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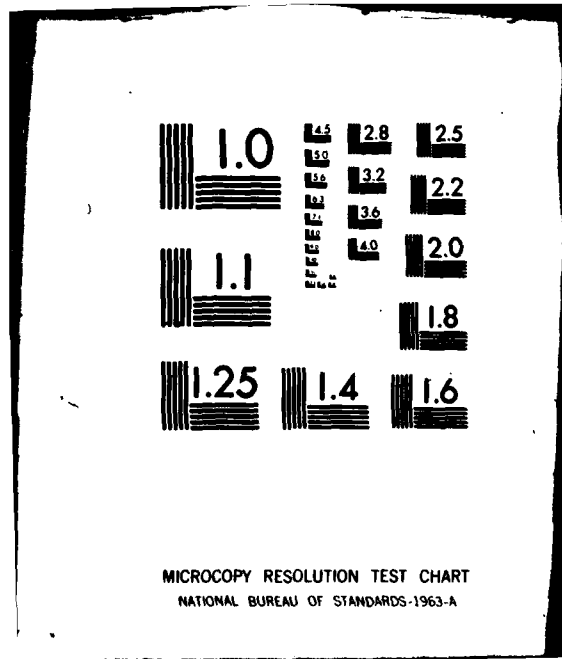
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RICHARD N. MCDONALD and DONALD W. SETSER

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20. ABSTRACT (Continue on reverse side if necessary and identify by block number) Following construction and testing of a flowing afterglow (FA) apparatus, two hypoivalent anion radicals, cyclopentadienylidene ⁻ ($\underline{c-C_5H_4}^-$) 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 PA's and ΔH_f° 's of $\underline{c-C_5H_4}^-$ and PhN^- were obtained as well as limits of their		

20.

hydrogen atom affinities. Compared to cyclopentadienyl anion ($\underline{c}\text{-C}_5\text{H}_5^-$), $\underline{c}\text{-C}_5\text{H}_4^-$ is a much stronger Bronsted base and a somewhat stronger nucleophile in both $\text{S}_{\text{N}}2$ displacement and conjugate (1,4) addition reactions. Since PhN^- has smaller H^+ and $\text{H}\cdot$ affinities than $\underline{c}\text{-C}_5\text{H}_4^-$, 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 $\text{C}=\text{O}$) is followed by a radical β -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 $\text{C}=\text{O}$ containing compound. From the group fragmentation order ($\text{CH}_3\text{O}\cdot > \text{CH}_3\text{CO}\cdot > \text{H}\cdot > \text{CH}_3\cdot > \text{CF}_3\cdot$), the $\text{D}^\circ(\text{C}-\text{R})$ of the anion-radical addition intermediate must be similar to those of the starting $\text{C}=\text{O}$ 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 $\text{PhNH}\cdot + \text{RO}^-(\text{HOR})$.

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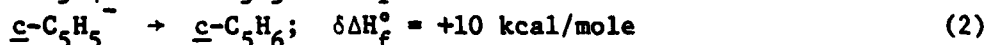
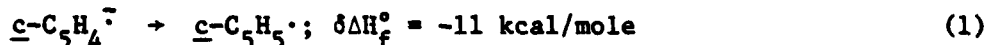
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I. Construction and testing of the flowing afterglow apparatus (FA) was accomplished in the first 1.9 years of the 3-year grant period. Certain features of the FA distinguish it from those used by other investigators: (1) the quadrupole mass spectrometer (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 ($\underline{c}\text{-C}_5\text{H}_4\bar{\cdot}$), (b) cyclopentadienyl anion ($\underline{c}\text{-C}_5\text{H}_5^-$), and (c) phenyl-nitrene anion radical ($\text{PhN}\bar{\cdot}$). Our usual reaction conditions are helium as the buffer gas, $P_{\text{He}} = 0.5$ torr, $\bar{v} = 80 \text{ m s}^{-1}$, and 298 K. The results from each of these studies are outlined below.

(a) $\underline{c}\text{-C}_5\text{H}_4\bar{\cdot}$ was produced from diazocyclopentadiene ($\underline{c}\text{-C}_5\text{H}_4\text{N}_2$) by dissociative electron attachment. Increasing the flow (concentration) of $\underline{c}\text{-C}_5\text{H}_4\text{N}_2$ past the ionizer showed the presence of three negative ions in the helium buffer gas flow, $\underline{c}\text{-C}_5\text{H}_4\bar{\cdot}$ (>98%), $\underline{c}\text{-C}_5\text{H}_4 = \underline{c}\text{-C}_5\text{H}_4\bar{\cdot}$ (m/z 128, <1%), and $\underline{c}\text{-C}_5\text{H}_4\text{N} = \underline{c}\text{-C}_5\text{H}_4\bar{\cdot}$ (m/z 156, 1%). The latter two ions were shown to result from primary reactions of $\underline{c}\text{-C}_5\text{H}_4\bar{\cdot}$ with $\underline{c}\text{-C}_5\text{H}_4\text{N}_2$ by similar processes described for the solution reactions of carbene anion radicals with their parent diazo compounds.

