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FINAL TECHNICAL REPORT
RICHARD N. MCDONALD AND DONALD W. SETSER
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The Chemistry of Energetic Fragments

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Flaming afterglow apparatus Ion-neutral clusters
Ion-molecule reactions Nucleophilic reactions
Hypovalent anion radicals Addition/fragmentation reactions
Cyclopentadienylidene anion radical 1,2-and 1,4-addition
Phenylnitrene anion radical

Following construction and testing of a flowing afterglow (FA) apparatus, two hypovalent anion radicals, cyclopentadienylidene$^-$ ($c-C_5H_4^-)$ and phenyl-nitrene$^-$ ($PhN^-$), were produced in the FA and the ion-molecule chemistry of these two species was determined. From the results of bracketing reactions, the FA's and $\Delta H_f^s$'s of $c-C_5H_4^-$ and $PhN^-$ were obtained as well as limits of their
hydrogen atom affinities. Compared to cyclopentadienyl anion ($c-C_5H_5^-$), $c-C_5H_4^-$ is a much stronger Bronsted base and a somewhat stronger nucleophile in both $S_N^2$ displacement and conjugate (1,4) addition reactions. Since PhN$^-$ has smaller H$^+$ and H- affinities than $c-C_5H_4^-$, reactions of PhN$^-$ could be examined with a larger variety of neutral molecules. Using the special feature of the hypovalent anion radicals that addition (e.g. to a C=O) is followed by a radical $\beta$-fragmentation process, the reactions with several aldehydes, ketones, and esters were examined. The products of such addition/fragmentation reactions are acyl anilide anions (PhNCOR$^-$) containing one of the R groups attached to the original C=O containing compound. From the group fragmentation order (CH$_3$O$^-$ > CH$_3$CO$^-$ > H$^-$ > CH$_3^-$ > CF$_3^-$), the D$(C-R)$ of the anion-radical addition intermediate must be similar to those of the starting C=O containing compound toward radical abstraction. PhN$^-$ formed clusters with simple alcohols which underwent a cluster-to-cluster anion-switch process in a second bimolecular reaction with a molecule of alcohol yielding PhNH$^-$ + RO$^-$ (HOR).
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I. Construction and testing of the flowing afterglow apparatus (FA) was accomplished in the first 1.9 years of the 3-year grant period. Certain features of the FA distinguish it from those used by other investigators: (1) the quadrupole mass spectrometer (MS) has a full set of lenses and its own ionizer (turned off during FA operation) for directing the ion beam into the mass filter, (2) the presence of the ionizer in front of the lenses and mass filter and a direct leak into the MS compartment allows the conventional, low-pressure, positive and/or negative ion mass spectrum of inletted reagents to be measured, and (3) the neutral reactants in the ion-molecule reactions in the FA are added via an inlet adjustable over the entire length of the flow tube (see Figs. 1 and 2).

II. Three studies have been completed: those of (a) cyclopentadienylidene anion radical (c-C₅H₄⁻), (b) cyclopentadienyl anion (c-C₅H₅⁻), and (c) phenyl-nitrene anion radical (PhN⁻). Our usual reaction conditions are helium as the buffer gas, Pₗₜ = 0.5 torr, v = 80 m s⁻¹, and 298 K. The results from each of these studies are outlined below.

(a) c-C₅H₄⁻ was produced from diazocyclopentadiene (c-C₅H₄N₂) by dissociative electron attachment. Increasing the flow (concentration) of c-C₅H₄N₂ past the ionizer showed the presence of three negative ions in the helium buffer gas flow, c-C₅H₄⁻ (>98%), c-C₅H₄⁺ c-C₅H₄⁻ (m/z 128, <1%), and c-C₅H₄⁺ NC c-C₅H₄⁻ (m/z 156, 1%). The latter two ions were shown to result from primary reactions of c-C₅H₄⁻ with c-C₅H₄N₂ by similar processes described for the solution reactions of carbene anion radicals with their parent diazo compounds.

