$	0.02	-3.7
$CF_3CO_2CH_3$	157	-14.6

[a] See text for how these values were calculated.

[b] ΔH_{rx}s were calculated for the formation of the acylanilide anion and the radical products. For those reactions involving more than one such channel, ΔH_{rx} for the major carbonyl addition/fragmentation channel is given; see reference 67.

these same substrates in the condensed phase; and (c) a general correlation between $k_{rel}^{C=O}$ and the exothermicity of the major product forming channel of carbonyl addition/fragmentation was absent. For the fastest of the reactions in Table 4 (with $CF_3CO_2CH_3$), the total rate constant was 57% of the collision limited rate constant calculated using the average dipole orientation theory.[85] Even here the selectivity for carbonyl addition/fragmentation vs S_N2 displacement was complete, 100%.[86] This fact assures us that mechanism selectivity by $PhN^{-\cdot}$ will be high in the other slower reactions listed in Table 3. The relative reactivity range of 7850 in this series of reactions is unusual for gas-phase ion-molecule reactions and stretches the FA to its limit with a kinetic window of 10^4.

The observation of the reactivity order $CH_3CHO > (CH_3)_2C{=}O > CH_3CO_2CH_3$ under the same conditions was encouraging. As a further check on this order, the reaction of $PhN^{-\cdot}$ with the α-dicarbonyl compound methyl pyruvate was examined. In this fast reaction ($k_{total} = 6.7 \times 10^{-10}$ cm^3 molecule^{-1} s^{-1}; 61% of the collision limit), the negative ion products at *m/z* 101 ($CH_2{=}C(O^-)CO_2CH_3$; 2%), 134 ($PhN{=}C(O^-)CH_3$; 83%), 150 ($PhN{=}C(O^-)OCH_3$); 8%), 162 ($PhN{=}C(O^-)COCH_3$; 4%), and 178 ($PhN{=}C(O^-)CO_2CH_3$; 3%) were observed. The product ions at *m/z* 134 and 178 were considered to be formed by ketone carbonyl addition/fragmentation (86%), those at *m/z* 150 and 162 by ester carbonyl addition/fragmentation (12%), and that at *m/z* 101 by H^+ transfer (2%). On this basis, nucleophilic addition of $PhN^{-\cdot}$ to the two carbonyl groups in $CH_3COCO_2CH_3$ favored that of the ketone vs that of the ester group by a factor of 7 in this intramolecular example.

The absence of a general correlation between $k_{rel}^{C=O}$ and the exothermicity of the overall reaction of carbonyl addition/fragmentation in Table 4 was most clearly seen in the reactions of $PhN^{-\cdot}$ with $(CH_3)_2C{=}O$ ($k_{rel}^{C=O} = 1$, $\Delta H_{rx} = -19$ kcal mol^{-1}) and with $CF_3CO_2CH_3$ ($k_{rel}^{C=O} = 157$, $\Delta H_{rx} = -14.6$ kcal mol^{-1}). This fact, however, was believed to be consistent with the involvement of adducts, **8**, in these carbonyl addition/fragmentation reactions. A three minimum potential surface was suggested for these reactions with the formation of the adduct being the principal contributor to the total rate constant. In this way, the rate constant for the reaction was effectively 'insulated' from the overall exothermicity.

One problem with the use of $PhN^{-\cdot}$ to determine the reactivities of carbonyl centers was that the very slow reaction with $CH_3CO_2CH_3$ was at the lower limit of determination in the FA apparatus. The kinetic part of this problem may be solved with the use of $Ph_2C^{-\cdot}$[48] as illustrated in its reaction with HCO_2CH_3 shown in Eqn 21. This reaction was 100 times faster than the analogous reaction of $PhN^{-\cdot}$.[67] However, the larger PA of $Ph_2C^{-\cdot}$ compared to $PhN^{-\cdot}$ introduces additional difficulties with neutral substrates containing modestly acidic C—H bonds as we see in the reactions with $CH_3CO_2CH_3$ in Eqns 22 and 23. The 3% addition/fragmentation channel in reaction 22 corresponds to $k^{C=O} = 4 \times 10^{-12}$ cm³ molecule⁻¹ s⁻¹ which is ≈30 times greater than $k^{C=O}$ in reaction 23.

$$\underset{(m/z\,166)}{Ph_2C^{-\cdot}} + HCO_2CH_3 \rightarrow \underset{(m/z\,195)}{Ph_2C{=}C(O^-)H} + {\cdot}OCH_3 \tag{21}$$

$$(k_{\text{total}} = 1.5 \times 10^{-10}\ \text{cm}^3\ \text{molecule}^{-1}\ \text{s}^{-1})$$

$$\underset{(m/z\,166)}{Ph_2C^{-\cdot}} + CH_3CO_2CH_3 \xrightarrow{0.03} \underset{(m/z\,209)}{Ph_2C{=}C(O^-)CH_3} + {\cdot}OCH_3 \tag{22a}$$

$$\xrightarrow{0.97} \underset{(m/z\,73)}{CH_2{=}C(O^-)OCH_3} + Ph_2CH{\cdot} \tag{22b}$$

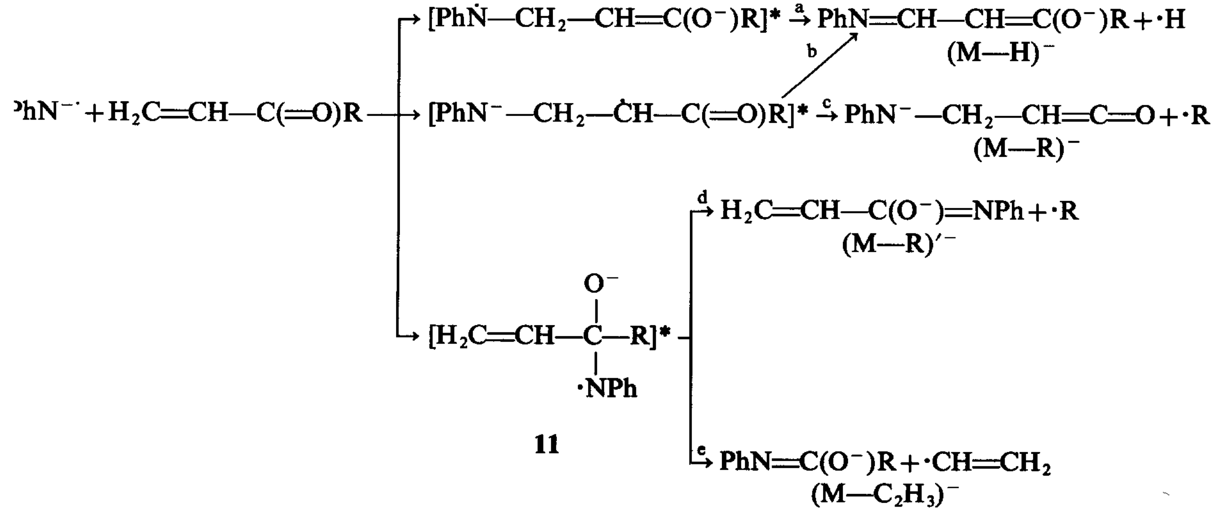
$$(k_{\text{total}} = 1.3 \times 10^{-10}\ \text{cm}^3\ \text{molecule}^{-1}\ \text{s}^{-1})$$