The $\text{PA}(\underline{c}\text{-C}_5\text{H}_4\bar{\cdot}) = 378 \pm 2$ kcal/mole was determined by ion-molecule bracketing reactions of $\underline{c}\text{-C}_5\text{H}_4\bar{\cdot}$ with various alcohols. From this value, $\Delta H_f^\circ(\underline{c}\text{-C}_5\text{H}_4\bar{\cdot}) = 71 \pm 3$ kcal/mole is calculated. The increased basicity of $\underline{c}\text{-C}_5\text{H}_4\bar{\cdot}$ compared to that of the corresponding carbanion $\underline{c}\text{-C}_5\text{H}_5^-$ ($\delta\text{PA} = 21$ kcal/mole) results from the $\delta\Delta H_f^\circ$'s of these two anions and their respective neutral products of protonation:



Experiments to determine the $\text{H}\cdot$ affinity (HA) of $\underline{c}\text{-C}_5\text{H}_4\bar{\cdot}$ were not as successful as those yielding it PA. It appears that a barrier exists in the $\text{H}\cdot$ abstraction reactions of $\underline{c}\text{-C}_5\text{H}_4\bar{\cdot}$. However, a lower limit of this physical property is obtained from the reaction with CH_3OH which occurs rapidly and exclusively by $\text{H}\cdot$ abstraction from the O-H group. This yields $\Delta H_f^\circ(\underline{c}\text{-C}_5\text{H}_4\bar{\cdot}) \geq 68 \pm 3$ kcal/mole, in good agreement with the value calculated from the PA data.

$\underline{c}\text{-C}_5\text{H}_4\bar{\cdot}$ undergoes addition/fragmentation reactions with $\text{H}_2\text{C}=\text{CH}-\text{X}$ molecules. With $\text{X}=\text{CN}$ and CO_2CH_3 , the principal product channel yields the (M-H) adduct of

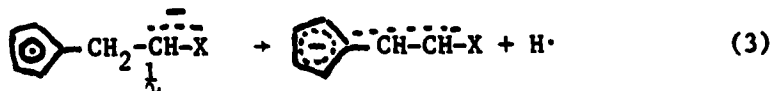
conjugate addition. With vinyl chloride (X=Cl), the exclusive formation of Cl^- is also considered to be formed by conjugate addition followed by fragmentation and rearrangement of the neutral species. No reaction was observed between $\underline{\text{C}}\text{-C}_5\text{H}_4^-$ with vinyl fluoride or ethylene. Comparison of the relative rate constants of these reactions requires that $\underline{\text{C}}\text{-C}_5\text{H}_4^-$ adds as a nucleophile (not a radical).

The ionization potential of $\underline{\text{C}}\text{-C}_5\text{H}_4^- = \text{EA}(\underline{\text{C}}\text{-C}_5\text{H}_4)$ was bracketed as $\leq 54 \pm 2$, $\geq 41.5 \pm 7$ kcal/mole by studies of its ability to electron transfer to neutral reactants.

The cyclic structure and electronic configuration ($\sigma^1\pi^2$) of $\underline{\text{C}}\text{-C}_5\text{H}_4^-$ were established by its reaction with CH_3OH yielding $\underline{\text{C}}\text{-C}_5\text{H}_5^-$ (same ion as produced from $\underline{\text{C}}\text{-C}_5\text{H}_6 + \text{CH}_3\text{O}^-$), and its PA cannot be that predicted for the alternative $\sigma^2\pi^1$ electronic configuration.

