

between the order of overtone intensities and the Franck–Condon factors.

### Conclusion

The present study of the  $[\text{MnO}_4]^-$  ion illustrates the potential of resonance Raman band excitation profiles in determining the nature and magnitude of geometric changes in simple species consequent on excitation from the ground to the relevant excited state. These changes are more accurately defined in this way than they are from the absorption spectrum since the excitation profiles relate to a single mode and are thus better resolved than an absorption spectrum, which consists of a convolution of bands

arising from a variety of vibrational modes. The change so deduced in the equilibrium MnO bond length for the  $[\text{MnO}_4]^-$  ion on  ${}^1\text{T}_2 \leftarrow {}^1\text{A}_1$  excitation ( $\sim 9.1$  pm) is nevertheless similar to that estimated from the intensity distribution of the vibronic components of the  ${}^1\text{T}_2 \leftarrow {}^1\text{A}_1$  absorption band ( $\sim 10$  pm).<sup>9</sup>

**Acknowledgment.** We thank the Science Research Council and the University of London for financial support, the Ramsay Memorial Fellowships Trust for a fellowship (to B.S.), and Dr. D. G. Cobbold for carrying out some of the experimental work.

(9) Ballhausen, C. J. *Theoret. Chim. Acta* 1963, 1, 285.

## Gas-Phase Generation of Phenylnitrene Anion Radical—Proton Affinity and $\Delta H_f^\circ$ of $\text{PhN}^-$ and Its Clustering with ROH Molecules<sup>1</sup>

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**Abstract:** Phenylnitrene anion radical ( $\text{PhN}^-$ ) was prepared in a flowing afterglow apparatus by dissociative electron attachment to phenyl azide ( $\text{PhN}_3$ ).  $\text{PhN}^-$  undergoes a very slow reaction with  $\text{PhN}_3$ , producing  $\text{PhN}_4\text{Ph}^-$  and  $\text{PhN}_2\text{Ph}^-$  in a ratio of 4:1. The proton affinity of  $\text{PhN}^-$  was bracketed from kinetic studies with various potential proton donors,  $\text{PA}(\text{PhN}^-) = 372 \pm 2$  kcal mol<sup>-1</sup>, from which  $\Delta H_f^\circ(\text{PhN}^-) = 60 \pm 2$  kcal mol<sup>-1</sup> was calculated. With alcohols which are too weakly acidic to directly protonate  $\text{PhN}^-$  [ $\text{CH}_3\text{OH}$ ,  $\text{C}_2\text{H}_5\text{OH}$ ,  $n\text{-C}_3\text{H}_7\text{OH}$ , and  $(\text{CH}_3)_3\text{COH}$ ], a sequence of bimolecular reactions is observed involving  $\text{ROH}$ ;  $\text{PhN}^- \rightarrow \text{PhN}^-(\text{HOR}) \rightarrow \text{PhNH} \cdot + \text{RO}^-(\text{HOR}) \rightarrow \text{RO}^-(\text{HOR})_x$ . Although the first step of the sequence is slow, the second step, a cluster-to-cluster transformation, is fast. The related reaction sequence of  $\text{PhN}^-$  reacting with  $\text{HOH}$  involves the ions  $\text{PhN}^- \rightarrow \text{PhN}^-(\text{HOH}) \rightarrow \text{PhN}^-(\text{HOH})_2 \rightarrow \text{PhNH} \cdot + \text{HO}^-(\text{HOH})_2 \rightarrow \text{HO}^-(\text{HOH})_x$  with the third reaction as the fast step. The relationship of these sequential processes to acidities and basicities found in solution is discussed. Of the five observed reaction channels for  $\text{PhN}^-$  with  $\text{CH}_3\text{CN}$ , the major channel yields the adduct  $m/z$  132 and a minor channel produces the  $M - 1$  species,  $m/z$  131. Additions by  $\text{PhN}^-$  to  $\text{C}_\alpha$  or N or  $\text{CH}_3\text{CN}$  are considered to account for these product anions. The reaction of  $\text{PhN}^-$  with  $(\text{CH}_3)_3\text{CCN}$  also yields its adduct.

In the physical-organic chemistry of heteroatom-centered hypovalent ion radicals, the group 5a elements (N, P, As) are of interest since variations of the single attached alkyl or aryl groups permit studies of changes in the physical and chemical properties of these ion radicals. The simplest member of the series of nitrogen-centered hypovalent anion radicals,  $\text{HN}^-$ , has been generated in the gas phase and thermodynamically characterized.<sup>2</sup> Our previous success in cleanly generating a carbene anion radical,  $\text{c-C}_5\text{H}_4^-$ , by dissociative electron attachment to the corresponding diazo compound,  $\text{c-C}_5\text{H}_4\text{N}_2$ ,<sup>3</sup> led us to consider the isoelectronic organic azides as precursors to nitrene anion radicals. To reduce the potential for  $\text{N}_3^-$  ion formation, as observed from electron attachment to  $\text{HN}_3$ ,<sup>2</sup> an aryl azide with a stronger C– $\text{N}_\alpha$  bond appeared to be desirable. The chemical<sup>4</sup> and electrochemical<sup>5</sup> reductions of phenyl azide ( $\text{PhN}_3$ ) gave products consistent with formation of phenylnitrene anion radical ( $\text{PhN}^-$ ) as the first-formed intermediate. In the present work, we have successfully used the gas-phase electron attachment of  $\text{PhN}_3$  to generate  $\text{PhN}^-$  in a flowing afterglow apparatus and study the room temperature reactions of  $\text{PhN}^-$  with  $\text{PhN}_3$  and potential proton donors. In

later papers, we will report the results of studies of addition reactions of  $\text{PhN}^-$  with various unsaturated molecules.<sup>1</sup>

### Experimental Section

The flowing afterglow used in the investigation has been previously described.<sup>3</sup> Briefly, gas-phase anions are prepared by dissociative electron attachment to neutral reagents added to the helium buffer gas in the upstream end of flow tube. The carrier gas pressure ( $P_{\text{He}}$ ) and flow velocity ( $\bar{v}$ ) were maintained in the stainless steel flow tube ( $120 \times 7.15$  cm i.d.) by a Stokes Roots blower-mechanical pump system (Model 1722-S). However, these two parameters could be varied from  $P_{\text{He}} = 0.2$ –1.2 torr and  $\bar{v} = 36$ –80 m/s by throttling a gate valve and/or altering the helium inlet flow. Our standard operating conditions were  $P_{\text{He}} = 0.5$  torr and  $\bar{v} = 80$  m/s at 298 K.