$$\underset{(m/z\,91)}{PhN^{-\cdot}} + CH_3CO_2CH_3 \xrightarrow{0.88} \underset{(m/z\,134)}{PhN{=}C(O^-)CH_3} + {\cdot}OCH_3 \tag{23a}$$

$$\xrightarrow{0.12} \underset{(m/z\,73)}{CH_2{=}C(O^-)OCH_3} + PhNH{\cdot} \tag{23b}$$

$$(k_{\text{total}} \approx 1.5 \times 10^{-13}\ \text{cm}^3\ \text{molecule}^{-1}\ \text{s}^{-1})$$

3.4.3. 1,2- vs 1,4-*Addition with α,β-unsaturated molecules.* The single report dealing with this topic involved the reactions of $PhN^{-\cdot}$ with acrylonitrile, methyl acrylate, methyl vinyl ketone, and acrolein.[87] The utility of the hypovalent species again makes use of the radical β-fragmentation reaction following the addition step. As shown in Scheme 4, three different negative ion products,



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Scheme 4.

$(M—H)^-$, $(M—R)^- = (M—R)'^-$, and $(M—C_2H_3)^-$, could potentially result from 1,2- and 1,4-addition of $PhN^{-\cdot}$ to an α,β-unsaturated carbonyl containing molecule. The $(M—H)^-$ ion can only be formed by radical β-fragmentation of the adducts of 1,4-conjugate addition ($R \neq H$) with $PhN^{-\cdot}$ adding either as an anion or a radical. While we believe that addition of $PhN^{-\cdot}$ as a radical is unlikely, cleavage of such an adduct by pathway c forming the $(M—R)^-$ product ion can be ruled out on the basis of the $\Delta H_{rx} = +27.7$ kcal mol^{-1} for the model reaction $\cdot CH_2C(=O)CH_3 \rightarrow H_2C=C=O + \cdot CH_3$.[88] Therefore, $(M—H)^-$ is the only probable product negative ion formed by 1,4-conjugate addition of $PhN^{-\cdot}$. Thus, it should be possible to distinguish between these two mechanistic paths.

The reaction of $PhN^{-\cdot}$ with $CH_2=CHCN$ rapidly ($k_{total} = 1.4 \times 10^{-10}$ cm^3 molecule^{-1} s^{-1}) and exclusively yielded the ion at m/z 143, the $(M—H)^-$ product. With the ester $CH_2=CHCO_2CH_3$, the reaction was considerably slower ($k_{total} = 5.9 \times 10^{-12}$ cm^3 molecule^{-1} s^{-1}) and produced two ions at m/z 146 (90%) and 176 (10%) which were assigned the structures of the $(M—OCH_3)^-$ and $(M—H)^-$ products, respectively, in Eqn 24. Based on the above arguments and Scheme 4, 1,2-addition to the carbonyl center was favored over 1,4-conjugate addition by a factor of 9.

$$\underset{(m/z\,91)}{PhN^{-\cdot}} + CH_2=CHCO_2CH_3 \xrightarrow{0.90} \underset{(m/z\,146)}{CH_2=C=CHC(O^-)=NPh} + \cdot OCH_3 \quad (24a)$$

$$\xrightarrow{0.10} \underset{(m/z\,176)}{PhN=CH—CH=C(O^-)OCH_3} + \cdot H \quad (24b)$$

The faster reaction ($k_{total} = 5.8 \times 10^{-11}$ cm^3 molecule^{-1} s^{-1}) of $PhN^{-\cdot}$ with methyl vinyl ketone gave four product ions at m/z 69, 134, 146, and 160 which are shown in Eqn 25 with their assigned structures. The ion at m/z 69 is the conjugate base of the starting ketone formed by H^+ transfer. Thus, 89% of the product ions result from the two addition/fragmentation mechanisms. Of these processes, the product ion structures (and their masses) clearly show that only 2% occurred by 1,4-conjugate addition while 87% occurred by 1,2-addition to the carbonyl group.

$$\underset{(m/z\,91)}{PhN^{-\cdot}} + CH_2=CHC(=O)CH_3 \xrightarrow{0.02} \underset{(m/z\,160)}{PhN=CH—CH=C(O^-)CH_3} + \cdot H \quad (25a)$$

$$\xrightarrow{0.82} \underset{(m/z\,146)}{PhN=C(O^-)—CH=CH_2} + \cdot CH_3 \quad (25b)$$

$$\xrightarrow{0.05} \underset{(m/z\,134)}{PhN=C(O^-)CH_3} + \cdot CH=CH_2 \quad (25c)$$

$$\xrightarrow{0.11} \underset{(m/z\,69)}{CH_2=C(O^-)—CH=CH_2} + PhNH\cdot \quad (25d)$$

The reaction of $PhN^{-\cdot}$ with the α,β-unsaturated aldehyde acrolein was also fast ($k_{total} = 2.1 \times 10^{-10}$ cm^3 molecule^{-1} s^{-1}). Two product ions were formed at m/z 120 and 146 and their assigned structures are given in Eqn 26. The minor ion product at m/z 120 was the $(M—C_2H_3)^-$ ion and was considered to have been formed from 1,2-addition to the carbonyl group followed by fragmentation of the vinyl radical. The major product ion at m/z 146 is the $(M—H)^-$ species; however, in reaction 26, $(M—H)^- = (M—R)'^-$ from Scheme 4. Therefore, in the absence of the results from the reaction of $PhN^{-\cdot}$ with a specially deuterated acrolein molecule, e.g. $CH_2=CHCDO$, it is not possible to quantitate the percentages of 1,2- vs 1,4-addition in reaction 26.

$$\underset{(m/z\,91)}{\mathrm{PhN^{-\cdot}}} + \mathrm{CH_2{=}CHCHO} \xrightarrow{0.97}$$

$$\mathrm{PhN{=}C(O^-){-}CH{=}CH_2 \text{ and/or } PhN{=}CH{-}CH{=}C(O^-)H} + {}^{\cdot}\mathrm{H} \quad (m/z\,146) \tag{26a}$$

$$\xrightarrow{0.03} \underset{(m/z\,120)}{\mathrm{PhN{=}C(O^-)H}} + {}^{\cdot}\mathrm{CH{=}CH_2} \tag{26b}$$

Qualitatively, however, the rate constant for 1,4-conjugate addition of $\mathrm{PhN^{-\cdot}}$ to methyl vinyl ketone ($k_{\mathrm{total}} \times 0.02 = 1.2 \times 10^{-12}\ \mathrm{cm^3\ molecule^{-1}\ s^{-1}}$) and acrolein should be very similar while the rate constant for 1,2-addition to the aldehydic carbonyl of acrolein will be greater than to the carbonyl of the ketone ($k_{\mathrm{total}} \times 0.87 = 5.0 \times 10^{-11}\ \mathrm{cm^3\ molecule^{-1}\ s^{-1}}$) (see Table 4). These considerations suggest that the increase in the rate constant in the reaction of $\mathrm{PhN^{-\cdot}}$ with acrolein compared to methyl vinyl ketone by a factor of 4 is due only to an increase in $k^{\mathrm{C{=}O}}$ in the aldehyde reaction. Based on this kinetic argument, we conclude that >99% of reaction 26 occurred by 1,2-addition to the carbonyl group of acrolein.