The PA(c-C₅H₄⁻) = 378+2 kcal/mole was determined by ion-molecule bracketing reactions of c-C₅H₄⁻ with various alcohols. From this value, ΔH_f²(c-C₅H₄⁻) = 71±3 kcal/mole is calculated. The increased basicity of c-C₅H₄⁻ compared to that of the corresponding carbanion c-C₅H₅⁻ (ΔPA = 21 kcal/mole) results from the δΔH_f²'s of these two anions and their respective neutral products of protonation:

\[
\begin{align*}
\text{c-C₅H₄⁻} & \rightarrow \text{c-C₅H₅⁺} \quad \delta \Delta H_f² = -11 \text{ kcal/mole} \\
\text{c-C₅H₅⁻} & \rightarrow \text{c-C₅H₆} \quad \delta \Delta H_f² = +10 \text{ kcal/mole}
\end{align*}
\] (1)

Experiments to determine the H⁺ affinity (HA) of c-C₅H₄⁻ were not as successful as those yielding it PA. It appears that a barrier exists in the H⁺ abstraction reactions of c-C₅H₄⁻. However, a lower limit of this physical property is obtained from the reaction with CH₃OH which occurs rapidly and exclusively by H⁺ abstraction from the O-H group. This yields ΔH_f²(c-C₅H₄⁻) > 68±3 kcal/mole, in good agreement with the value calculated from the PA data.

c-C₅H₄⁻ undergoes addition/fragmentation reactions with H₂C=CH-X molecules. With X=CN and CO₂CH₃, the principal product channel yields the (M-H) adduct of
conjugate addition. With vinyl chloride (X=Cl), the exclusive formation of Cl⁻ is also considered to be formed by conjugate addition followed by fragmentation and rearrangement of the neutral species. No reaction was observed between c-C₅H⁻ with vinyl fluoride or ethylene. Comparison of the relative rate constants of these reactions requires that c-C₅H⁻ adds as a nucleophile (not a radical).

The ionization potential of c-C₅H₄⁻ = EA(c-C₅H₄) was bracketed as ≤ 54±2, > 41.5±7 kcal/mole by studies of its ability to electron transfer to neutral reactants.

The cyclic structure and electronic configuration (σ²π¹) of c-C₅H₄⁻ were established by its reaction with CH₃OH yielding c-C₅H₅⁻ (same ion as produced from c-C₅H₆ + CH₃O⁻), and its PA cannot be that predicted for the alternative σ¹π² electronic configuration.

(b) The study of the carbanion c-C₅H₅⁻ was carried out to compare/contrast with those results observed for the carbene anion radical c-C₅H₄⁻. We have already noted that c-C₅H₄⁻ is a much stronger base toward proton donors than is c-C₅H₅⁻ (δPA = 21 kcal/mole). Also, c-C₅H₄⁻ was found to be kinetically a more powerful nucleophile with methyl halides (S₈₂) and H₂C=CH-X (conjugate addition) by krel of 60 - 100. The increased nucleophilicity of c-C₅H₄⁻ compared to c-C₅H₅⁻ as with the greater PA of c-C₅H₄⁻, is considered to be the thermochemistry of these processes, since electrons in similar HOMO orbitals are involved. Therefore, we believe that this comparative reactivity of c-C₅H₄⁻ vs c-C₅H₅⁻ is that of π-delocalization of the free radicals product from the former species contrasted to the simply polyene product from the latter species reactions.

A significant difference was also found in the types of products formed in the reactions of c-C₅H₄⁻ or c-C₅H₅⁻ with α,β-unsaturated molecules, e.g. H₂C=CHCN and H₂C=CHCO₂CH₃. With c-C₅H₄⁻, the ion-molecule reaction products from both substrates were the (M-H) anion adducts. However, c-C₅H₅⁻ reacted with H₂C=CHCN to yield c-C₅H₅CH₂CHCN⁻, the (M) adduct, and with H₂C=CHCO₂CH₃ to produce c-C₅H₄CHCHCO₂CH₃⁻, the (M-2H) adduct. These results establish the "special" and useful nature of the addition/fragmentation reactions of c-C₅H₄⁻ with these α,β-unsaturated molecules. If we assume nucleophilic addition takes place to yield intermediate 1, the radical β-fragmentation reaction producing the (N-H)