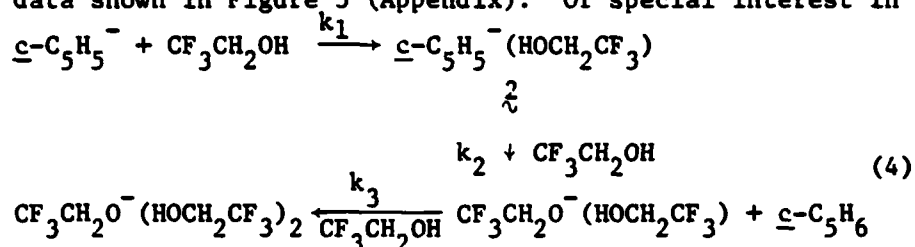
(b) The study of the carbanion $\underline{\text{C}}\text{-C}_5\text{H}_5^-$ was carried out to compare/contrast with those results observed for the carbene anion radical $\underline{\text{C}}\text{-C}_5\text{H}_4^-$. We have already noted that $\underline{\text{C}}\text{-C}_5\text{H}_4^-$ is a much stronger base toward proton donors than is $\underline{\text{C}}\text{-C}_5\text{H}_5^-$ ($\delta\text{PA} = 21$ kcal/mole). Also, $\underline{\text{C}}\text{-C}_5\text{H}_4^-$ was found to be kinetically a more powerful nucleophile with methyl halides ($\text{S}_{\text{N}}2$) and $\text{H}_2\text{C}=\text{CH-X}$ (conjugate addition) by k_{rel} of 60 - 100. The increased nucleophilicity of $\underline{\text{C}}\text{-C}_5\text{H}_4^-$ compared to $\underline{\text{C}}\text{-C}_5\text{H}_5^-$ as with the greater PA of $\underline{\text{C}}\text{-C}_5\text{H}_4^-$, 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 $\underline{\text{C}}\text{-C}_5\text{H}_4^-$ vs $\underline{\text{C}}\text{-C}_5\text{H}_5^-$ 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 $\underline{\text{C}}\text{-C}_5\text{H}_4^-$ or $\underline{\text{C}}\text{-C}_5\text{H}_5^-$ with α, β -unsaturated molecules, e.g. $\text{H}_2\text{C}=\text{CHCN}$ and $\text{H}_2\text{C}=\text{CHCO}_2\text{CH}_3$. With $\underline{\text{C}}\text{-C}_5\text{H}_4^-$, the ion-molecule reaction products from both substrates were the (M-H) anion adducts. However, $\underline{\text{C}}\text{-C}_5\text{H}_5^-$ reacted with $\text{H}_2\text{C}=\text{CHCN}$ to yield $\underline{\text{C}}\text{-C}_5\text{H}_5\text{CH}_2\text{CHCN}^-$, the (M) adduct, and with $\text{H}_2\text{C}=\text{CHCO}_2\text{CH}_3$ to produce $\underline{\text{C}}\text{-C}_5\text{H}_4\text{CHCHCO}_2\text{CH}_3^-$, the (M-2H) adduct. These results establish the "special" and useful nature of the addition/fragmentation reactions of $\underline{\text{C}}\text{-C}_5\text{H}_4^-$ with these α, β -unsaturated molecules. If we assume nucleophilic addition takes place to yield intermediate I , the radical β -fragmentation reaction producing the (M-H)



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 ($\Delta H_{\text{acid}}^\circ$) of CH_3OH , $\text{C}_2\text{H}_5\text{OH}$, $(\text{CH}_3)_3\text{COH}$, $\text{CF}_3\text{CH}_2\text{OH}$, and $\underline{\text{C}}\text{-C}_5\text{H}_6$, these alcohols cannot directly protonate $\underline{\text{C}}\text{-C}_5\text{H}_5^-$. Therefore, we were surprised to find that a reasonably fast reaction ($k_1 = (2.7 \pm 0.2) \times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$) was observed between $\underline{\text{C}}\text{-C}_5\text{H}_5^-$ and $\text{CF}_3\text{CH}_2\text{OH}$ and that the major reaction products were the clusters $\text{CF}_3\text{CH}_2\text{O}^-(\text{HOCH}_2\text{CF}_3)_n$ 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 $\text{CF}_3\text{CH}_2\text{O}^-(\text{HOCH}_2\text{CF}_3)$ is that derived from N of $(\text{IN})^-$, not I^- . This anion-switching mechanism accounts for the absence of the unsolvated $\text{CF}_3\text{CH}_2\text{O}^-$ 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_1 is the observed decay constant for $\underline{\text{C}}\text{-C}_5\text{H}_5^-$. It is the extra binding energy of $\text{CF}_3\text{CH}_2\text{O}^-(\text{HOCH}_2\text{CF}_3)$ over that of cluster 2 that allows step 2 to occur; the direct proton transfer from $\text{CF}_3\text{CH}_2\text{OH}$ to $\underline{\text{C}}\text{-C}_5\text{H}_5^-$ is endothermic by 8.3 ± 3 kcal/mole.

Anion $\underline{\text{C}}\text{-C}_5\text{H}_5^-$ also formed 1:1 clusters with CH_3OH , $\text{C}_2\text{H}_5\text{OH}$, and $(\text{CH}_3)_3\text{COH}$. However, the anion-switching reactions of these clusters with a second alcohol molecule were not observed. The endoergicities of the direct proton transfers between $\underline{\text{C}}\text{-C}_5\text{H}_5^-$ and these alcohols vary from 17 ± 3 to 23 ± 3 kcal/mole. Apparently, the binding energies of these homoconjugate clusters ($\text{RO}^-(\text{HOR})$) are not sufficient to overcome the endoergicity of the proton transfer process.

