is typically found[22] and is due to the fact that d functions are especially important in describing the triple bonds of the separated CO molecules. Electron correlation has a relatively small effect on the predicted value of D_e (OC – CO), which is increased by 8.3 kcal to 73.7 kcal (DZ + P CI). Finally, the Davidson correction for unlinked clusters[29] increases the predicted dissociation energy by 0.5 kcal to 74.2 kcal.

In contrast, $^3\Sigma_g^-$ ethylenedithione is the *absolute* minimum on the C_2S_2 energy hypersurface. This result is predicted at each of the five levels of theory considered here. As with C_2O_2, however, the predicted value of the dissociation energy is significantly reduced by the addition of d functions to the basis set. Relative to the lowest CS + CS triplet dissociation limit, the 4-31G and DZ + P SCF values of D_e (SC – CS) are 154.5 and 117.1 kcal, respectively. The dissociation energy relative to two ground-state CS molecules is similarly reduced from 75.4 kcal (4-31G) to only 38.0 kcal (DZ + P). These DZ + P SCF dissociation energies are, however, somewhat increased when the effects of electron correlation are variationally considered.

Concluding Remarks

A very simple and crude bond-energy argument presented in the introduction suggests that S=C=C=S might have a thermochemical stability (relative to the dissociation limit CS + CS) much greater than the analogous oxygen compound O=C=C=O, which lies energetically above two ground-state CO molecules. This seemingly naive suggestion has been confirmed in the present theoretical study, in the sense that the $^3\Sigma_g^-$ ground state of ethylenedithione is predicted to be the absolute minimum on the C_2S_2 potential energy hypersurface, lying 39 kcal below $X^1\Sigma^+$ CS + $X^1\Sigma^+$ CS. Therefore, we are convinced that C_2S_2 is a "makable" molecule and look forward to experimental efforts to this end. Since the monomer CS itself is not a very stable species, we appreciate that the production of gram quantities of C_2S_2 is unlikely. However, matrix-isolation infrared spectroscopy,[17] electron spin resonance techniques,[38] or molecular beam studies[39] would all appear to be viable approaches to the experimental identification of ethylenedithione. Although the $^3\Sigma_g^-$ state of C_2O_2 lies ~65 kcal above $X^1\Sigma^+$ CO + $X^1\Sigma^+$ CO, this metastable species nevertheless lies 74 kcal below its lowest spin-allowed dissociation limit and should also be detectable in a carefully designed experiment.

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Gas-Phase Nucleophilic Reactivities of Phenylnitrene ($PhN^{-}\cdot$) and Sulfur Anion Radicals ($S^{-}\cdot$) at sp^3 and Carbonyl Carbon[1]

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Abstract: The reactions of $PhN^{-}\cdot$ with a series of carbonyl-containing molecules (aldehydes, ketones, and esters) were shown to proceed via an addition/fragmentation mechanism, $PhN^{-}\cdot + R_2C{=}O \rightarrow [Ph\dot{N}C(O^-)R_2] \rightarrow PhN{=}C(O^-)R + \cdot R$, producing various acyl anilide anion products. In several cases, the tetrahedral intermediate anion radicals were observed as minor ions. The *intrinsic* reactivity of the carbonyl-containing molecules was aldehydes > ketones > esters, where similar R groups were involved. The overall exothermicities of these reactions did not appear to play the major role in determining the relative rates ($k_{rel}^{C=O}$) for these reactions. From the reaction of $PhN^{-}\cdot$ with cyclobutanone, a new type of anion radical, $PhN{=}C(O^-)CH_2\cdot$ (m/z 133) (+ C_2H_4), was produced; the loss of C_2H_4 was considered due to the ring strain in the ketone. With cyclopentanone, cyclohexanone, and cycloheptanone, the anion radicals $PhN{=}C(O^-)(CH_2)_n\cdot$ (n = 4–6) were the exclusive product ions. $PhN^{-}\cdot$ was shown to be a poor nucleophile in S_N2 displacement reactions with CH_3X molecules (X = Cl, Br, O_2CCF_3). $S^{-}\cdot$ was shown to exhibit modest S_N2 nucleophilicity with CH_3Cl and CH_3Br. The reactions of $S^{-}\cdot$ with CF_3CO_2R proceeded via both S_N2 displacement and carbonyl addition/fragmentation mechanisms: with R = CH_3, the anion products were 65% $CF_3CO_2^-$ and 35% CF_3COS^-; from R = C_2H_5, the product ions were 4% $CF_3CO_2^-$ and 96% CF_3COS^-. These data yield the ratio $k_{CH_3}/k_{C_2H_5}$ = 16 for S_N2 displacement by $S^{-}\cdot$ at these alkyl groups. The reactions of $PhN^{-}\cdot$ with CO_2, COS, CS_2, and O_2 are also reported. The reaction of $PhN^{-}\cdot$ with CS_2 to produce $S^{-}\cdot$ as a major channel was used as the source of this atomic anion radical. In several reactions occurring at nearly the collison limit, selectivity was observed for (a) which of two reaction centers were attacked to give products and (b) which of two mechanisms would be dominant in the overall reaction.