In the present experiments,  $\text{PhN}_3$  ( $\sim 10^{12}$  molecules cm<sup>-3</sup>) was introduced into the helium buffer gas before the carrier gas flowed past the electron gun. The negative ion composition of the flow monitored with an Extranuclear quadrupole mass spectrometer was  $m/z$  91 ( $\sim 99\%$ ) and  $m/z$  26 ( $\sim 1\%$ ,  $\text{CN}^-$ ). When  $\text{SF}_6$  was added to this flow via a port located 10 cm downstream of the electron gun, no  $\text{SF}_6^-$  signal was observed, indicating high efficiency for electron attachment by the  $\text{PhN}_3$  molecules; furthermore, destruction of the  $\text{He}^*(2^1\text{s})$  atoms generated by the electron gun also must be efficient.

The  $m/z$  91 anions were thermalized by numerous collisions with the buffer gas as they flowed downstream (30 cm). At this point neutral reactant gases,  $Q$ , were added through a fixed inlet 61 cm from the first sampling nose cone; this is the ion–molecule reaction distance (time). Since this distance (time) is held constant during the experiment, variable concentrations of  $Q$  are added and the  $m/z$  91 and product ion signals are recorded at each concentration of  $Q$  added to the flow. The slope from the log  $[\text{PhN}^-]$  vs.  $Q$  concentration plot is then converted into the

(1) Paper 10 in the series "Hypovalent Radicals". For paper 9, see: McDonald, R. N.; Chowdhury, A. K. *J. Am. Chem. Soc.* 1981, 103, 674.

(2) Engelking, P. C.; Lineberger, W. C. *J. Chem. Phys.* 1976, 65, 4323 and references therein.

(3) McDonald, R. N.; Chowdhury, A. K.; Setser, D. W. *J. Am. Chem. Soc.* 1980, 102, 6491.

(4) Kauffman, T.; Hage, S. M. *Angew. Chem., Int. Ed. Engl.* 1963, 2, 156.

(5) McDonald, R. N.; Herbranson, D.; Hawley, M. D., unpublished results.

Table I. Summary of Kinetic and Product Data for Proton-Transfer Reactions to Phenylnitrene Anion Radical

ion + neutral reactants	products [assumed neutral]	fraction of product ion signal	$k_{\text{total}}^a$ cm <sup>3</sup> molecule <sup>-1</sup> s <sup>-1</sup>	$\Delta H^{\circ}_{\text{acid of neutral}}^b$ kcal mol <sup>-1</sup>
PhN <sup>-</sup> + (CF <sub>3</sub> ) <sub>2</sub> CHOH	(CF <sub>3</sub> ) <sub>2</sub> CHO <sup>-</sup> [+ PhNH <sup>·</sup> ]	1.00	$(8.4 \pm 0.5) \times 10^{-10} c$	<351
PhN <sup>-</sup> + CF <sub>3</sub> CH <sub>2</sub> OH	CF <sub>3</sub> CH <sub>2</sub> O <sup>-</sup> [+ PhNH <sup>·</sup> ]	1.00	$(8.8 \pm 0.8) \times 10^{-10} c$	364.4
PhN <sup>-</sup> + CH <sub>3</sub> CHO	CH <sub>2</sub> CHO <sup>-</sup> [+ PhNH <sup>·</sup> ]	0.10 <sup>d</sup>	$(7.4 \pm 0.7) \times 10^{-11} c$	366.4
PhN <sup>-</sup> + CH <sub>3</sub> COCH <sub>3</sub>	CH <sub>2</sub> COCH <sub>3</sub> <sup>-</sup> [+ PhNH <sup>·</sup> ]	0.19 <sup>d</sup>	$(6.4 \pm 0.4) \times 10^{-12} c$	368.8
PhN <sup>-</sup> + CH <sub>3</sub> CO <sub>2</sub> CH <sub>3</sub>	CH <sub>2</sub> CO <sub>2</sub> CH <sub>3</sub> <sup>-</sup> [+ PhNH <sup>·</sup> ]	0.12 <sup>d</sup>	$\sim 1.5 \times 10^{-13}$	371.0
PhN <sup>-</sup> + CH <sub>3</sub> CN	CH <sub>2</sub> CN <sup>-</sup> [+ PhNH <sup>·</sup> ]	0.03 <sup>d</sup>	$(3.2 \pm 0.1) \times 10^{-11} c$	372.2
PhN <sup>-</sup> + (CH <sub>3</sub> ) <sub>2</sub> SO	no reaction		$<10^{-13}$	372.7

<sup>a</sup> Rate constants are for the decay of PhN<sup>-</sup> ion signal and are estimated to be accurate to  $\pm 30\%$ . Errors given are deviations from multiple runs. <sup>b</sup> From ref 13,  $\pm 2$  kcal mol. <sup>c</sup> Increasing  $P_{\text{He}}$  from 0.5 to 1.1 torr produced no change in  $k_{\text{total}}$  or the relative fractions of the product ion signals. <sup>d</sup> See ref 14.

bimolecular ion-molecule reaction rate constant as previously described.<sup>3</sup> The rate constants have ca.  $\pm 5\%$  reproducibility but are considered to have  $\pm 30\%$  absolute uncertainty. Flow rates of neutrals,  $Q$ , are measured by determining the increase of pressure in a calibrated volume as a function of time.

Gas purities and suppliers were as follows: helium, 99.99%, Welder Products; (CF<sub>3</sub>)<sub>2</sub>CHOH, Du Pont; CF<sub>3</sub>CH<sub>2</sub>OH, Halocarbon Products; other alcohols, CH<sub>3</sub>CN, CH<sub>3</sub>CO<sub>2</sub>CH<sub>3</sub>, CH<sub>3</sub>CHO, CH<sub>3</sub>COCH<sub>3</sub>, and (CH<sub>3</sub>)<sub>2</sub>SO, Fisher; (CH<sub>3</sub>)<sub>2</sub>CCN, Aldrich. All liquids were distilled and a center-cut, constant boiling point sample was transferred to a gas storage bulb after three freeze-pump-thaw degassing cycles. The helium buffer gas was purified by passage through two traps filled with Davison 4A molecular sieves cooled with liquid nitrogen and then warmed to room temperature in a glass coil prior to introduction into the flow tube.

**Preparation of Phenyl Azide.** The preparation of PhN<sub>3</sub> from the reaction of PhNHNH<sub>2</sub> + HONO<sup>6</sup> was found to contain small quantities of PhOH as indicated by the presence of  $m/z$  93 (PhO<sup>-</sup>) in our first experiments. The PhOH was readily removed from an ether solution of PhN<sub>3</sub> by extraction with base prior to distillation [bp 30 °C (10 torr)]. PhN<sub>3</sub> was stored in a freezer at -23 °C for up to 40 days with no apparent decomposition. No problems were experienced in the handling of this compound. The glass, gas-phase storage reservoir was covered with black cloth to eliminate photodecomposition.