From this limited study with the α,β-unsaturated carbonyl containing molecules methyl acrylate, methyl vinyl ketone, and acrolein, we conclude that the intramolecular kinetic competition for 1,2- vs 1,4-addition by a nucleophile is greatly favored (>9 : 1) by 1,2-addition at the carbonyl center.

3.5. *Generation, thermodynamics, and chemistry of diazoalkane anion radicals*

To fill the gap between the above results obtained in the gas phase and those reported in the condensed phase, it would be most useful if we could generate and study the diazoalkane and carbene anion radicals derived from the same neutral diazo compound. However, as we have pointed out in Section 3.2., the attachment of thermal energy electrons with the diazo compounds $\mathrm{CF_3CH{=}N_2}$, $\mathrm{(CF_3)_2C{=}N_2}$, $c\text{-}\mathrm{C_5H_4{=}N_2}$, $\mathrm{Ph_2C{=}N_2}$, and $\mathrm{Fl{=}N_2}$ occurred dissociatively with formation of the corresponding carbene anion radicals. It appeared that this was a general process where the EA of the diazoalkane exceeded the binding energy of the $\mathrm{N_2}$ molecule in the intermediate diazoalkane anion radical.

3.5.1. *Generation of some diazoalkane anion radicals.* We were, therefore, surprised to find that associative electron attachment occurred when the diazo compounds $\mathrm{EtO_2CCH{=}N_2}$ and $\mathrm{PhCH{=}N_2}$ were introduced to the FA at inlet 1 (Eqns 27 and 28). While the handling of $\mathrm{EtO_2CCH{=}N_2}$ and generation of $\mathrm{EtO_2CCHN_2^{-\cdot}}$ were clean, the apparent lower stability of $\mathrm{PhCH{=}N_2}$ led to considerable decomposition in the gas inlet and inside of the flow tube with this diazo compound. Therefore, the subsequent studies proceeded exclusively using $\mathrm{EtO_2CCHN_2^{-\cdot}}$.

$$\mathrm{EtO_2CCH{=}N_2} + \mathrm{e^-} \rightarrow \underset{(m/z\,114)}{\mathrm{EtO_2CCHN_2^{-\cdot}}} \tag{27}$$

$$\mathrm{PhCH{=}N_2} + \mathrm{e^-} \rightarrow \underset{(m/z\,118)}{\mathrm{PhCHN_2^{-\cdot}}} \tag{28}$$

It appeared likely that $\mathrm{EtO_2CCHN_2^{-\cdot}}$ could be used as a 'soft' electron transfer reagent in reactions with other $\mathrm{R_2C{=}N_2}$ molecules where $\mathrm{EA(R_2C{=}N_2)} > \mathrm{EA(EtO_2CCH{=}N_2)}$ to yield the new diazoalkane anion radicals. In such cases, the excess energy deposited in $\mathrm{R_2CN_2^{-\cdot}}$ will be the difference $\mathrm{EA(R_2C{=}N_2)} - \mathrm{EA(EtO_2CCH{=}N_2)}$. Since, as we will show, $\mathrm{EA(EtO_2CCH{=}N_2)} = 18.7\ \mathrm{kcal\ mol^{-1}}$,[89] the excess energy in $\mathrm{R_2CN_2^{-\cdot}}$ might be less than the $D^\circ(\mathrm{R_2C^-{-}N_2})$ and a stable $\mathrm{R_2CN_2^{-\cdot}}$ would result. This approach was successful with the diazo compounds shown in Eqns 29–31, but failed with $\mathrm{PhN_3}$ (Eqn 32).[49] This means that the EAs of $c\text{-}\mathrm{C_5H_4N_2}$, $\mathrm{Ph_2CN_2}$, and

FlN_2 are greater than 18.7 kcal mol^{-1} while EA(PhN_3) is less than this value.[90]

$$\text{EtO}_2\text{CCHN}_2^{-\cdot}+c\text{-C}_5\text{H}_4{=}\text{N}_2 \rightarrow c\text{-C}_5\text{H}_4\text{N}_2^{-\cdot}+\text{EtO}_2\text{CCH}{=}\text{N}_2 \tag{29}$$

$$\text{EtO}_2\text{CCHN}_2^{-\cdot}+\text{Ph}_2\text{C}{=}\text{N}_2 \rightarrow \text{Ph}_2\text{CN}_2^{-\cdot}+\text{EtO}_2\text{CCH}{=}\text{N}_2 \tag{30}$$

$$\text{EtO}_2\text{CCHN}_2^{-\cdot}+\text{Fl}{=}\text{N}_2 \rightarrow \text{FlN}_2^{-\cdot}+\text{EtO}_2\text{CCH}{=}\text{N}_2 \tag{31}$$

$$\text{EtO}_2\text{CCHN}_2^{-\cdot}+\text{PhN}_3 \rightarrow \text{no reaction} \tag{32}$$

To point out a further complication in such reactions, we calculate that the reaction (a) $\text{CH}_2{=}\text{N}_2+\text{e}^- \rightarrow \text{H}_2\text{C}^{-\cdot}+\text{N}_2$ is *endothermic* by 6.8 kcal mol^{-1}.[94] However, the dissociative electron transfer reaction (b) $\text{EtO}_2\text{CCHN}_2^{-\cdot}+\text{CH}_2{=}\text{N}_2 \rightarrow \text{H}_2\text{C}^{-\cdot}+\text{N}_2+\text{EtO}_2\text{CCH}{=}\text{N}_2$ is *exothermic* by 12.9 kcal mol^{-1} due to the factor of the EA($\text{EtO}_2\text{CCH}{=}\text{N}_2$) in this latter equation. Assuming that $\text{CH}_2{=}\text{N}_2$ has a positive EA, which is most likely less than EA($\text{EtO}_2\text{CCH}{=}\text{N}_2$), an endothermic electron transfer could occur within the collision complex [$\text{EtO}_2\text{CCHN}_2^{-\cdot}/\text{CH}_2{=}\text{N}_2$] since such complexes are stabilized by 10–20 kcal mol^{-1} due to the attractive ion-dipole and ion-induced dipole forces. The resulting charge transfer complex [$\text{EtO}_2\text{CCHN}_2/\text{CH}_2\text{N}_2^{-\cdot}$] could not separate (endothermic), but could dissociate to yield the products of reaction (b) above. Thus, $\text{H}_2\text{C}^{-\cdot}$ would be the only negative ion product under the electron transfer conditions. The EA($\text{CH}_2{=}\text{N}_2$) does not bear on the thermochemistry of reactions (a) or (b), but is important in the electron transfer required for reaction (b) to operate.