Studies of S_N2 displacement reactions by closed-shell nucleophiles in the gas phase have been reported.[2-10] Predominant inversion of configuration was established in displacement of Br^- by Cl^- from an RBr molecule,[5] a relative kinetic nucleophilicity order was established,[6,7] and a double-minimum model for the potential surface of the gas-phase S_N2 mechanism was developed.[8,9]

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(1) Paper 13 in the series "Hypovalent Radicals". For paper 12, see: McDonald, R. N.; Chowdhury, A. K. *J. Phys. Chem.* **1982**, *86*, 3641-3645.

(2) Bohme, D. K.; Young, L. B. *J. Am. Chem. Soc.* **1970**, *92*, 7354-7358.

(3) Young, L. B.; Lee-Ruff, E.; Bohme, D. K. *J. Chem. Soc., Chem. Commun.* **1973**, 35-36.

(4) Bohme, D. K.; Mackay, G. I.; Payzant, J. D. *J. Am. Chem. Soc.* **1974**, *96*, 4027-4028.

(5) (a) Lieder, C. A.; Brauman, J. I. *J. Am. Chem. Soc.* **1974**, *96*, 4028-4030. (b) See also: Hall, D. G.; Gupta, C.; Morton, T. H. *Ibid.* **1981**, *103*, 2416-2417, where it was concluded that inversion of configuration occurred in the reaction $ROH + ROH_2^+ \rightarrow R_2OH^+ + H_2O$.

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(7) Tanaka, K.; Mackay, G. I.; Payzant, J. D.; Bohme, D. K. *Can. J. Chem.* **1976**, *54*, 1643-1659.

(8) Olmstead, W. M.; Brauman, J. I. *J. Am. Chem. Soc.* **1977**, *99*, 4219-4228.

(9) Pellerite, M. J.; Brauman, J. I. *J. Am. Chem. Soc.* **1980**, *102*, 5993-5999.

(10) Bohme, D. K.; MacKay, G. I. *J. Am. Chem. Soc.* **1981**, *103*, 978-979.

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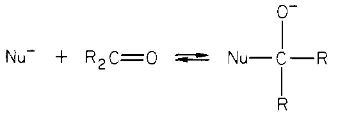
The effect of anion solvation on reaction I was interpreted as a

$$HO^-(H_2O)_n + CH_3Br \rightarrow Br^-(H_2O)_n + CH_3OH \qquad (I)$$

mechanistic continuum linking gas-phase and solution data,[10] and various comparisons between gas-phase and condensed-phase nucleophilicities have been presented. Therefore, our understanding of many of the factors involved in this mechanism in both phases is reasonably solid.

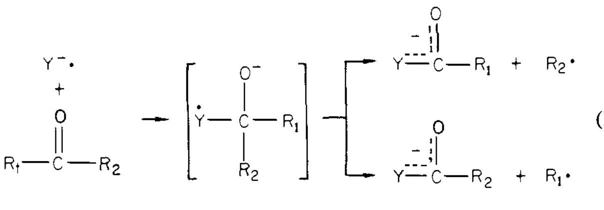
However, in the area of addition reactions of nucleophiles to carbonyl groups of molecules, the information from both condensed[11] and gas-phase[12] studies is considerably more limited primarily due to the fact that this addition reaction is reversible (eq II). In solution studies, this equilibrium problem has been



$$Nu^- + R_2C{=}O \rightleftharpoons Nu-\overset{O^-}{\underset{R}{C}}-R \qquad (II)$$

overcome by using various metal hydrides. However, the precise nature of certain of these processes and, in some cases, the structure of the hydride donor(s) is controversial.[11]

Our approach to determining the *intrinsic* gas-phase reactivities of carbonyl-containing molecules was to utilize nucleophilic reagents that would undergo radical β fragmentation of the tetrahedral intermediate in competition with or to the exclusion of retroaddition. To this end, the hypovalent species $R_2C^-\cdot$, $RN^-\cdot$, $O^-\cdot$, and $S^-\cdot$ could function as such reagents, $Y^-\cdot$. These hypovalent anion radicals formally have the anion electron pair and the radical unpaired electron on the same nuclear center. If $Y^-\cdot$ adds to the carbon of the C=O group, the radical site of the intermediate can induce β fragmentation of an R· yielding characteristic fragment anions (eq III). Of the hypovalent anion radicals



(III)

considered, $R_2C^-\cdot$ and $O^-\cdot$ did not appear to be useful with a wide range of carbonyl-containing molecules due to their large calculated H atom ($HA(Y^-\cdot) = D°(Y^--H)$) and H^+ affinities (PA).[13,14,17] However, phenylnitrene anion radical[18] ($PhN^-\cdot$) and $S^-\cdot$[19] have smaller calculated values of HA and PA, and $PhN^-\cdot$ has already been shown to undergo carbonyl addition followed by fragmentation (eq III) as the major reaction channel with methyl vinyl ketone.[1] Bohme et al.[7] had demonstrated that $S^-\cdot$ was of "medium nucleophilicity" in its S_N2 displacement reactions with CH_3Cl and CH_3Br.