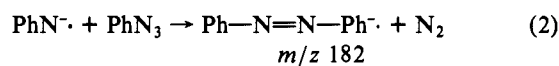
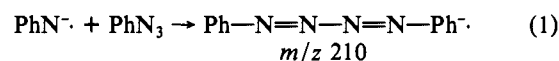
## Results and Discussion

**Generation of Phenylnitrene Anion Radical and Its Reaction with Phenyl Azide.** Dissociative electron attachment with PhN<sub>3</sub> in the flowing afterglow yields  $m/z$  91 along with <1% of a signal  $m/z$  26 attributed to CN<sup>-</sup>. This is in contrast to the anion composition when PhN<sub>3</sub> is added directly to the ionizer region of our quadrupole mass spectrometer ( $\sim 10^{-7}$  torr) with nominal 3.3-eV electron energy where  $m/z$  26 is the major ion observed and  $m/z$  91 is only 7% of the total product signal. The difference presumably is a consequence of the difference in the mean electron energy in the two experiments.

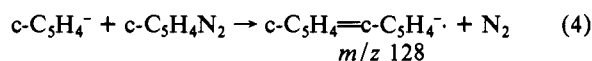
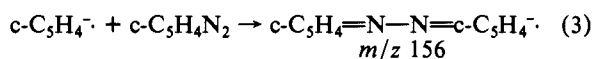
The structure of the anion  $m/z$  91 is assigned as PhN<sup>-</sup> from the following considerations. First, the relative intensity of  $m/z$  91 and its  $M + 1$  isotope signal,  $m/z$  92, is 1/0.070 (theoretical 1/0.069)<sup>7</sup> which establishes that the ions composition is C<sub>6</sub>H<sub>5</sub>N<sup>-</sup>. Addition of an electron to neutral phenylnitrene (PhN) forming the doublet PhN<sup>-</sup> not only removes the multiplicity problem of PhN but reduces the probability for molecular rearrangement in PhN<sup>-</sup> since there is no vacant orbital on N in this open-shell anion radical.<sup>8</sup> The doublet electronic state of PhN<sup>-</sup> is considered to have the electronic configuration of triplet PhN<sup>10</sup> with the ad-

ditional electron placed in the delocalized, out-of-plane 3b<sub>2</sub> orbital. This electronic configuration of PhN<sup>-</sup> has the basic (nucleophilic) pair of electrons and the lone (radical) electron localized on N with a second pair of electrons in the delocalized 3b<sub>2</sub> orbital.

When excess PhN<sub>3</sub> is flowed past the electron gun or is added through the downstream inlet port, a very slow reaction between PhN<sup>-</sup> and PhN<sub>3</sub> occurred ( $k = 2.3 \times 10^{-12}$  cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup>). Two product ions were observed at  $m/z$  182 [ $m/z$  183 ( $M + 1$ ), observed 1:0.151, theory 1:0.141],<sup>7</sup> C<sub>12</sub>H<sub>10</sub>N<sub>2</sub><sup>-</sup>, and  $m/z$  210 [ $m/z$  211 ( $M + 1$ ), observed 1:0.151, theory 1:0.147],<sup>7</sup> C<sub>12</sub>H<sub>10</sub>N<sub>4</sub><sup>-</sup>, in a ratio of 1:4. Increasing the helium pressure and decreasing the flow velocity ( $P_{\text{He}} = 1.2$  torr,  $\bar{v} : 50$  m/s) gave proportionate changes in both product ion signals with no change in the rate constant. Since the rate constant and the product-branching ratio were independent of changes in the flow velocity and pressure, both products must be formed in primary reaction channels and each is a stable, bound structure.



The structure of the ion  $m/z$  182 is assigned as azobenzene<sup>-</sup>, a major product from certain electrochemical reductions of PhN<sub>3</sub>,<sup>5</sup> formed by reaction of PhN<sup>-</sup> at N<sub>α</sub> of PhN<sub>3</sub>. The structure of the major product ion,  $m/z$  210, which incorporates all four nitrogen atoms is assigned as 1,4-diphenyltetraazadiene<sup>-</sup> produced by reaction of PhN<sup>-</sup> at N<sub>γ</sub> of PhN<sub>3</sub>. These structural assignments bear a striking resemblance to the condensation products observed in the reactions of cyclopentadienylidene anion radical (c-C<sub>5</sub>H<sub>4</sub><sup>-</sup>) with its precursor diazo compound (c-C<sub>5</sub>H<sub>4</sub>N<sub>2</sub>).<sup>3</sup> Even the product branching ratio of 1:3 for  $m/z$  128 and 156 (eq 3 and 4) is similar to the ratio observed from the reaction of PhN<sup>-</sup> with PhN<sub>3</sub>.

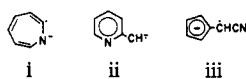


These results suggest that reduction of PhN<sub>3</sub> in the condensed phase may proceed by formation of an (Ph-N=N-)<sub>2</sub><sup>-</sup> species. PhN=NPh<sup>-</sup> could also be produced from (Ph-N=N-)<sub>2</sub><sup>-</sup> by either a stepwise or concerted loss of N<sub>2</sub>. Also, formation of (Ph-N=N-)<sub>2</sub> has been proposed as an intermediate in the reaction of PhN with PhN<sub>3</sub> in the thermal and photochemical decompositions of PhN<sub>3</sub> in solution.<sup>11</sup> Our gas-phase evidence, although dealing with the reduced PhN<sup>-</sup> species, is the first available data suggesting that this proposal may be correct. It is interesting to note that the gas-phase rate constant for the reaction of PhN<sup>-</sup> with PhN<sub>3</sub> (eq 1 and 2) is the same as that reported for the gas-phase reaction of PhN + PhN<sub>3</sub> → PhN=NPh ( $k \approx 10^{12}$  cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup>) where azobenzene formation was monitored.<sup>12</sup> We consider the identity of these rate constants

(6) Lindsay, R. O.; Allen, C. F. H. *Org. Synth. Collect. Vol. III* 1955, 710.

(7) Beynon, J. H.; Williams, A. E. "Mass Abundance Tables for Use in Mass Spectrometry"; Elsevier: New York, 1963.

(8) Alternate molecular structures i, ii, and iii might be considered for C<sub>6</sub>H<sub>5</sub>N<sup>-</sup> using known rearrangement product structures from PhN chemistry.<sup>9</sup> However, all three are readily eliminated as possibilities on the basis of H<sup>+</sup> and H<sup>-</sup> affinities measured for  $m/z$  91 prepared by this method



(9) Wentrup, C. *Top. Curr. Chem.* 1976, 62, 173.

(10) (a) Reiser, A.; Bowes, G.; Horne, R. J. *Trans. Faraday Soc.* 1966, 62, 3162. (b) Berry, R. S. In "Nitrenes"; Lwowski, W., Ed.; Wiley-Interscience: New York, 1970; Chapter 2.

(11) Smith, P. A. S. In "Nitrenes"; Lwowski, W., Ed.; Wiley-Interscience: New York, 1970; Chapter 4.