3.5.2. *Thermodynamic data of* $\text{EtO}_2\text{CCHN}_2^{-\cdot}$ *and* $c\text{-C}_5\text{H}_4\text{N}_2^{-\cdot}$. The PAs of $\text{EtO}_2\text{CCHN}_2^{-\cdot}$ and $c\text{-C}_5\text{H}_4\text{N}_2^{-\cdot}$ and the EAs of $\text{EtO}_2\text{CCH}{=}\text{N}_2$ and $c\text{-C}_5\text{H}_4{=}\text{N}_2$ given in Table 5 were determined using the bracketing method with neutral substrates of known gas-phase acidities[54] and EAs[95,96], respectively.

The PA($c\text{-C}_5\text{H}_4\text{N}_2^{-\cdot}$) and EA($c\text{-C}_5\text{H}_4{=}\text{N}_2$) allow for the direct comparison with those values of the corresponding carbene anion radical $c\text{-C}_5\text{H}_4^{-\cdot}$ and the carbene $c\text{-C}_5\text{H}_4$. From the PA data in Tables 2 and 5, we observe that $c\text{-C}_5\text{H}_4^{-\cdot}$ is the *stronger Bronsted base by 31 kcal mol*$^{-1}$. We believe that this will be a general trend in the basicities of carbene anion radicals compared to their

Table 5. Thermodynamic data of $\text{EtO}_2\text{CCHN}_2^{-\cdot}$ and $c\text{-C}_5\text{H}_4\text{N}_2^{-\cdot}$

Substrate	PA($\text{R}_2\text{CN}_2^{-\cdot}$) kcal mol^{-1}	EA($\text{R}_2\text{C}{=}\text{N}_2$), kcal mol^{-1}
$\text{EtO}_2\text{CCHN}_2^{-\cdot}$[a]	355 ± 4[b]	18.7 ± 3[c,g]
$c\text{-C}_5\text{H}_4\text{N}_2^{-}$[d]	346 ± 2[e]	27.3 ± 4[f,g]

[a] Reference 89.

[b] Bracketed between H_2S (PA = 353.4 ± 2 kcal mol^{-1}; H$^+$ transfer) and $c\text{-C}_5\text{H}_6$ (PA = 356.1 ± 2 kcal mol^{-1}; no H$^+$ transfer).[54]

[c] Determined from the equilibrium constant for electron transfer between $\text{EtO}_2\text{CCH}{=}\text{N}_2$ and biacetyl anion radical (EA = 15.9 kcal mol^{-1}).[95]

[d] Reference 97.

[e] Bracketed between HCO_2H (PA = 345.2 ± 2 kcal mol^{-1}; H$^+$ transfer) and $\text{C}_2\text{H}_5\text{CO}_2\text{H}$ (PA = 346.5 ± 2 kcal mol^{-1}; no H$^+$ transfer) [54]

[f] Bracketed between $m\text{-FC}_6\text{H}_4\text{NO}_2$ (EA = 28.4 ± 2.3 kcal mol^{-1}; e$^-$ transfer) and $o\text{-ClC}_6\text{H}_4\text{NO}_2$ (EA = 26.3 ± 2.3 kcal mol^{-1}; no e$^-$ transfer).[95]

[g] This value assumes no significant entropy change between the neutral diazo compound and its anion radical.

precursor diazoalkane anion radicals while the absolute difference will change with the molecular system. This difference should prove useful in condensed-phase experiments where selective protonation may be accomplished. Although the bracketed EA of the carbene $c\text{-}C_5H_4$ is broad,[39] $EA(c\text{-}C_5H_4) > EA(c\text{-}C_5H_4{=}N_2)$ by at least 20 kcal mol^{-1}. This expected relationship between the EAs results from the fact that the electrons in the carbene anion radical are in bonding MOs while the electron added to the diazoalkane must enter a π^* MO.

In the determination of the PA of $EtO_2CCHN_2^{-\cdot}$,[89] it was observed that the sole product negative ion formed in the reaction with CH_3SH was the ion at *m/z* 46. This ion contained a sulfur atom as characterized by the isotope signals at *m/z* 47 (≈1%) and 48 (4%). The *m/z* 46 ion was assigned the structure $H_2CS^{-\cdot}$ and was considered formed by H_2^+ transfer from CH_3SH to $EtO_2CCHN_2^{-\cdot}$ *in a single collision encounter* (see section 3.3 for related H_2^+ transfer reactions with carbene anion radicals).[98] The likely overall reaction is shown in Eqn 33.

$$EtO_2CCHN_2^{-\cdot} + CH_3SH \rightarrow H_2CS^{-\cdot} + EtO_2CCH_3 + N_2 \tag{33}$$

3.5.3. $EtO_2CCHN_2^{-\cdot}$ *and* $c\text{-}C_5H_4N_2^{-\cdot}$ *as nucleophiles.* $EtO_2CCHN_2^{-\cdot}$ was studied as a nucleophile in reactions with CH_3X derivatives and with several carbonyl containing molecules. However, $c\text{-}C_5H_4N_2^{-\cdot}$ has only been examined as an S_N2 nucleophile at this time.

3.5.3.1. S_N2 *Reactions.* Both $EtO_2CCHN_2^{-\cdot}$ and $c\text{-}C_5H_4N_2^{-\cdot}$ failed to react with CH_3Br ($k_{total} < 10^{-13}$ cm^3 molecule^{-1} s^{-1}). A slow reaction ($k_{total} = 8.4 \times 10^{-12}$ cm^3 molecule^{-1} s^{-1}) between $EtO_2CCHN_2^{-\cdot}$ and the more reactive CH_3X substrate $CF_3CO_2CH_3$ was observed, but occurred exclusively by the carbonyl addition/fragmentation mechanism[89] (see next section). The reaction of $c\text{-}C_5H_4N_2^{-\cdot}$ with $CF_3CO_2CH_3$ did produce $CF_3CO_2^-$ (*m/z* 113) at a slow rate ($k_{total} < 10^{-12}$ cm^3 molecule^{-1} s^{-1}).[97] We conclude that the two diazo anion radicals $EtO_2CCHN_2^{-\cdot}$ and $c\text{-}C_5H_4N_2^{-\cdot}$ are very poor S_N2 nucleophiles. The much greater reactivity of $c\text{-}C_5H_4^{-\cdot}$ compared to $c\text{-}C_5H_4N_2^{-\cdot}$ with CH_3Br by $> 10^3$ is striking and may prove useful in condensed-phase studies to identify the presence of carbene anion radicals.