\[
\begin{align*}
\text{CH}_2\overline{\text{CH}} &= \frac{\text{CH}}{} \\
\text{CH} &= \overline{\text{CH}} \quad + \quad \overline{\text{CH}} \quad + \quad \text{H} \quad + \quad \text{H} \\
\end{align*}
\]

adduct and a hydrogen atom is easily understood. This addition/fragmentation sequence should prove valuable in all of our studies with hypovalent anion radicals and can be extrapolated to predict certain chemistry of hypovalent cation radicals.
From the known acidities ($\Delta H_{acid}^{o}$) of CH$_3$OH, C$_2$H$_5$OH, (CH$_3$)$_3$COH, CF$_3$CH$_2$OH, and c-C$_5$H$_6$, these alcohols cannot directly protonate c-C$_5$H$_5^-$. Therefore, we were surprised to find that a reasonably fast reaction ($k_1 = (2.7\pm0.2) \times 10^{-10}$ cm$^3$ molecule$^{-1}$ s$^{-1}$) was observed between c-C$_5$H$_5^-$ and CF$_3$CH$_2$OH and that the major reaction products were the clusters CF$_3$CH$_2$O$^-$((HOCH$_2$CF$_3$)$_n$) where $n=1$ and 2. A careful examination of this reaction revealed the reaction sequence shown in eq. (4) with the data shown in Figure 3 (Appendix). Of special interest in this mechanism is that the anion transferred from cluster 2 in step 2 yielding CF$_3$CH$_2$O$^-$((HOCH$_2$CF$_3$)$_2$) is that derived from N of (IN), not I$^-$. This anion-switching mechanism accounts for the absence of the unsolvated CF$_3$CH$_2$O$^-$ in this reaction.

Computer fitting of the maxima of the data in Figure 3 yields the rate constants for the three consecutive pseudo-first-order steps of this mechanism, $k_1 = k_3 = \frac{1}{2}k_2$, where $k_2$ is the observed decay constant for c-C$_5$H$_5^-$. It is the extra binding energy of CF$_3$CH$_2$O$^-$((HOCH$_2$CF$_3$)$_2$) over that of cluster 2 that allows step 2 to occur; the direct proton transfer from CF$_3$CH$_2$OH to c-C$_5$H$_5^-$ is endothermic by $8.3\pm3$ kcal/mole.

Anion c-C$_5$H$_5^-$ also formed 1:1 clusters with CH$_3$OH, C$_2$H$_5$OH, and (CH$_3$)$_3$COH. However, the anion-switching reactions of these clusters with a second alcohol molecule were not observed. The endergicities of the direct proton transfers between c-C$_5$H$_5^-$ and these alcohols vary from $17\pm3$ to $23\pm3$ kcal/mole. Apparently, the binding energies of these homoconjugate clusters (RO$^-$(HOR)) are not sufficient to overcome the endergicity of the proton transfer process.

We believe that these gas-phase results and the proposed mechanism for protonation of c-C$_5$H$_5^-$ by CF$_3$CH$_2$OH closely mimic this reaction in solution. In solution the proton donor would be the solvate CF$_3$CH$_2$OH(HOCH$_2$CF$_3$)$_X$, and the homoconjugate product would be CF$_3$CH$_2$O$^-$((HOCH$_2$CF$_3$)$_X$, both of which are structurally analogous to the species of the ion-cluster steps described here.

(c) Phenyl nitrene anion radical (PhN$^-$) was cleanly prepared by dissociative electron attachment to phenyl azide (PhN$_3$). From bracketing reaction studies using neutral molecules of known acidities, PA(PhN$^-$) = $372\pm2$ kcal/mole was determined, which gives $\Delta H_e^o(PhN^-) = 60\pm2$ kcal/mole. Similar attempts to bracket
the H⁺ affinity of PhN⁻ failed; no example of an ion-molecule H⁺ transfer was found yielding the upper limit of \( D^\circ(\text{PhN}^--\text{H}) < 96 \text{ kcal/mole} \).