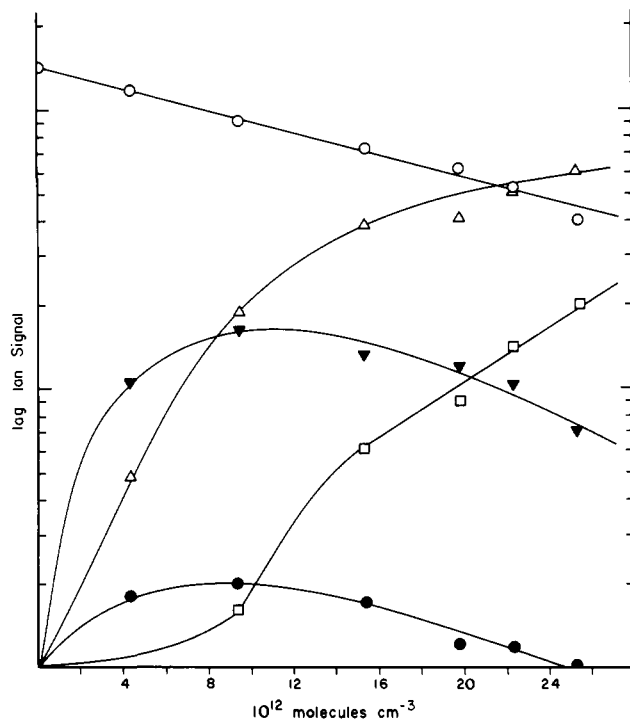


Figure 1. Semilog plot of the decay of PhN<sup>-</sup> (O) and formation of the product ions [*m/z* 123 (●), 63 (▼), 95 (Δ), and 127 (□)] for the reaction of PhN<sup>-</sup> + CH<sub>3</sub>OH vs. added alcohol. Ion signals are in arbitrary units taken directly from the mass spectrometer intensities.

to be more than fortuitous and indicative of related processes and energetics.

**Proton Affinity and  $\Delta H_f^\circ$  of Phenylnitrene Anion Radical.** To determine the PA of PhN<sup>-</sup>, the reactions of PhN<sup>-</sup> with a series of proton donors of known acidity<sup>13</sup> were examined. The results of these PA bracketing studies for the proton-transfer reaction channel<sup>14</sup> are listed in Table I. This gives PA(PhN<sup>-</sup>) = 372 ± 2 kcal mol<sup>-1</sup> from which  $\Delta H_f^\circ$ (PhN<sup>-</sup>) = 60 ± 2 kcal mol<sup>-1</sup> was calculated<sup>15</sup> from eq 5. The basicity (toward H<sup>+</sup> donors) of PhN<sup>-</sup>

$$\Delta H_f^\circ(\text{PhN}^-) = \text{PA}(\text{PhN}^-) + \Delta H_f^\circ(\text{PhNH}\cdot) - \Delta H_f^\circ(\text{H}^+) \quad (5)$$

is 5 kcal mol<sup>-1</sup> greater than that of the closed-shell anilide anion [PA(PhNH<sup>-</sup>) = 367.1 ± 2 kcal mol<sup>-1</sup>]<sup>13</sup> on the same scale. While this  $\delta$ PA is much smaller than that found for c-C<sub>3</sub>H<sub>4</sub><sup>-</sup> and c-C<sub>3</sub>H<sub>5</sub><sup>-</sup> ( $\delta$ PA = 21 kcal mol<sup>-1</sup>),<sup>3</sup> the difference of 16 kcal mol<sup>-1</sup> between these two systems of hypovalent anion radicals and the corresponding anions is the difference in the bond energies of the anions [*D*<sup>o</sup>(PhN<sup>-</sup> - H) and *D*<sup>o</sup>(c-C<sub>3</sub>H<sub>4</sub><sup>-</sup> - H)]<sup>17</sup> and probably of the radicals, PhNH<sup>•</sup> and c-C<sub>3</sub>H<sub>5</sub><sup>•</sup>.

The reactions with the two alcohols, (CF<sub>3</sub>)<sub>2</sub>CHOH and CF<sub>3</sub>-CH<sub>2</sub>OH, gave the corresponding alkoxide anions (eq 6 and 8) followed by the cluster formation sequences (eq 7, 9, and 10). The

(12) Lehman, P. A.; Berry, R. S. *J. Am. Chem. Soc.* **1973**, *95*, 8614. Contamination by PhOH in the samples of PhN<sub>3</sub> used by these authors could have given the apparent "induction process" mentioned.

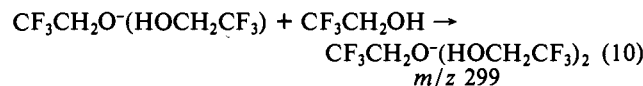
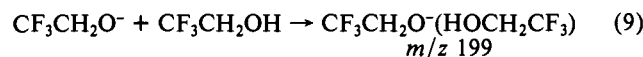
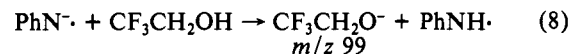
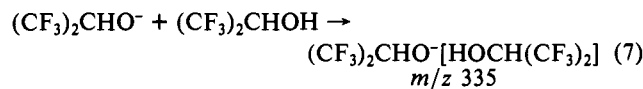
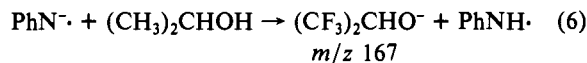
(13) Bartmess, J. E.; McIver, R. T. In "Gas Phase Ion Chemistry"; Bowers, M. T., Ed.; Academic Press: New York, 1979; Vol. 2, Chapter 11.

(14) The remaining reaction channels with the carbonyl containing compounds (CH<sub>3</sub>COCH<sub>3</sub>, CH<sub>3</sub>CHO, and CH<sub>3</sub>CO<sub>2</sub>CH<sub>3</sub>) yield acylanilide anions (PhNCOR<sup>-</sup>) formed by addition of PhN<sup>-</sup> to the carbonyl group followed by radical  $\beta$  fragmentation. The results of these processes will be discussed shortly in a separate publication. For a preliminary report, see ref 1. Also see: McDonald, R. N.; Chowdhury, A. K. *J. Am. Chem. Soc.* **1980**, *102*, 6146.

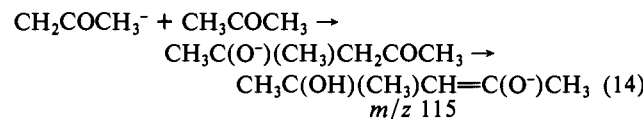
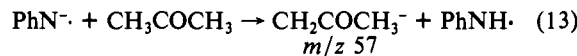
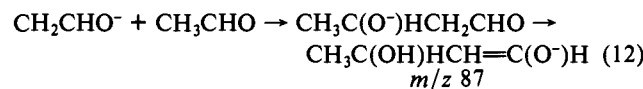
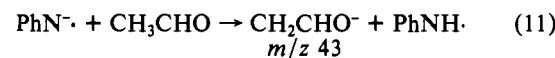
(15) (a)  $\Delta H_f^\circ$ (PhNH<sup>•</sup>) = 55.0 kcal/mol.<sup>16a</sup> (b)  $\Delta H_f^\circ$ (H<sup>+</sup>) = 367.2 kcal/mol.<sup>16b</sup>

(16) (a) O'Neal, H. E.; Benson, S. W. In "Free Radicals"; Kochi, J. K., Ed.; Wiley: New York, 1973; Vol. 2, Chapter 17. (b) "JANAF Thermochemical Tables", *Natl. Stand. Ref. Data. Ser., Natl. Bur. Stand.* **1971**, No. 37.