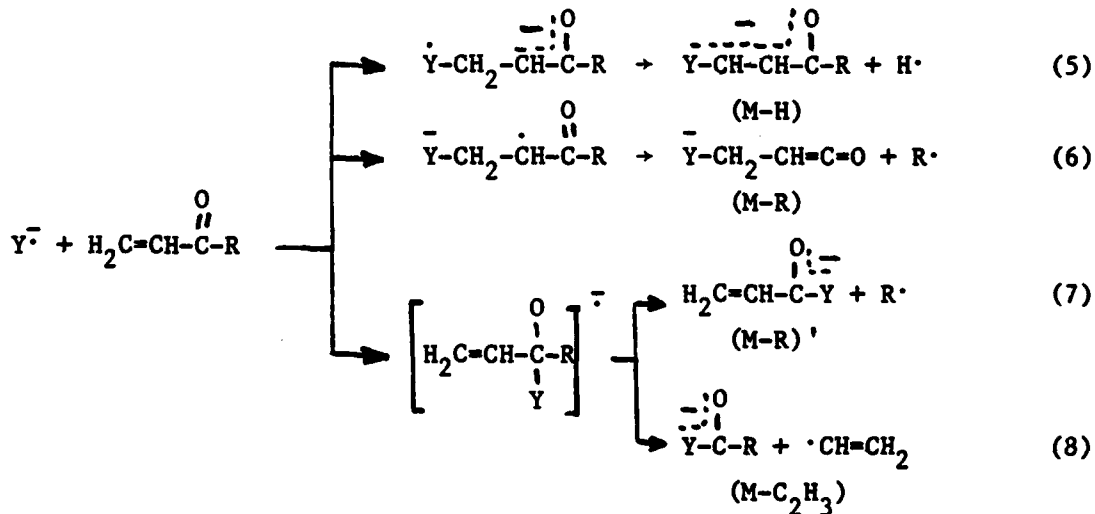
We believe that these gas-phase results and the proposed mechanism for protonation of $\underline{\text{C}}\text{-C}_5\text{H}_5^-$ by $\text{CF}_3\text{CH}_2\text{OH}$ closely mimic this reaction in solution. In solution the proton donor would be the solvate $\text{CF}_3\text{CH}_2\text{OH}(\text{HOCH}_2\text{CF}_3)_x$,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

(c) Phenylnitrene 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, $\text{PA}(\text{PhN}^-) = 372 \pm 2$ kcal/mole was determined, which gives $\Delta H_f^\circ(\text{PhN}^-) = 60 \pm 2$ 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^o(PhN⁻-H) ≤ 96 kcal/mole.

PhN⁻ was shown to react slowly with PhN₃ giving two products, C₁₂H₁₀N₄⁻ and C₁₂H₁₀N₂⁻, 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=NPh⁻ is directly related to formation of azine anion radicals (R₂C=N=N=CR₂⁻) from the reaction of R₂C⁻ with R₂CN₂ 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-C₅H₄⁻ 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 α,β-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)



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 H₂C=CHCN occurred rapidly (k = (1.4 ± 0.2) × 10⁻¹⁰ cm³ molecule⁻¹ s⁻¹) and exclusively by 1,4-addition/fragmentation yielding the (M-H) adduct. With H₂C=CHCO₂CH₃ 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 $\text{H}_2\text{C}=\text{CHCONPh}^-$ (M-OCH₃) and 10% $\text{PhNCHCHCO}_2\text{CH}_3$ (M-H). At this time, we are unable to tell whether (M-OCH₃) is (M-R) (as structure is given) or (M-R)' (eqs. 6 and 7).

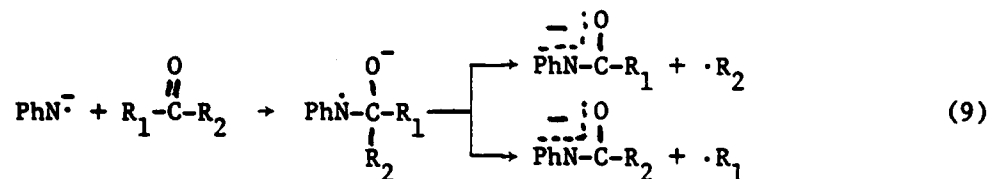
The reaction between PhN^- and methyl vinyl ketone produced three product ions from addition/fragmentation processes, (M-CH₃) (82%), (M-C₂H₃) (5%), and (M-H) (2%), and the product of proton transfer $\text{CH}_2=\text{CHCOCH}_2^-$ (11%). Observation of the (M-C₂H₃) product ion requires the 1,2-addition/fragmentation mechanism via the tetrahedral intermediate of eq. 8. We have further shown that the (M-CH₃) adduct has the structure of the (M-R)' adduct of eq. (7) which is also formed from this same tetrahedral intermediate. The structure of the (M-CH₃) adduct was identified by determining its proton affinity, which is calculated to be considerably smaller than that of the (M-R) adduct formed by eq. (6). Thus, 97% of the addition processes occurring in the reaction of PhN^- with $\text{H}_2\text{C}=\text{CHCOCH}_3$ take place at the C=O group (1,2-addition).