PhN⁻ was shown to react slowly with PhN₃ giving two products, \( C_{12}H_{10}N^+ \) and \( C_{12}H_{10}N_2^- \), assigned the structures of 1,4-diphenyltetrazadiene and azobenzene anion radicals, respectively. This is the first evidence for a tetrazadiene structure in the organic chemistry of nitrogen containing compounds. Formation of PhN=N-N=NPh⁻ is directly related to formation of azine anion radicals \( (R_2C=N-N=CR_2^-) \) from the reaction of \( R_2C^- \) with \( R_2CN_2 \) observed in solution and in the gas phase (see section (a)).

The somewhat lower basicity (toward proton donors) and markedly lower H⁺ affinity of PhN⁻ compared to \( c-C_5H_4^- \) should make possible a much larger number and types of neutral molecules with which to study in ion-molecule reactions. Our first such study was with several \( \alpha,\beta \)-unsaturated molecules. With a suitable, nucleophilic hypovalent anion radical, it appeared possible that the competitive 1,2- and 1,4-addition reaction could be observed since such a reagent undergoes the sequence of addition followed by fragmentation. The four product forming reaction channels associated with addition/fragmentation are shown in eqs. (5) - (8). Since both 1,4- and 1,2-addition/fragmentation processes (eqs. 6 and 7)

\[
\begin{align*}
\text{Y}^- + H_2C=CH-C-R & \rightarrow \text{Y}^-CH_2=CH-C-R + H^+ \quad (5) \\
& \rightarrow \text{Y}^-H_2C=CH-C-R + \text{Y}^-CH-CH-C-R + H^+ (M-H) \\
& \rightarrow \text{Y}^-H_2C=CH-C-R + \text{Y}^-CH-CH-C=O + R^- (M-R) \\
& \rightarrow \text{H}_2\text{C}=\text{CH-C}-\text{Y}^- + \text{R}^- (M-R)' \\
& \rightarrow \text{H}_2\text{C}=\text{CH-C}-\text{Y}^- + \text{R}^- (M-R)' \\
& \rightarrow \text{Y}^-C-R + \cdot \text{CH}=\text{CH}_2 (M-C_2H_3) \\
\end{align*}
\]

could conceivably yield isomeric (M-R) and (M-R)' adducts, the test for 1,2-addition would be observation of the (M-C₂H₃) ion.

As expected, the reaction of PhN⁻ with \( H_2C=CHCN \) occurred rapidly \( (k = (1.4 \pm 0.2) \times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}) \) and exclusively by 1,4-addition/fragmentation yielding the (M-H) adduct. With \( H_2C=CHCO_2CH_3 \) as the neutral
reactants, a slower reaction was observed \(((5.9 \pm 0.2) \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1})\) yielding 90% of \(\text{H}_2\text{C}=\text{CHCONPh}^- \text{ (M-OCH}_3\text{)}\) and 10% \(\text{PhNCHCO}_2\text{CH}_3 \text{ (M-H)}\). At this time, we are unable to tell whether \(\text{M-OCH}_3\) is \(\text{M-R}\) (as structure is given) or \(\text{M-R}'\) (eqs. 6 and 7).

The reaction between \(\text{PhN}^-\) and methyl vinyl ketone produced three product ions from addition/fragmentation processes, \(\text{M-CH}_3\) (82%), \(\text{M-C}_2\text{H}_3\) (5%), and \(\text{M-H}\) (2%), and the product of proton transfer \(\text{CH}_2=\text{CHCOCH}_2^-\) (11%). Observation of the \(\text{M-C}_2\text{H}_3\) product ion requires the 1,2-addition/fragmentation mechanism via the tetrahedral intermediate of eq. 8. We have further shown that the \(\text{M-CH}_3\) adduct has the structure of the \(\text{M-R}'\) adduct of eq. (7) which is also formed from this same tetrahedral intermediate. The structure of the \(\text{M-CH}_3\) adduct was identified by determining its proton affinity, which is calculated to be considerably smaller than that of the \(\text{M-R}\) adduct formed by eq. (6). Thus, 97% of the addition processes occurring in the reaction of \(\text{PhN}^-\) with \(\text{H}_2\text{C}=\text{CHCOCH}_3\) take place at the \(\text{C}=\text{O}\) group (1,2-addition).