(17) (a) *D*<sup>o</sup>(PhN<sup>-</sup> - H) = 91.3 ± 2 kcal/mol calculated using  $\Delta H_f^\circ$ (PhNH<sup>•</sup>) = 20.7 ± 2 kcal/mol.<sup>13</sup> (b) *D*<sup>o</sup>(c-C<sub>3</sub>H<sub>4</sub><sup>-</sup> - H) = 104 ± 5 kcal/mol.<sup>3</sup>

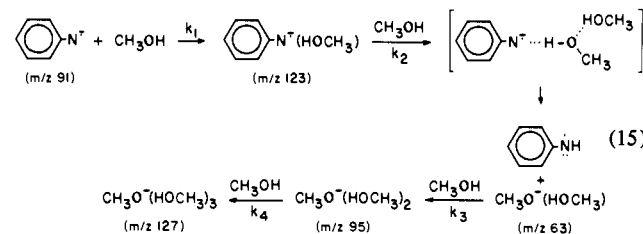


reaction products from CH<sub>3</sub>CHO and CH<sub>3</sub>COCH<sub>3</sub> were the expected enolate anions (eq 11 and 13) along with small amounts of higher mass ions (*m/z* 87 and 115, respectively) in accord with the aldol condensation product of the enolate anion adding to the neutral carbonyl reagent (eq 12 and 14). Since the first con-



denation step in eqs 12 and 14 are calculated to have only small exoergicities (3–4 kcal mol<sup>-1</sup>),<sup>18</sup> prototropic rearrangement to the condensed hydroxy-enolate anions would appear to be required for stabilization.

**Cluster Formation of Phenylnitrene Anion Radical with Alcohols and Water.** Considering the lower acidities (larger  $\Delta H^\circ_{\text{acid}}$ 's) for the alcohols CH<sub>3</sub>OH, C<sub>2</sub>H<sub>5</sub>OH, CH<sub>3</sub>(CH<sub>2</sub>)<sub>2</sub>OH, and (CH<sub>3</sub>)<sub>3</sub>COH compared to the PA(PhN<sup>-</sup>), it was somewhat surprising to find that reactions occurred between PhN<sup>-</sup> and these alcohols with modest rate constants (Table II). Since direct proton transfer in these ion-molecule reactions is endoergic, more careful analysis of the data is required. A set of data is shown in Figure 1 for the reaction of PhN<sup>-</sup> with CH<sub>3</sub>OH. The series of sequential reactions formulated to explain these results with CH<sub>3</sub>OH is given in eq 15. For all of these reactions, the first observed product



is the PhN<sup>-</sup>·(HOR) cluster. The second common step in these reactions is a cluster-to-cluster transformation which occurs in a collision of PhN<sup>-</sup>·(HOR) with an ROH molecule. In this step, a proton is transferred to PhN<sup>-</sup> yielding *directly* the RO<sup>-</sup>(HOR) cluster and PhNH<sup>•</sup>; note, the anion PhN<sup>-</sup> of the original cluster is *switched* for RO<sup>-</sup> in forming the product cluster RO<sup>-</sup>(HOR)

(18)  $\Delta H_f^\circ$ 's for CH<sub>3</sub>CH(O<sup>-</sup>)CH<sub>2</sub>CHO (-82.7 kcal/mol) and CH<sub>3</sub>CO<sup>-</sup>(C-H<sub>3</sub>)CH<sub>2</sub>COCH<sub>3</sub> (-105.5 kcal/mol) were calculated from  $\Delta H_f^\circ$  group additivity for their corresponding alcohols<sup>19</sup> and using  $\Delta H^\circ_{\text{acid}}$  of *i*-PrOH (374.1 kcal/mol)<sup>13</sup> and *t*-BuOH (373.3 kcal/mol),<sup>13</sup> respectively.

(19) Benson, S. W. "Thermochemical Kinetics", 2nd ed., Wiley: New York, 1976.

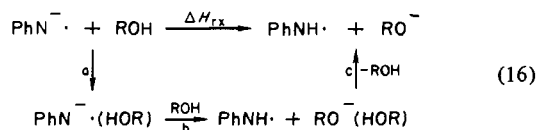
Table II. Summary of Kinetic and Product Data for the Cluster-Forming Reactions of Phenylnitrene Anion Radical with Alcohols and Water

ion + neutral reactants	product ions listed in sequence obsd, <sup>d</sup> <i>m/z</i>	<i>k</i> <sub>total</sub> , <sup>a</sup> cm <sup>3</sup> molecule <sup>-1</sup> s <sup>-1</sup>	$\Delta H^{\circ}_{\text{acid}}$ , <sup>b</sup> kcal mol <sup>-1</sup>	$\Delta H_{\text{rx}}$ , <sup>c</sup> kcal mol <sup>-1</sup>
PhN <sup>-</sup> + (CH <sub>3</sub> ) <sub>3</sub> COH	165, 147, 221	(3.9 ± 0.1) × 10 <sup>-11</sup>	373.3	+1.3
PhN <sup>-</sup> + CH <sub>3</sub> (CH <sub>2</sub> ) <sub>2</sub> OH	151, 119, 179	(4.0 ± 0.1) × 10 <sup>-11</sup>	374.7	+2.7
PhN <sup>-</sup> + C <sub>2</sub> H <sub>5</sub> OH	137, 183	(2.1 ± 0.1) × 10 <sup>-11</sup>	376.1	+4.1
PhN <sup>-</sup> + CH <sub>3</sub> OH	123, 63, 96, 127	(9.8 ± 0.2) × 10 <sup>-12</sup>	379.2	+7.2
PhN <sup>-</sup> + H <sub>2</sub> O	109, 53, 71, 89	(7.5 ± 0.4) × 10 <sup>-13</sup>	390.8	+18.8

<sup>a</sup> Same description as footnote *a* in Table I. <sup>b</sup> From ref 13. <sup>c</sup> Calculated endoergicities from the direct proton transfer from ROH to PhN<sup>-</sup>: [ $\Delta H^{\circ}_{\text{acid}}(\text{ROH}) - \text{PA}(\text{PhN}^{\cdot-})$ ]. <sup>d</sup> The full extent of the sequence of cluster formation was checked under throttled conditions ( $P_{\text{He}} = 1.1$  torr,  $\bar{v} = 50$  m/s).