3.5.3.2. *Additions to carbonyl groups.* Only $EtO_2CCHN_2^{-\cdot}$ has been investigated in this reaction type.[89] No reaction was observed between $EtO_2CCHN_2^{-\cdot}$ and CH_3CHO or $(CH_3)_2C{=}O$ ($k_{total} < 10^{-13}$ cm^3 molecule^{-1} s^{-1}). With the more reactive α-diketone biacetyl (established kinetically with $PhN^{-\cdot}$ [67]), two product forming channels were observed (Eqn 34) with $k_{total} = 2.4 \times 10^{-11}$ cm^3 molecule^{-1} s^{-1}.

$$\underset{(m/z\,114)}{EtO_2CCHN_2^{-\cdot}} + (CH_3C({=}O))_2 \xrightarrow{0.77} \underset{(m/z\,129)}{EtO_2CCH{=}C(O^-)CH_3} + N_2 + CH_3CO\cdot \tag{34a}$$

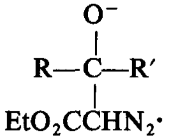
$$\xrightarrow{0.23} \underset{(m/z\,86)}{(CH_3C({=}O))_2^{-\cdot}} + EtO_2CCH{=}N_2 \tag{34b}$$

With $CF_3CO_2CH_3$, which had reacted at the collision limit with $PhN^{-\cdot}$ by the carbonyl addition/fragmentation mechanism, $EtO_2CCHN_2^{-\cdot}$ reacted slowly ($k_{total} = 8.4 \times 10^{-12}$ cm^3 molecule^{-1} s^{-1}) to yield the enolate anion $EtO_2CCH{=}C(O^-)CF_3$ at *m/z* 183 (Eqn 35). The same product negative ion was formed with the same rate constant in the reaction of $EtO_2CCHN_2^{-\cdot}$ with the ethyl ester $CF_3CO_2C_2H_5$.

$$\underset{(m/z\,114)}{EtO_2CCHN_2^{-\cdot}} + CF_3CO_2R \rightarrow \underset{(m/z\,183)}{EtO_2CCH{=}C(O^-)CF_3} + N_2 + \cdot OR \tag{35}$$

$$R = CH_3 \text{ or } C_2H_5$$

In these reactions of $EtO_2CCHN_2^{-\cdot}$ with carbonyl containing substrates, two mechanisms were considered possible. (a) Direct addition of C_α of $EtO_2CC_\alpha HN_2^{-\cdot}$ to the carbonyl center would give adduct **12** which would expel N_2 and fragment R· or R'· to give the product enolate anion. Or (b) N_2 is ejected in forming the collision complex yielding the excited ternary complex $[EtO_2C\text{-}CH^{-\cdot}/N_2/RR'C{=}O]^*$ which then competitively returns to the starting materials or yields the products via addition/fragmentation of $EtO_2CCH^{-\cdot}$ with the carbonyl compound. This competition within the ternary complex would be required to explain the slow reaction rates.



$$R{-}\overset{\overset{\displaystyle O^-}{|}}{\underset{\underset{\displaystyle EtO_2CCHN_2\cdot}{|}}{C}}{-}R'$$

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The following observations and rationale are offered to *rule out mechanism* (*b*) *as the operating mechanism* in these reactions of $EtO_2CCHN_2^{-\cdot}$. First, total adduct negative ion products, $[EtO_2CCHN_2^{-\cdot}\cdot HR]$, were observed in the reactions of $EtO_2CCHN_2^{-\cdot}$ with the neutral molecules CF_3CH_2OH, CH_3NO_2, and $HCCl_3$ which were too weakly acidic to H^+ transfer to the diazoalkane anion radical.[89] Obviously, N_2 was not lost in generating these complexes which are probably weak hydrogen bonded cluster structures. Second, the nature of the products and the rate constants for reactions 35 ($R = CH_3$ and C_2H_5) are not those expected for the intermediacy of the excited ternary complex $[EtO_2CCH_2^{-\cdot}/N_2/CF_3CO_2R]^*$. The methyl cation affinity (MCA) of $^-CH_2CO_2CH_3$ at C_α is calculated to be 271.5 kcal mol^{-1} and should be the lower limit for $MCA(EtO_2CCH^{-\cdot})$. This means that $EtO_2CCH^{-\cdot}$ should be kinetically a good to excellent S_N2 nucleophile and would be expected to rapidly produce the negative ion displacement product $CF_3CO_2^-$ (*m*/*z* 113) from the ternary complex given above. Since no ion product at *m*/*z* 113 was observed in these two slow reactions, it was concluded that mechanism (a) forming adduct **12** was operating.

Although the corresponding carbene anion radical $EtO_2CCH^{-\cdot}$ is not available for direct comparison, the author believes that the diazoalkane anion radicals will be considerably weaker Bronsted bases and much poorer nucleophiles in S_N2 displacement and carbonyl addition reactions than the corresponding carbene anion radicals. These factors should prove advantageous in future condensed-phase investigations of these reactive intermediates where the selective reactions of $R_2C^{-\cdot}$ in the presence of $R_2CN_2^{-\cdot}$ may be observed.

4. SUMMARY AND CONCLUSIONS

It is now possible to generate a number of diazoalkane anion radicals and the corresponding carbene anion radicals in condensed- and gas-phase experiments within certain limitations. In the condensed-phase, stabilization of the negative charge of the carbene anion radical by attached carbonyl groups or incorporation of the divalent center in a cyclopentadienyl ring (but not in fluorene) has proven successful to allow for expulsion of the N_2 molecule from the intermediate diazoalkane anion radical. The carbene anion radicals produced in the condensed phase to date are $(EtO_2C)_2C^{-\cdot}$,[28,30] 4,4-dimethyl-2,6-dioxocyclohexylidene anion radical,[29] $Ph(PhCO)C^{-\cdot}$,[30] $(NC)_4\text{-}c\text{-}C_5^{-\cdot}$,[13] and $Ph_4\text{-}c\text{-}C_5^{-\cdot}$.[32] The diazoalkane anion radicals $Ph_2CN_2^{-\cdot}$ and $FlN_2^{-\cdot}$ decompose by reactions other than the intramolecular loss of N_2.