The reaction of PhN^- with acrolein is simpler in that only two product ions are observed, the (M-H) (97%) and (M-C₂H₃) adducts (3%). However, the interpretation of how the (M-H) adduct is produced is more difficult since, in this case, all three of the adducts from eqs. (5)-(7) are (M-H). Determination of the PA of this ion rules out the ketene (M-R) structure as being present. To distinguish between the (M-H) (eq. 5) and (M-R)' (eq. 7) will require preparation of $\text{H}_2\text{C}=\text{CHCDO}$ and determination of whether or not deuterium is incorporated into the adduct. This experiment has not yet been carried out.

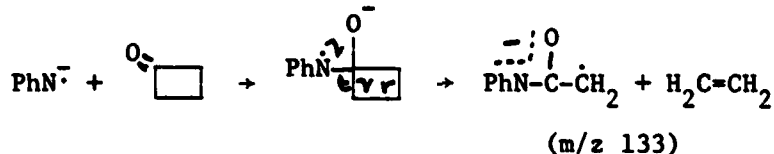
Since the results from the reactions of PhN^- with $\text{H}_2\text{C}=\text{CHCOCH}_3$ and $\text{H}_2\text{C}=\text{CHCHO}$ indicated that the major addition/fragmentation process occurred at the C=O group, we have studied the reactions of PhN^- with various aldehydes, ketones, and esters. Omitting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

	$k_{\text{rel}}^{\text{C=O}}$		$k_{\text{rel}}^{\text{C=O}}$
CH_3COCH_3	1.0	$\text{CH}_3\text{COCOCH}_3$	122
CH_3CHO	14	 =O	13
CF_3COCF_3	95	$\text{CF}_3\text{CO}_2\text{CH}_3$	176
CF_3COCH_3	88	$\text{CH}_3\text{CO}_2\text{CH}_3$	0.03

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 ($D^\circ(\text{C-R}_1)$ and $D^\circ(\text{C-R}_2)$) in the tetrahedral adduct in eq. (9) assuming that these addition adducts are at thermal energies.

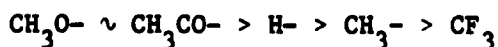


Several interesting points emerge from the absolute rate constants and the $k_{\text{rel}}^{\text{C=O}}$: (a) all of the rate constants are below the Langevin or ADO limits for ion-molecule collisions, (b) a range of almost 6,000 in $k_{\text{rel}}^{\text{C=O}}$ is observed, (c) in most respects, the 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.

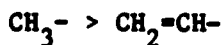


The large range in $k_{\text{rel}}^{\text{C=O}}$ observed is unusual in such a series of gas-phase ion-molecule reactions. Assuming a common mechanism of nucleophilic attack by PhN^- in these reactions, a barrier in the addition process is required. Since small, but discernible, ion signals for addition adducts were observed for a slow (CH_3COCH_3) and a fast (CF_3COCF_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):



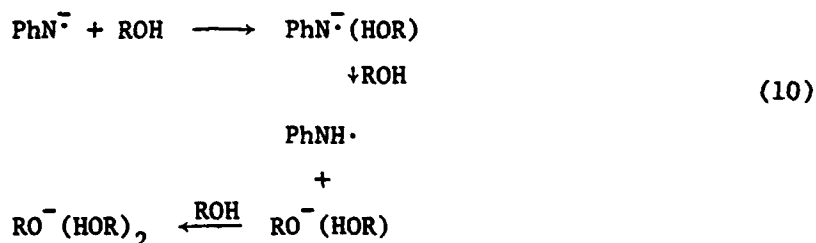
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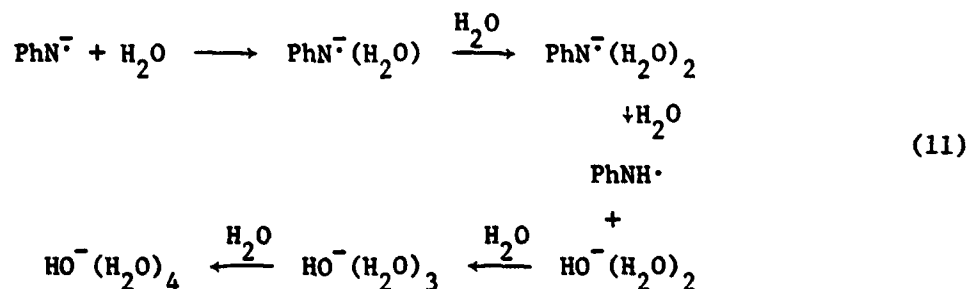
This fragmentation order, especially that of H, is consistent with the order observed for aldehydes for abstraction of H vs. R by free radicals. This suggests that attachment of two heteroatoms to the central quaternary carbon of these tetrahedral intermediates is similar, in many respects, to having 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 CH_3OH , $\text{C}_2\text{H}_5\text{OH}$, and $(\text{CH}_3)_3\text{COH}$ cannot directly protonate PhN^- , they do react initially to form clusters (as with $\underline{\text{C}}_5\text{H}_5^-$). The clusters then undergo a second bimolecular reaction with an ROH molecule in a cluster-to-cluster anion switch process yielding $\text{PhNH}\cdot$ and $\text{RO}^-(\text{HOR})$. This is followed by further clustering of $\text{RO}^-(\text{HOR})$.