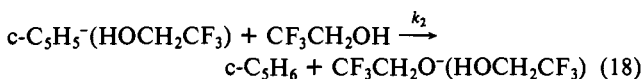
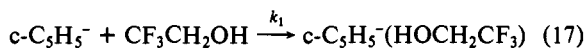
in this cluster-to-cluster process. The structure in brackets in eq 15 may be an intermediate or a transition state. Further clustering of the RO<sup>-</sup>(HOR) species then occurs to RO<sup>-</sup>(HOR)<sub>x</sub> with the extent of clustering of RO<sup>-</sup> apparently dependent on the alkyl group (see column 2 of Table II).

Computer simulation of the PhN<sup>-</sup> + CH<sub>3</sub>OH data presented in Figure 1 for the sequence in eq 15 gave a good fit with the following pseudo-first-order rate constants:  $k_2 = 30k_1$ ,  $k_3 = 8k_1$ , and  $k_4 = 1/2k_1$  where  $k_1 = k_{\text{total}}$ , the decay constant for PhN<sup>-</sup> (Table II). The fast reaction of PhN<sup>-</sup>(HOCH<sub>3</sub>) with CH<sub>3</sub>OH to yield the products of proton transfer [PhNH<sup>·</sup> + CH<sub>3</sub>O<sup>-</sup>(HOCH<sub>3</sub>)] is a reflection of the relative intrinsic binding energies of the clusters CH<sub>3</sub>O<sup>-</sup>(HOCH<sub>3</sub>) and PhN<sup>-</sup>(HOCH<sub>3</sub>) as shown in steps a and b of the thermochemical cycle in eq 16. The



cluster-to-cluster transformation (step b, eq 16) can only occur if the binding energy of the cluster RO<sup>-</sup>(HOR) exceeds that of the binding energy of PhN<sup>-</sup>(HOR) by more than  $\Delta H_{\text{rx}}$ ; in the case of R = CH<sub>3</sub>,  $D(\text{CH}_3\text{O}^- - \text{HOCH}_3) - D(\text{PhN}^{\cdot-} - \text{HOCH}_3) > 7.2$  kcal mol<sup>-1</sup>. If we assume that  $D(\text{CH}_3\text{O}^- - \text{HOCH}_3) = D(\text{HO}^- - \text{HOH}) = 24$  kcal mol<sup>-1</sup>,<sup>20</sup> a value of  $D(\text{PhN}^{\cdot-} - \text{HOCH}_3) \sim 10$  kcal mol<sup>-1</sup><sup>21</sup> would appear appropriate to still allow for step b to be reasonably exoergic.

The rate constant of the cluster-to-cluster transformation ( $k_2$  in eq 15) is 30 times greater than that of the original clustering reaction ( $k_1$ ) of PhN<sup>-</sup> with CH<sub>3</sub>OH. From the value of  $k_1$  in Table II, this gives  $k_2 = 3 \times 10^{-10}$  cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup> in this reaction sequence. The only analogous process of which we are aware to compare this result is the sequential reactions between the delocalized cyclopentadienyl anion (c-C<sub>5</sub>H<sub>5</sub><sup>-</sup>) with CF<sub>3</sub>CH<sub>2</sub>OH shown in eq 17 and 18 where  $k_1 = 2.7 \times 10^{-10}$  cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup> and  $k_2 = 2k_1 = 5.4 \times 10^{-10}$  cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup>.<sup>22</sup> In this



comparison, the  $k_1$ 's differ by greater than one order of magnitude in the two reactions (eq 15 and 17) while the  $k_2$ 's are essentially the same value. Both reactions show no dependence of rate constants  $k_1$  on  $P_{\text{He}}$  (0.4–1.1 torr), so we assume that both reactions are bimolecular processes.<sup>23</sup> That the second step ( $k_2$ ) in both cases should be bimolecular is readily understood since

(20) (a) Payzant, J. D.; Yamdagni, R.; Kebarle, P. *Can. J. Chem.* **1971**, *49*, 3308. (b) Yamdagni, R.; Kebarle, P. *J. Am. Chem. Soc.* **1971**, *93*, 7139.

(21) Binding enthalpies for other delocalized anion clusters X<sup>-</sup>(HOH) where X = CN<sup>-</sup>, NO<sub>2</sub><sup>-</sup>, and NO<sub>3</sub><sup>-</sup> range between 12.4 and 14.3 kcal/mol.<sup>20</sup>

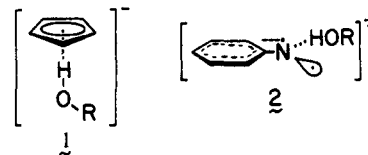
(22) McDonald, R. N.; Chowdhury, A. K.; Setser, D. W. *J. Am. Chem. Soc.* **1980**, *102*, 4836.

(23) The formation of ion clusters is normally considered to be a termolecular process requiring third-body stabilization of the cluster.<sup>20</sup> The absence of  $P_{\text{He}}$  dependency on our clustering rate constants means either that we are observing saturated termolecularity even at our lowest pressure or that the size of our anions and alcohols offer sufficient vibrational modes for stabilization of the bimolecularly formed clusters.

loss of the neutral fragment (PhNH<sup>·</sup> or c-C<sub>5</sub>H<sub>6</sub>) can carry off the excess vibrational energy.

While the clustering reaction between c-C<sub>5</sub>H<sub>5</sub><sup>-</sup> and CF<sub>3</sub>CH<sub>2</sub>OH is reasonably fast, although certainly less than the collision (ADO)<sup>24</sup> limit, the reasons for the much slower  $k_1$  for the clustering reaction of PhN<sup>-</sup> with CH<sub>3</sub>OH are not immediately obvious. That this is apparently not a function of the acid (ROH) and base (PhN<sup>-</sup> and c-C<sub>5</sub>H<sub>5</sub><sup>-</sup>) strengths of the components is seen in the results of their differences,  $\Delta H^{\circ}_{\text{acid}}(\text{CF}_3\text{CH}_2\text{OH}) - \text{PA}(\text{c-C}_5\text{H}_5^-) = 8.3 \pm 4$  kcal mol<sup>-1</sup> and  $\Delta H^{\circ}_{\text{acid}}(\text{CH}_3\text{OH}) - \text{PA}(\text{PhN}^{\cdot-}) = 7.2 \pm 4$  kcal/mol.<sup>13</sup> The  $\delta\Delta H^{\circ}_{\text{acid}}$  of CH<sub>3</sub>OH and C<sub>2</sub>H<sub>5</sub>OH is  $3.1 \pm 4$  kcal mol<sup>-1</sup>, and the rate constant decreases by only a factor of 2 with PhN<sup>-</sup>; a similar reduction of rate constant was observed for the reactions of these two alcohols with c-C<sub>5</sub>H<sub>5</sub><sup>-</sup> to yield the c-C<sub>5</sub>H<sub>5</sub><sup>-</sup>(HOR) clusters.<sup>22</sup> Therefore, the enthalpic difference of  $1.1 \pm 4$  kcal mol<sup>-1</sup> in the above comparison should have little, if any, effect on the rate constants  $k_1$  in eq 15 and 17.