The reaction of \(\text{PhN}^-\) with acrolein is simpler in that only two product ions are observed, the \(\text{M-H}\) (97%) and \(\text{M-C}_2\text{H}_3\) adducts (3%). However, the interpretation of how the \(\text{M-H}\) adduct is produced is more difficult since, in this case, all three of the adducts from eqs. (5)-(7) are \(\text{M-H}\). Determination of the PA of this ion rules out the ketene \(\text{M-R}\) structure as being present. To distinguish between the \(\text{M-H}\) (eq. 5) and \(\text{M-R}'\) (eq. 7) will require preparation of \(\text{H}_2\text{C}=\text{HCDO}\) and determination of whether or not deuterium is incorporated into the adduct. This experiment has not yet been carried out.

Since the results from the reactions of \(\text{PhN}^-\) with \(\text{H}_2\text{C}=\text{CHCOCH}_3\) and \(\text{H}_2\text{C}=\text{CHCHO}\) indicated that the major addition/fragmentation process occurred at the \(\text{C}=\text{O}\) group, we have studied the reactions of \(\text{PhN}^-\) with various aldehydes, ketones, and esters. Omitting the amounts of proton transfer which occur between \(\text{PhN}^-\) and some of these carbonyl containing reactants, we find the following rate constants for addition/fragmentation relative to that measured for acetone.

<table>
<thead>
<tr>
<th>C=O</th>
<th>(k_{rel})</th>
<th>C=O</th>
<th>(k_{rel})</th>
</tr>
</thead>
<tbody>
<tr>
<td>(\text{CH}_3\text{COCH}_3)</td>
<td>1.0</td>
<td>(\text{CH}_3\text{COCOCH}_3)</td>
<td>122</td>
</tr>
<tr>
<td>(\text{CH}_3\text{CHO})</td>
<td>13</td>
<td>(\text{CF}_3\text{COCH}_3)</td>
<td>95</td>
</tr>
<tr>
<td>(\text{CF}_3\text{COCF}_3)</td>
<td>13</td>
<td>(\text{CF}_3\text{CO}_2\text{CH}_3)</td>
<td>176</td>
</tr>
<tr>
<td>(\text{CF}_3\text{COCH}_3)</td>
<td>0.03</td>
<td>(\text{CH}_3\text{CO}_2\text{CH}_3)</td>
<td>0.03</td>
</tr>
</tbody>
</table>
The products of these reactions of PhN\(^{-}\) with carbonyl containing compounds are acyl anilide anions. The relative amounts of PhNCOR\(_1\)^- and PhNCOR\(_2\)^- product ions depend on the bond dissociation energies (D\(_0\)(C-R\(_1\)) and D\(_0\)(C-R\(_2\))) in the tetrahedral adduct in eq. (9) assuming that these addition adducts are at thermal energies.

\[
\text{PhN}^- + R_1\text{C}R_2^- + \text{PhN}^-C-R_1^- + \cdot R_2
\]

Several interesting points emerge from the absolute rate constants and the \(k_{\text{rel}}^{\text{C=O}}\): (a) all of the rate constants are below the Langevin or ADO limits for ion-molecule collisions, (b) a range of almost 6,000 in \(k_{\text{rel}}^{\text{C=O}}\) is observed, (c) in most respects, the relative reactivities of these carbonyl reactants with PhN\(^{-}\) in the gas phase are those observed or expected for nucleophilic additions in solution, (d) the absence of additivity for the substituent effect of the CF\(_3\) group, and (e) the addition/fragmentation process observed with the alicyclic cyclobutanone generates an interesting, new type of anion-radical m/z 133 for future studies.