An even more dramatic sequence is seen in the reaction between PhN^- with H_2O given in eq. (11). In this case, the endothermicity of proton transfer



cannot be overcome in the binding energy of $\text{HO}^-(\text{H}_2\text{O})_x$ until $x = 2$.

III. List of publications

R. N. McDonald, A. K. Chowdhury, and D. W. Setser, "Importance of Solvation on the Gas-Phase Proton-Transfer Reaction between Cyclopentadienyl Anion and Alcohols," J. Am. Chem. Soc., 102, 4836 (1980).

R. N. McDonald and A. K. Chowdhury, "Gas-Phase Generation of Phenylnitrene Anion Radical and Its Reaction with Phenyl Azide", J. Am. Chem. Soc., 102, 5118 (1980).

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

R. N. McDonald, A. K. Chowdhury, and D. W. Setser, "Gas-Phase Studies of the Ion-Molecule Reactions of Cyclopentadienylidene Anion Radical in a Flowing Afterglow", J. Am. Chem. Soc., 102, in press (1980).

R. N. McDonald and A. K. Chowdhury, "Gas-Phase Nucleophilic Addition Reactions of Phenylnitrene Anion Radical with Certain Carbonyl Containing Molecules," J. Am. Chem. Soc., submitted.

R. N. McDonald, A. K. Chowdhury, and D. W. Setser, "On the Mechanism of the Riveros Reaction", in preparation.

R. N. McDonald, A. K. Chowdhury, and D. W. Setser, "Preparation of Phenylnitrene Anion Radical in the Gas Phase and Determination of Its PA and ΔH_f° ", in preparation.

R. N. McDonald, A. K. Chowdhury, and D. W. Setser, "Gas-Phase Ion-Molecule Reactions of Cyclopentadienyl Anion," in preparation.