Consideration of the structures and electronic configurations of these two anions, c-C<sub>5</sub>H<sub>5</sub><sup>-</sup> and PhN<sup>-</sup>, offers an explanation for the difference in the cluster formation rate effects. In c-C<sub>5</sub>H<sub>5</sub><sup>-</sup>, the planar, symmetric  $\pi$ -delocalized anion should interact with ROH through hydrogen bonding to the  $\pi$  cloud of the anion, e.g., in 1, a structure that can naturally evolve from the loose ion-molecule collision complex. In PhN<sup>-</sup>, the delocalized  $\pi$ -HOMO



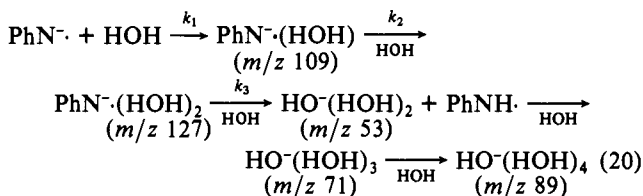
orbital will have the largest coefficient at N. Furthermore, the in-plane lone pair on N could, in fact, be the "basic" site to which hydrogen bonding with ROH takes place. If this is the case, specific orientation of ROH would be required to yield the hydrogen-bonded PhN<sup>-</sup>(HOR) cluster (2) from its loose ion-molecule collision complex. This rearrangement could have a barrier and account for the small rate constant for PhN<sup>-</sup>(HOR) formation.

The reaction of PhN<sup>-</sup> with HOH gave an even more spectacular example of how a sequence of anion-solvent clustering followed by a cluster-to-cluster transformation can overcome a large endoergic for the direct proton-transfer step. As listed in Table II, the observed ion-cluster sequence involved formation of PhN<sup>-</sup>(HOH) (*m/z* 109), HO<sup>-</sup>(HOH)<sub>2</sub> (*m/z* 53), HO<sup>-</sup>(HOH)<sub>3</sub> (*m/z* 71), and HO<sup>-</sup>(HOH)<sub>4</sub> (*m/z* 89). Since the cluster HO<sup>-</sup>(HOH) (*m/z* 35) was not observed in this reaction at any concentration of added HOH, we assume that it was not formed as a product ion cluster. Furthermore, in order for HO<sup>-</sup>(HOH) to be formed, as shown in eq 19, requires  $D(\text{PhN}^{\cdot-} - \text{HOH}) < 6.2$



kcal mol<sup>-1</sup>, and it is doubtful that PhN<sup>-</sup>(HOH) would be an observable, bound species in the FA experiment. The sequence proposed for the reaction of PhN<sup>-</sup> with HOH is shown in eq 20.

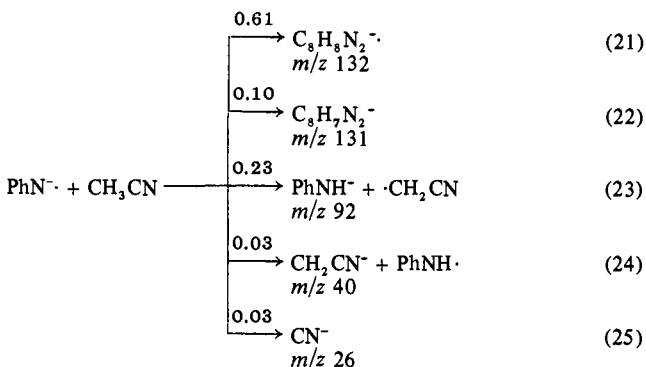
(24) Su, T.; Bowers, M. T. *J. Chem. Phys.* **1973**, *58*, 3027. *Int. J. Mass Spectrom. Ion Phys.* **1973**, *12*, 347.



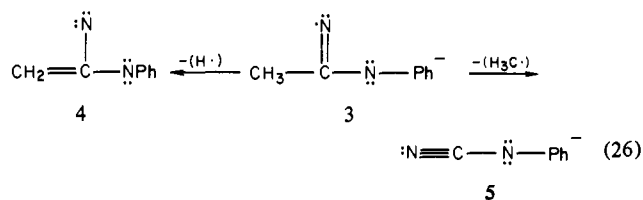
Failure to observe cluster  $\text{PhN}^{\cdot-}(\text{HOH})_2$  ( $m/z$  127) is not unexpected since the net binding energy of  $\text{HO}^-(\text{HOH})_2 \rightarrow \text{HO}^- + 2\text{HOH}$  is  $40.4 \text{ kcal mol}^{-1}$ ,<sup>20</sup> leading to a large exoergicity for this third step in eq 20, and  $k_3$  for this step is expected to be of the magnitude of  $k_2$ 's in eq 15 and 18, ca.  $10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ . The slow clustering of  $\text{PhN}^{\cdot-}$  with HOH is a result of the lower acidity of HOH compared to the alcohols and the orientation factor discussed above.

The graphic demonstrations of the above cluster-to-cluster transformations where proton transfer is induced to occur by interaction with an additional "solvent" molecule closely mimic such proton-transfer reactions in protic solutions. This is clearly depicted in the proposed structure of the collision complex for the second step in eq 15 of the reaction of  $\text{PhN}^{\cdot-}$  with  $\text{CH}_3\text{OH}$ . In methanol solution, the proton donor would be the solvate  $\text{CH}_3\text{OH}(\text{HOCH}_3)_x$  and the homoconjugate product would be  $\text{CH}_3\text{O}^-(\text{HOCH}_3)_x$ , both of which are structurally analogous to the sequentially produced species described in this gas-phase study. The present results further display the dependence of structural effects on acidity, basicity, and other properties of molecules measured in solution relative to those same *intrinsic* properties determined in the gas phase.<sup>25</sup> The ability to overcome a 19-kcal  $\text{mol}^{-1}$  thermochemical barrier to protonation of  $\text{PhN}^{\cdot-}$  by three associated HOH molecules is impressive as an effect of solvation. It is, therefore, not at all surprising that *different* acidity orders exist for the series of alcohols<sup>26</sup> and amines<sup>27</sup> from solution and gas-phase measurements.

**Reactions of Phenylimide Anion Radical with Acetonitrile and Trimethylacetone.** The reaction of  $\text{PhN}^{\cdot-}$  with acetonitrile proceeded with a modest rate constant (Table I) and formation of five product ions (eq 21–25) with the fraction of the total product signals for that channel given above each arrow. The major process is production of the adduct  $\text{C}_8\text{H}_8\text{N}_2^{\cdot-}$  ( $m/z$  132).