In the gas phase, the most general route to generating carbene anion radicals (see Table 2) involves dissociative electron attachment to diazo compounds; by analogy, PhN_3 yields $PhN^{-\cdot}$. The notable exceptions were $EtO_2CCH{=}N_2$ and $PhCH{=}N_2$ which formed their respective diazoalkane anion radicals. $EtO_2CCHN_2^{-\cdot}$ served as a 'soft' electron transfer reagent ($EA(EtO_2CCH{=}N_2) = 18.7$ kcal mol^{-1}) in its reactions with other diazo compounds and the formation of several diazoalkane anion radicals resulted. Of special interest here is the availability of the pairs $c\text{-}C_5H_4^{-\cdot}/c\text{-}C_5H_4N_2^{-\cdot}$, $Ph_2C^{-\cdot}/Ph_2CN_2^{-\cdot}$, and $Fl^{-\cdot}/FlN_2^{-\cdot}$ for direct comparisons of each pairs thermodynamic properties (PA, ΔH_f°, and EA of the neutral species) and their ion-molecule chemistry with the same neutral substrates under the same experimental conditions. Some preliminary data for the $c\text{-}C_5H_4^{-\cdot}/c\text{-}C_5H_4N_2^{-\cdot}$ pair are presented and discussed.

The kinetic S_N2 nucleophilicities of the carbene anion radicals and $PhN^{-\cdot}$ vary from good to poor depending on their structure and are correlated with their methyl cation affinities. In this reaction type, both diazoalkane anion radicals, $c\text{-}C_5H_4N_2^{-\cdot}$ and $EtO_2CCHN_2^{-\cdot}$, proved to be very poor S_N2 nucleophiles, a fact that is likely to be general for other $R_2CN_2^{-\cdot}$ species.

The carbene anion radicals and $PhN^{-\cdot}$ are excellent to good nucleophiles in adding to carbonyl centers of neutral substrates. The kinetic investigations in this area take advantage of the fast radical β-fragmentation of the adduct formed by nucleophilic addition of the HIR negative ion to the carbonyl group. In these studies, the kinetic reactivity order $RCHO > R_2C{=}O > RCO_2R'$ toward nucleophilic addition for the same alkyl substituents was determined which is the same order observed in the condensed phase. The reactions of $PhN^{-\cdot}$ with the α,β-unsaturated carbonyl molecules methyl acrylate, methyl vinyl ketone, and acrolein established the high regioselectivity in nucleophilic addition at the carbonyl centers compared to 1,4-conjugate addition.

Of the two diazoalkane anion radicals examined to date, comparison of the thermodynamic properties and reaction kinetics of $c\text{-}C_5H_4N_2^{-\cdot}$ with those of the corresponding carbene anion radical $c\text{-}C_5H_4^{-\cdot}$ show that $c\text{-}C_5H_4^{-\cdot}$ is the stronger Bronsted base, better S_N2 nucleophile, and $EA(c\text{-}C_5H_4) > EA(c\text{-}C_5H_4{=}N_2)$. The second diazoalkane anion radical, $EtO_2CCHN_2^{-\cdot}$, was also found to be kinetically a very poor nucleophile in S_N2 displacement reactions with CH_3X molecules. $EtO_2CCHN_2^{-\cdot}$ did effect several carbonyl addition/fragmentation processes with the more reactive carbonyl group containing substrates with small rate constants. The product anions from these latter reactions strongly suggested that C_α of $EtO_2CCHN_2^{-\cdot}$ is the nucleophilic center which adds to the carbonyl group of the neutral substrate.

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REFERENCES

[1] We define a hypovalent ion radical as a charged radical species containing *less* than the number of attached substituents found in the uncharged free radical system normally associated with the central atom in the radical.
[2] Jugelt, W. and Pragst, F. *Angew. Chem. Internatl Ed.* **1968,** *7,* 290.
[3] Jugelt, W. and Pragst, F. *Tetrahedron* **1968,** *24,* 5123.
[4] Jugelt, W. and Pragst, F. *Electrochim. Acta* **1970,** *15,* 1543.
[5] Pragst, F., Huebner, W. and Jugelt, W. *J. Prakt. Chem.* **1970,** *312,* 105.
[6] Berseck, L., Jugelt, W., Pragst, F. and Schmidt, D. *J. Prakt. Chem.* **1970,** *312,* 117.
[7] Pragst, F. and Jugelt, W. *Electrochim. Acta* **1970,** *15,* 1769.
[8] Rodina, L. L., Pragst, F. and Jugelt, W. *J. Prakt. Chem.* **1974,** *316,* 286.
[9] Elofson, R. M., Gadallah, F. F., Cantu, A A. and Schulz, K. F. *Can. J. Chem* **1974,** *52,* 2430.
[10] Fry, A. J. In *The Chemistry of Diazonium and Diazo Groups*; Patai, S., Ed.; Wiley: New York, 1978; Chapter 10.
[11] Parker, V. D. and Bethell, D. *J. Am. Chem. Soc.* **1987,** *109,* 5066.
[12] Ahmad, I., Bethell, D. and Parker, V. D., *J. Chem. Soc. Perkin Trans. II,* **1984,** 1527.
[13] Webster, O. W *J. Am. Chem. Soc.* **1966,** *88,* 4055.
[14] Sargent, G. D., Tatum, C. M. and Castner, S. M. *J. Am. Chem. Soc.* **1972,** *94,* 7174.
[15] Sargent, G. D., Tatum, C. M. and Scott, R. P. *J. Am. Chem. Soc.* **1974,** *96,* 1602.
[16] Kauffmann, T. and Hage, S. M. *Angew. Chem. Internat. Ed.* **1963,** *2,* 156.
[17] McDonald, R. N., January, J. R., Borhani, K. J. and Hawley, M. D. *J. Am. Chem. Soc.* **1977,** *99,* 1268.
[18] Triebe, F. M., Hawley, M. D. and McDonald, R. N. *J. Chem. Soc., Chem. Commun.* **1980,** 574.
[19] McDonald, R. N., Triebe, F. M., January, J. R., Borhani, K. J. and Hawley, M. D. *J. Am. Chem. Soc.* **1980,** *102,* 7867.
[20] Parker, V D. and Bethell, D. *Acta Chem Scand., Ser. B* **1980,** *B34,* 617.
[21] Parker, V. D. and Bethell, D. *Acta Chem Scand., Ser. B* **1981,** *B35,* 72.
[22] Parker, V. D. and Bethell, D. *Acta Chem. Scand., Ser B* **1981,** *B35,* 691.