APPENDICES

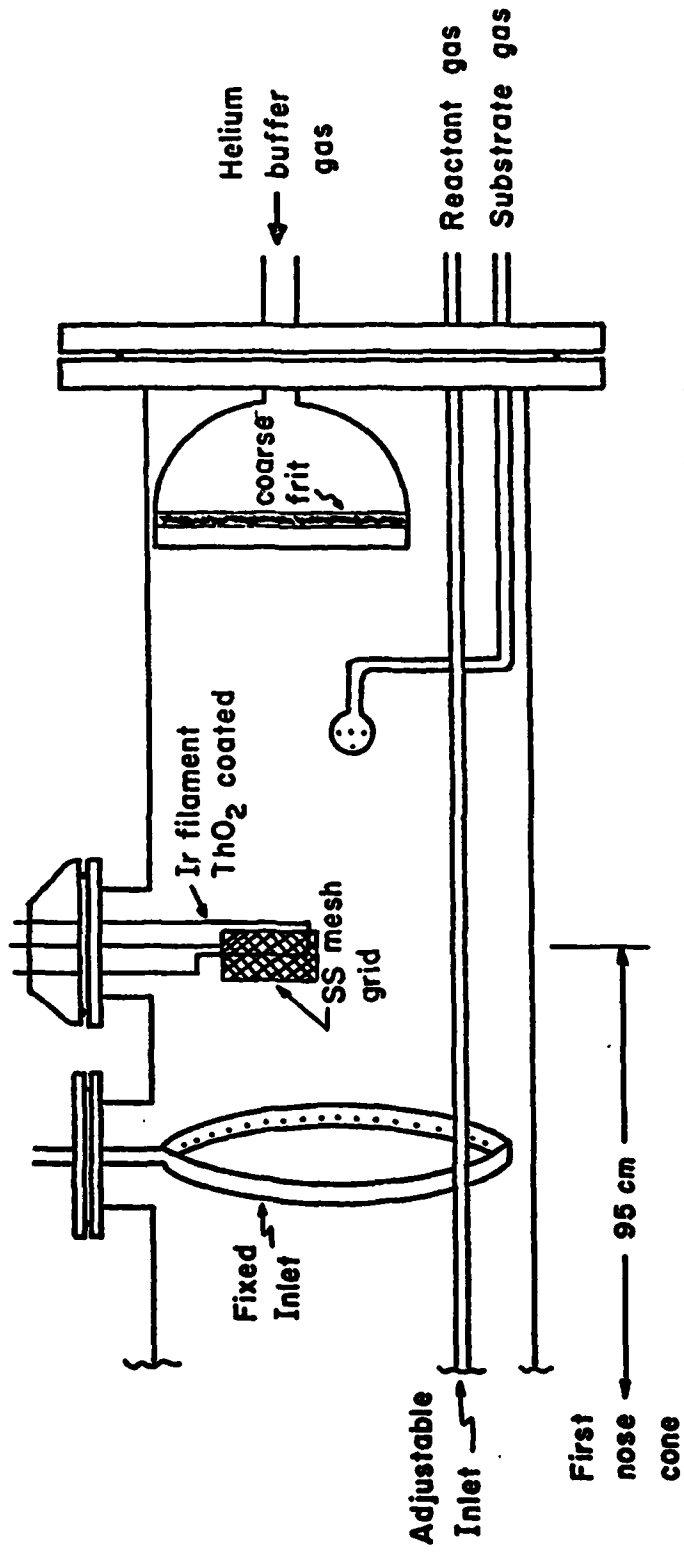


Figure 1. Ion preparation region of flowing afterglow apparatus.