The large range in \(k_{\text{rel}}^{\text{C=O}}\) observed is unusual in such a series of gas-phase ion-molecule reactions. Assuming a common mechanism of nucleophilic attack by PhN\(^{-}\) in these reactions, a barrier in the addition process is required. Since small, but discernible, ion signals for addition adducts were observed for a slow (CH\(_3\)COCH\(_3\)) and a fast (CF\(_3\)COCF\(_3\)) reactant, it is reasonable to assume that these adducts are tetrahedral anion-radicals rather than loose complexes, and that these addition/fragmentation reactions proceed via such an intermediate.

The fragmentation products from the acyclic carbonyl compounds studied establish the following group fragmentation order from the tetrahedral intermediate in eq. (9):

- CH\(_3\)O- \(\sim\) CH\(_3\)CO- \(\sim\) H- \(\sim\) CH\(_3\)- \(\sim\) CF\(_3\)

and

- CH\(_3\)- \(\sim\) CH\(_2\)=CH-
This fragmentation order, especially that of H, is consistent with the order observed for aldehydes for abstraction of H vs. R by free radicals. This suggests that attachment of two heteroatoms to the central quaternary carbon of these tetrahedral intermediates is similar, in many respects, to having an oxygen doubly-bonded (C=O) to that central carbon.

Through the use of these open-shell hypovalent anion radicals, we are able for the first time to examine a variety of nucleophilic processes common in condensed-phase organic chemistry. Such studies with conventional, closed-shell nucleophiles would either be very difficult or impossible to carry out in the gas phase.

Although the simple alcohols CH₃OH, C₂H₅OH, and (CH₃)₃COH cannot directly protonate PhN⁻, they do react initially to form clusters (as with c=C₅H₅⁻). The clusters then undergo a second bimolecular reaction with an ROH molecule in a cluster-to-cluster anion switch process yielding PhNH⁺ and RO⁻(HOR). This is followed by further clustering of RO⁻(HOR).

\[
\begin{align*}
\text{PhN}^- + \text{ROH} & \rightarrow \text{PhN}^-(\text{HOR}) \\
& \quad \uparrow \text{ROH} \\
& \quad \text{PhNH}^+ \\
& \quad + \\
& \text{RO}^-(\text{HOR})_2 \leftarrow \text{ROH} \quad \text{RO}^-(\text{HOR})
\end{align*}
\]

An even more dramatic sequence is seen in the reaction between PhN⁻ with H₂O given in eq. (11). In this case, the endothermicity of proton transfer

\[
\begin{align*}
\text{PhN}^- + \text{H}_2\text{O} & \rightarrow \text{PhN}^-\text{(H}_2\text{O}) \quad \text{H}_2\text{O} \\
& \rightarrow \text{PhN}^-\text{(H}_2\text{O})_2 \quad \text{H}_2\text{O} \\
& \quad \uparrow \text{H}_2\text{O} \\
& \quad \text{PhNH}^+ \\
& \quad + \\
& \text{HO}^-(\text{H}_2\text{O})_4 \leftarrow \text{HO}^-(\text{H}_2\text{O})_3 \leftarrow \text{HO}^-(\text{H}_2\text{O})_2
\end{align*}
\]

cannot be overcome in the binding energy of HO⁻(H₂O)ₓ until x = 2.
III. List of publications


R. N. McDonald and A. K. Chowdhury, "Identification of Nucleophilic 1,2- and 1,4-Addition Processes with \( \alpha, \beta \)-Unsaturated Molecules in the Gas Phase", J. Am. Chem. Soc., 102, 6146 (1980).


Figure 1. Ion preparation region of flowing afterglow apparatus.
Figure 2. Differentially pumped analysis section of flowing afterglow apparatus
Figure 3. Semi-log plot of the reaction of cyclopentadienyl anion with 2,2,2-trifluoroethanol