[23] Bethell, D. and Parker, V. D. *J. Chem. Soc. Perkin Trans. 2* **1982**, 842.
[24] Bethell, D., McDowall, L. J. and Parker, V. D. *J. Chem. Soc. Perkin Trans. 2* **1984**, 1531.
[25] Bethell, D. and Parker, V. D. *J. Am. Chem. Soc.* **1986**, *108*, 895.
[26] van Galen, D. A., Young, M. P. and Hawley, M. D. *J Electroanal. Chem.* **1984**, *175*, 53.
[27] Cheng, S. and Hawley, M. D. *J. Org. Chem.* **1986**, *51*, 3799.
[28] van Galen, D. A., Young, M. P., Hawley, M. D. and McDonald, R. N. *J. Am. Chem. Soc.* **1985**, *107*, 1465.
[29] van Galen, D. A. and Hawley, M. D. *J. Electroanal. Chem.* **1987**, *218*, 227
[30] Bethell, D. and Parker, V. D. *J. Am. Chem. Soc.* **1986**, *108*, 7194.
[31] Bethell, D., McDowall, L. J. and Parker, V. D. *J. Chem. Soc., Chem. Commun.* **1984**, 308.
[32] Bethell, D. and Parker, V. D. *J. Chem. Res.* **1987**, 116.
[33] Hawley, M. D. private communication.
[34] Kebarle, P. *Annu. Rev. Phys. Chem.* **1977**, *28*, 445.
[35] Beauchamp, J. L. *Annu. Rev. Phys. Chem.* **1971**, *22*, 527.
[36] Lehman, T. A. and Bursey, M. M. *Ion Cyclotron Resonance Spectroscopy*; Wiley-Interscience: New York, 1976.
[37] Ferguson, E. E., Fehsenfeld, F. C and Schmeltekopf, A. L. *Adv. At. Mol. Phys.* **1969**, *5*, 1.
[38] For other reviews of the FA apparatus and data, see [a]Smith, D. and Adams, N. G. In *Gas Phase Ion Chemistry*; Bowers, M. T., Ed.; Academic Press: New York, 1979; Vol. 1, Chapter 1. [b]Ferguson, E. E., Fehsenfeld, F. C. and Albritton, D. L. In *Gas Phase Ion Chemistry*; Bowers, M. T., Ed.; Academic Press: New York, 1979; Vol. 1, Chapter 2. [c]Albritton, D. L. *At. Data Nucl. Data Tables* **1978**, *22*, 1.
[39] McDonald, R. N., Chowdhury, A. K. and Setser, D. W. *J. Am. Chem. Soc.* **1980**, *102*, 6491.
[40] McDonald, R. N. and Chowdhury, A. K. *Ibid.* **1985**, *1985*, 4123.
[41] In an attempt to generate $(EtO_2C)_2C^{-\cdot}$ from $(EtO_2C)_2C{=}N_2$ by dissociative electron attachment, the only product observed was the negative ion at m/z 113. This ion was considered to be $EtO_2C{-}C{\equiv}C{-}O^-$ formed by radical β-fragmentation of the carbene anion radical with loss of ·OEt.
[42] Jones, M. T., Dreiling, T. D., Setser, D. W. and McDonald, R. N. *J. Phys. Chem.* **1985**, *89*, 4501.
[43] Leopold, D. G., Murray, K. K., Miller, A. E. S. and Lineberger, W. C. *J. Chem. Phys.* **1985**, *83*, 4849.
[44] DePuy, C H., Barlow, S. E., Van Doren, J. M., Roberts, C. R. and Bierbaum, V. M. *J. Am. Chem. Soc.* **1987**, *109*, 4415.
[45] Lindinger, W., Albritton, D L., Fehsenfeld, F. C. and Ferguson, E. E. *J. Chem. Phys.* **1975**, *63*, 3238.
[46] Dawson, J. H. J. and Nibbering, N. M. M. *J. Am. Chem. Soc.* **1978**, *100*, 1928.
[47] Grabowski, J. J. and Melly, S. J. *Int. J. Mass Spectrom. Ion Phys.* **1987**, *81*, 147.
[48] McDonald, R. N. and Gung, W. Y. *J. Am. Chem. Soc* **1987**, *109*, 7328.
[49] McDonald, R. N. and Chowdhury, A K. unpublished results.
[50] McDonald, R. N. and McGhee, W. D. unpublished results.
[51] McDonald, R. N., Chowdhury, A. K. and McGhee, W. D. *J. Am. Chem. Soc.* **1984**, *106*, 4112.
[52] For a summary of the reactions of $O^{-\cdot}$ with various neutral substrates, see [a]Jennings, K. R. *Philos. Trans. R. Soc. London, Ser. A* **1979**, *293*, 125; [b]Bruins, A. P., Ferrer-Correia, A. J., Harrison, A. G., Jennings, K. R. and Mitchum, R. K. *Adv. Mass Spectrom.* **1978**, *7*, 355; [c]Dawson, J. H. J. and Jennings, K. R. *J. Chem. Soc., Faraday Trans. 2* **1976**, *72*, 700.
[53] Stull, D. R. and Prophet, H. JANAF Thermochemical Tables, *Natl. Stand. Ref. Data Ser., Natl. Bur. Stand.* No. 37 (1971). $\Delta H^\circ_{f,298}(O^-) = 24.3 \pm 0.5$ kcal mol^{-1} and $\Delta H^\circ_{f,298}(HO^-) = -34.4 \pm 1$ kcal mol^{-1}.
[54] Bartmess, J. E. and McIver, R. T In *Gas Phase Ion Chemistry*, Bowers, M. T., Ed.; Academic Press: New York; Vol. 2, 1979.
[55] McDonald, R. N., Chowdhury, A. K. and Setser, D. W. *J. Am. Chem. Soc.* **1981**, *103*, 6599.
[56] Furuyama, S., Golden, D. M. and Benson, S. W. *Int. J. Chem. Kinet.* **1971**, *3*, 237.
[57] Chandrasekhar, J., Kahn, R. A. and Schleyer, P. von R. *Chem. Phys. Lett.* **1982**, *85*, 493.
[58] DeFrees, D. J., McIver, R. T. and Hehre, W. J. *J. Am. Chem. Soc.* **1980**, *102*, 3334.
[59] Burnett, S. M., Stevens, A. E., Feigerle, C. S. and Lineberger, W. C. *Chem. Phys. Lett.* **1983**, *100*, 124.
[60] Sullivan, S. A. and Beauchamp, J. L. *J. Am. Chem. Soc.* **1976**, *98*, 1160.
[61] DePuy, C. H., Bierbaum, V M. and Damrauer, R. *J. Am. Chem. Soc.* **1984**, *106*, 4051.
[62] Jensen, P., Bunker, P. R. and Hoy, A. R. *J. Chem. Phys.* **1982**, *77*, 5370.
[63] $D^\circ(c\text{-}C_5H_4^{-}{-}H) = 103.9 \pm 5.2$ kcal mol^{-1}.[39]
[64] Drzaic, P. S and Brauman, J. I. *J. Phys. Chem.* **1984**, *88*, 5285.
[65] Jordan, K. D. and Burrow, P. D. *Acc. Chem. Res.* **1978**, *11*, 341.
[66] Drzaic, P. S. and Brauman, J I. *J. Am. Chem. Soc.* **1984**, *106*, 3443.
[67] McDonald, R. N. and Chowdhury, A. K. *J. Am. Chem. Soc.* **1983**, *105*, 198.
[68] Professors K. D. Jordan and P. D. Burrow (private communication) have estimated that $H_2C{=}S$ will have a positive EA.
[69] Engelking, P. C., Ellison, G. B. and Lineberger, W. C. *J. Chem. Phys.* **1978**, *69*, 1826.
[70] Brauman, J I., Olmstead, W. N. and Lieder, C. A. *J. Am. Chem. Soc.* **1974**, *96*, 4030.
[71] Tanaka, K., Mackay, G. I, Payzant, J. D. and Bohme, D. K. *Can. J. Chem.* **1976**, *54*, 1643.
[72] Olmstead, W. M. and Brauman, J. I. *J. Am Chem. Soc.* **1977**, *99*, 4219.
[73] Pellerite, M. J. and Brauman, J. I. *J. Am. Chem. Soc.* **1980**, *102*, 5993.
[74] Chandrasekhar, J., Smith, S. F. and Jorgensen, W. L. *J. Am. Chem. Soc.* **1984**, *106*, 3049.
[75] Chandrasekhar, J. and Jorgensen, W. L. *J. Am. Chem. Soc.* **1985**, *107*, 2974.
[76] McDonald, R. N., Chowdhury, A. K. and Setser, D. W. *J. Am. Chem. Soc.* **1981**, *103*, 7586.
[77] The thermodynamic values used in calculating the MCAs are $\Delta H^\circ_f(c\text{-}C_5H_4^{-\cdot}) = 70.7$ kcal mol^{-1},[39] $\Delta H^\circ_f(CH_3^+) = 262$ kcal mol^{-1},[78] $\Delta H^\circ_f(CH_3\text{-}c\text{-}C_5H_5) = 25.1$ kcal mol^{-1} calculated using group additivities,[79] $\Delta H^\circ_f(CH_3\text{-}c\text{-}C_5H_4\cdot) = 54.2$ kcal