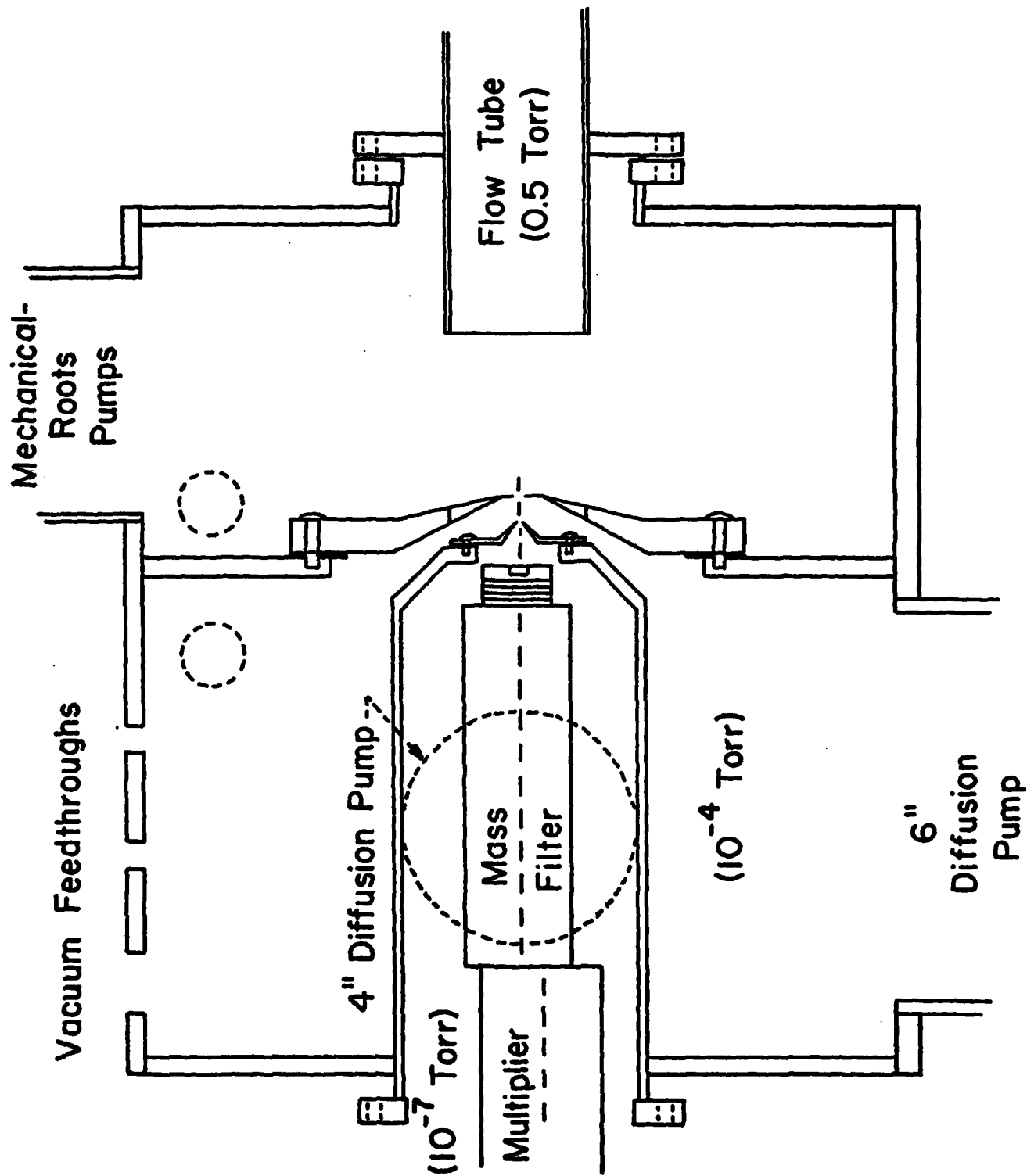


Figure 2. Differentially pumped analysis section of flowing afterglow apparatus

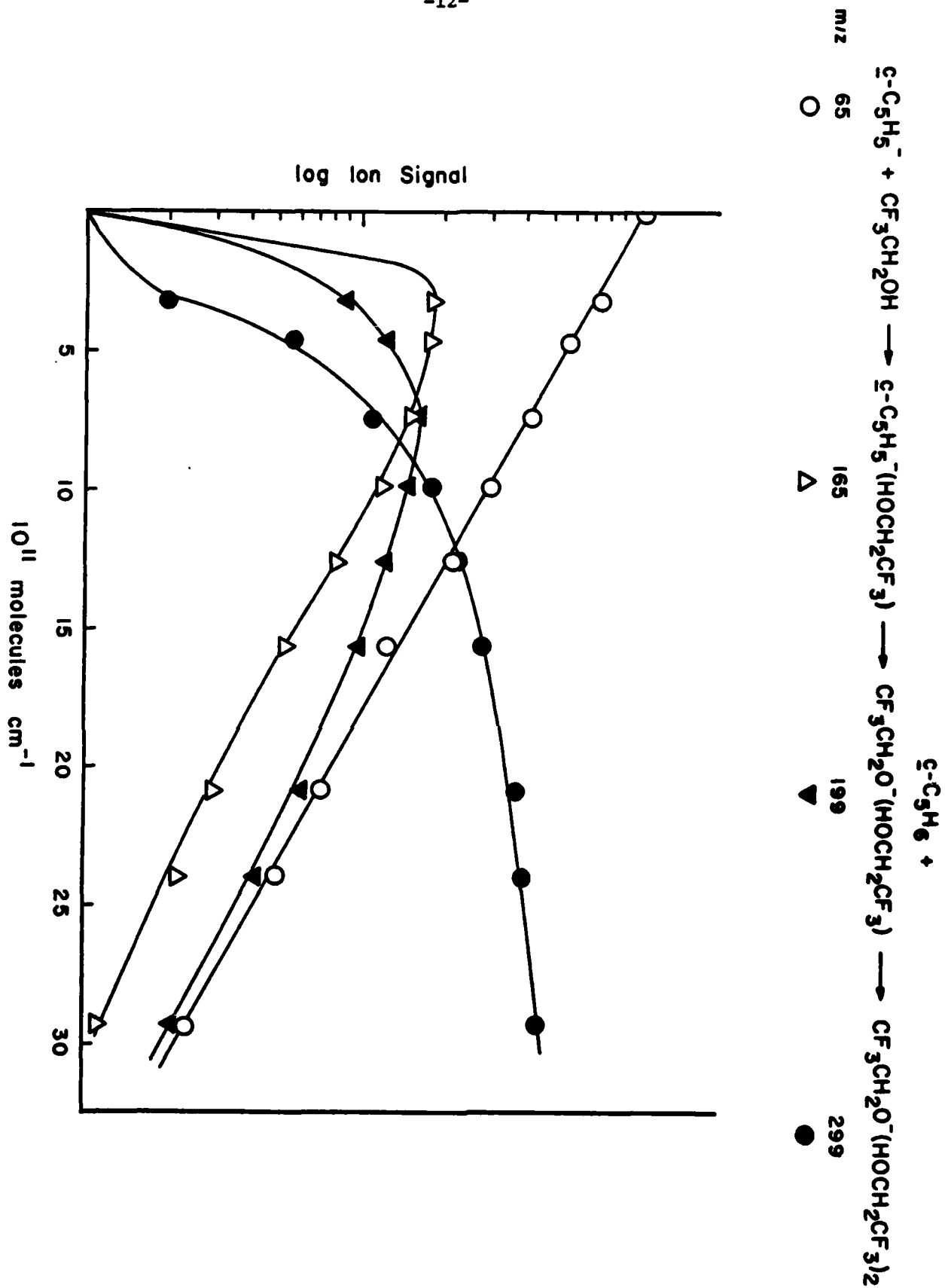


Figure 3. Semi-log plot of the reaction of cyclopentadienyl anion with 2,2,2-trifluoroethanol