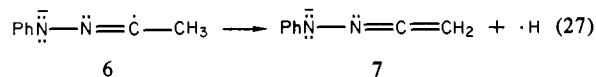


We would normally consider the structure of this adduct to arise by addition of  $\text{PhN}^{\cdot-}$  to  $\text{C}_1$  of  $\text{CH}_3\text{CN}$  yielding **3** because of the



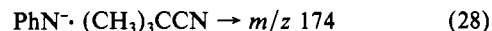
(25) (a) For gas-phase acidities of substituted phenols and benzoic acids, see: McMahon, T. B.; Kebarle, P. *J. Am. Chem. Soc.* **1977**, *99*, 2222. (b) For gas-phase acidities of substituted anilines, see: Bartmess, J. E.; Scott, J. A.; McIver, R. T. *J. Am. Chem. Soc.* **1979**, *101*, 6046 and ref 13.  
(26) Brauman, J. I.; Blair, L. K. *J. Am. Chem. Soc.* **1970**, *92*, 5986.  
(27) Brauman, J. I.; Blair, L. K. *J. Am. Chem. Soc.* **1971**, *93*, 3911.

large dipole moment in  $\text{CH}_3\text{CN}$ . However, this structure does not appear to have a reasonable pathway to produce the  $M-1$  adduct,  $\text{C}_8\text{H}_7\text{N}_2^{\cdot-}$  ( $m/z$  131); a structure such as **4** (or its resonance contributors) appears most unlikely to be a stable species. Also, radical  $\beta$  fragmentation of a  $\cdot\text{CH}_3$  group from **3** (eq 26) would be expected to be a more favorable energetic process yielding the phenylcarbodiimidyl anion (**5**), which is not observed. However, if the addition reaction site on  $\text{CH}_3\text{CN}$  is at N, ion-radical **6** would be produced (eq 27), and  $\beta$  fragmentation of H $\cdot$  would yield the

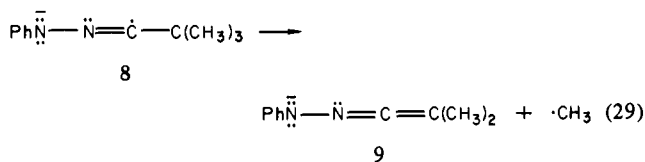


delocalized anion **7**, the conjugate base of a ketene phenylhydrazone. Although the adduct ion-radical  $m/z$  132 may be composed of **3** and/or **6**, structure **7** seems to be the best possibility to represent the  $M-1$  ion  $m/z$  131.

An attempt to determine whether reaction of  $\text{PhN}^{\cdot-}$  was more favorable at  $\text{C}_\alpha$  or N of  $\text{CH}_3\text{CN}$ , the reaction of  $\text{PhN}^{\cdot-}$  with  $(\text{CH}_3)_3\text{CCN}$  was investigated. Here, the *tert*-butyl vs.  $\text{CH}_3$  steric effect should better control the reaction of  $\text{PhN}^{\cdot-}$  toward addition at N of the cyano group. The single product ion formed was that of the adduct  $m/z$  174 (eq 28). We had hoped that if adduct



**8** were formed, that  $\beta$  fragmentation of the  $\text{H}_3\text{C}\cdot$  groups would also be observed to yield ion **9** according to eq 29. If **8** is the



structure of the adduct  $m/z$  174, apparently the increased mass and vibrational levels offered by replacing three  $\beta$ -H's in **6** by  $\text{CH}_3$ 's in **8** sufficiently stabilizes this species prior to third-body collisional stabilization of the ion-radical adduct.<sup>23,28</sup> Although these reaction site and structural assignments are by no means certain, they reflect our opinions at this time.<sup>29</sup>

The second major product forming channel in the reaction of  $\text{PhN}^{\cdot-}$  with  $\text{CH}_3\text{CN}$  involves H $\cdot$  transfer (eq 23). For this reaction,  $\Delta H_{rx} = -8 \text{ kcal/mol}$ .<sup>30</sup> This reaction agrees with the calculated, low H $\cdot$  affinity of  $\text{PhN}^{\cdot-}$ .  $D^\circ(\text{PhN}^{\cdot-} - \text{H}) = 91.4 \pm 3 \text{ kcal/mol}$ .

Formation of anion  $\text{CH}_2\text{CN}^-$  represents only 3% of the total anion products from the reaction of  $\text{PhN}^{\cdot-}$  with  $\text{CH}_3\text{CN}$ . The fact that no reaction was observed with  $(\text{CH}_3)_2\text{SO}$  (Table I) offers a tight bracket on the PA of  $\text{PhN}^{\cdot-}$  previously discussed. The formation of  $\text{CH}_2\text{CN}^-$  by proton transfer to  $\text{PhN}^{\cdot-}$  is reasonable since  $\text{PhN}^{\cdot-}$  is the strongest base that can be present in the flow under thermal conditions, e.g.,  $\text{PA}(\text{PhNH}^-) = 367.1 \text{ kcal mol}^{-1}$ .<sup>13</sup>

The pathway for the minor amount of  $\text{CN}^-$  observed as the fifth product is unknown. However, it is unlikely that it involves an  $\text{S}_{\text{N}}2$  displacement by  $\text{PhN}^{\cdot-}$  on  $\text{CH}_3\text{CN}$ , even though this reaction has  $\Delta H_{rx} = -7 \text{ kcal mol}^{-1}$ .<sup>31</sup> We have previously shown that  $\text{PhN}^{\cdot-}$  is a very poor nucleophile toward the methyl halides<sup>32</sup> whose reactions are considerably more exoergic than is this one.

**Acknowledgment.** We thank the U.S. Army Research Office and the National Science Foundation (equipment grant) for their support of this research.

(28) A somewhat similar stabilizing effect was observed in the reactions of carbonyl-containing molecules where the ion-radical adducts were observed.<sup>1</sup>

(29) Since the product ions  $m/z$  132 and 131 are present even at low concentrations of added  $\text{CH}_3\text{CN}$ , we discount the possibility that a reaction of  $\text{PhNH}^- + \text{CH}_3\text{CN}$  could produce them.

(30)  $\Delta H_f^\circ(\text{CH}_3\text{CN}) = 19 \pm 1 \text{ kcal/mol}$ ,<sup>19</sup>  $\Delta H_f^\circ(\cdot\text{CH}_2\text{CN}) = 51.1 \text{ kcal/mol}$ ,<sup>16a</sup> and  $\Delta H_f^\circ(\text{PhNH}^-) = 20.7 \pm 2 \text{ kcal/mol}$ .<sup>13</sup>

(31)  $\Delta H_f^\circ(\text{PhNCH}_3) = 53.3 \text{ kcal/mol}$ <sup>16a</sup> and  $\Delta H_f^\circ(\text{CN}^-) = 18.2 \text{ kcal/mol}$ .<sup>13</sup>

(32) See footnote 4 in ref 1.