mol^{-1} calculated assuming $D°(CH_3$-*c*-C_5H_4—H) = $D°$(*c*-C_5H_5—H) = 81.2 kcal mol^{-1},[56] and $\Delta H_f°$(*c*-$C_5H_5^-$) = 21.3 kcal mol^{-1}.[54]

[78] Rosenstock, H. M., Draxl, K., Steiner, B. W. and Herron, H. T. *J. Phys. Chem. Ref. Data* **1977**, *6*, Suppl 1.

[79] Benson, S. W. *Thermochemical Kinetics*; Wiley: New York, 1976; 2nd ed.

[80] Asubiojo, O. I. and Brauman, J. I. *J. Am Chem. Soc.* **1979**, *101*, 3715.

[81] Han, C.-C and Brauman, J. I. *J. Am. Chem. Soc.* **1987**, *109*, 589.

[82] Bohme, D. K., Mackay, G. I. and Tanner, S. D. *J. Am. Chem. Soc.* **1980**, *102*, 407.

[83] McDonald, R. N. and Chowdhury, A. K. *J. Am. Chem. Soc.* **1983**, *105*, 7267.

[84] The $\Delta H_f°$s of *n*-$C_3H_7\cdot$, $\cdot CH_3$, and C_2H_4 are from reference 79.

[85] Su, T and Bowers, M. T. In *Gas Phase Ion Chemistry*; Academic Press: New York, 1979; Vol. 1, Chapter 3.

[86] It was shown in Section 3.4.1. that $PhN^{-\cdot}$ was a poor S_N2 nucleophile.

[87] McDonald, R. N. and Chowdhury, A. K. *J. Phys. Chem.* **1982**, *86*, 3641.

[88] $\Delta H_f°$- and $D°(CH_3C({=}O)CH_2$—H) are from references 54 and 79.

[89] McDonald, R. N. and Chowdhury, A. K. *Tetrahedron* **1986**, *42*, 6253.

[90] Electron transfer from $EtO_2CCHN_2^-$ to $Fe(CO)_5$ occurred dissociatively as shown in Eqn (i). Sufficient thermodynamic exist

$$EtO_2CCHN_2^- + Fe(CO)_5 \rightarrow (OC)_4Fe^{-\cdot} + CO + EtO_2CCH{=}N_2 \qquad \text{(i)}$$

($\Delta H_f°(Fe(CO)_5) = -173.0 \pm 1.5$ kcal mol^{-1},[91] $\Delta H_f°(CO) = -26.42 \pm 0.04$ kcal mol^{-1},[91] $D°((OC)_4Fe$—$(CO)) = 41 \pm 2$ kcal mol^{-1},[92] and EA $(Fe(CO)_4) = 55.3 \pm 7$ kcal mol^{-1}[93]) for the components of reaction (i) to allow calculation of ΔH_{rx}(i) = -34 ± 10.5 kcal mol^{-1}. This is the sum of —EA($EtO_2CCH{=}N_2$) and the exothermicity of the dissociative electron attachment to $Fe(CO)_5$ forming $(OC)_4Fe^{-\cdot}$ and CO (-14.3 ± 10.5 kcal mol^{-1}).

[91] Cox, J. D. and Pilcher, G. *Thermochemistry of Organic and Organometallic Compounds*; Academic Press· New York, 1970.

[92] Lewis, K. E., Golden, D. M. and Smith, G. P. *J. Am. Chem. Soc.* **1984**, *106*, 3905.

[93] Engelking, P. C. and Lineberger, W. C. *J. Am. Chem. Soc.* **1979**, *101*, 5569.

[94] $\Delta H_f°(CH_2{=}N_2) = 71$ kcal mol^{-1}.[79]

[95] Kebarle, P. and Chowdhury, S *Chem. Rev.* **1987**, *87*, 513.

[96] Drzaic, P S., Marks, J. and Brauman, J I. In *Gas Phase Ion Chemistry*, Bowers, M. T., Ed.; Academic Press: New York; 1979, Vol. 3, Chapter 21.

[97] McDonald, R. N. and Reed, D. J. unpublished results.

[98] Under the high dilution and time constraints of the FA experiments, the probability for a neutral product from an ion/molecule reaction to encounter a second ion is zero

NOTE ADDED IN PROOF. Since this manuscript was submitted, Lineberger *et al.* (Murray, K. K., Leopold, D. G., Miller, T. M. and Lineberger, W. C. *J. Chem. Phys.* **1988**, *89*, 5442) reported the photoelectron spectroscopy results for HCF^-, $HCCl^{-\cdot}$, $HCBr^{-\cdot}$, HCI^-, $F_2C^{-\cdot}$ and $Cl_2C^{-\cdot}$ yielding the EAs of the corresponding carbenes, and a review of the condensed-phase studies directed toward $R_2C^{-\cdot}$ and $R_2C^{+\cdot}$ appeared (Bethell, D. and Parker, V. D. *Acc. Chem. Res.* **1988**, *21*, 400).