Experimental Section

The flowing afterglow (FA) used in these investigations has been previously described.[13] Gas-phase anions were prepared by dissociative electron attachment (DEA) in the upstream end of the stainless steel flow tube (120 × 7.15 cm i.d.) by adding small amounts of neutral reagent gases to the helium buffer gas and flowing this mixture past the electron gun. Alternatively, the anion of interest could be generated by an ion-molecule reaction between the ion produced by DEA with a second neutral reagent added via a port located just downstream of the electron gun. The flow pressure (P_{He}) and flow velocity ($\bar{v}$) were maintained in the flow tube by a Stokes Roots blower-mechanical pump system (Model 1722-S) but could be varied from P_{He} = 0.2–1.2 torr and $\bar{v}$ = 30–80 m s^{-1} by throttling a gate valve and/or altering the helium inlet flow. Our standard operating conditions were P_{He} = 0.5 torr and $\bar{v}$ = 80 m s^{-1} at 298 K. A quadrupole mass spectrometer monitors the ion composition of the flow.

In the present experiments, $PhN^-\cdot$ was prepared by dissociative electron attachment of PhN_3 that was flowed past the electron gun.[18] $S^-\cdot$ was produced by the ion-molecule reaction of $PhN^-\cdot$ with CS_2 (see text). Sufficient CS_2 was added through an inlet located 10 cm downstream from the electron gun to completely remove $PhN^-\cdot$ within 10 cm of the flow tube. The anions (I^-) are thermalized by numerous collisions with the buffer gas as they flow 25 cm downstream before neutral reactants gases (N) are added to the flow through a fixed inlet. The inlet for N is located 61 cm from the first sampling nose cone and is the distance (time) for the pseudo-first-order (N in large excess) ion-molecule reaction to occur. This reaction distance is held constant as variable concentrations of N are added, and the ion signals of I^- and the products are recorded at each concentration of N. The slope of the plot of log I^- vs. concentration of N is then converted into the bimolecular rate constant for the ion-molecule reaction $I^- + N$ by the equations previously described.[13]

The helium used in this study was 99.99% purity and was supplied by Welders Products. All of the gas and liquid carbonyl-containing compounds used were obtained from commercial sources (Fisher, Eastman, Aldrich, and PCR). The liquid substrates were freshly distilled, and a constant boiling, center-cut fraction was used in the experiments. These liquid fractions were then transferred to their gas storage bulbs after three freeze-pump-thaw degassing cycles; the gas substrates were used directly.

Results

The kinetic and product data for the ion-molecule reactions of $PhN^-\cdot$ are summarized in Table I, and those data for $S^-\cdot$ are summarized in Table II. In all cases, clean pseudo-first-order decay plots of the log ion signal of $PhN^-\cdot$ (m/z 91) or $S^-\cdot$ (m/z 32) vs. concentration of neutral reactants were observed. The product ion distribution in Tables I and II are the relative ion signals observed from the mass spectrometer.

Discussion

Reactions of $PhN^-\cdot$ and $S^-\cdot$ with Methyl Halides. The reactions of $PhN^-\cdot$ with CH_3Br and CH_3Cl were examined to place $PhN^-\cdot$ on the scale of kinetic nucleophilicities toward sp^3 carbon developed by Bohme et al.[7] The reaction of $PhN^-\cdot$ with CH_3Br yielded Br^- as the only product anion (reaction 1, Table I). No ion-molecule reaction was observed for the reaction of $PhN^-\cdot$ with CH_3Cl (reaction 2).

If we assume that the reaction of $PhN^-\cdot$ with CH_3Br proceeded by S_N2 nucleophilic displacement of Br^-, the exothermicity of reaction 1 is calculated to be 48.2 kcal mol^{-1}.[18,22,23,25] The

$$PhN^-\cdot + CH_3Br \rightarrow Br^- + Ph\dot{N}CH_3 \qquad (1)$$

corresponding reaction of $PhN^-\cdot$ with CH_3Cl is 40.4 kcal mol^{-1} exothermic.[18,22,23,25] These large exothermicities and the slow rate constant for the $PhN^-\cdot$ with CH_3Br reaction (no reaction observed

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[11] March, J. "Advanced Organic Chemistry", 2nd ed.; McGraw-Hill: New York, 1977; Chapter 16 and many other general references of organic reactions.

[12] Bowie, J. H. *Acc. Chem. Res.* **1980**, *13*, 76–82 and references therein.

[13] McDonald, R. N.; Chowdhury, A. K.; Setser, D. W. *J. Am. Chem. Soc.* **1980**, *102*, 6491–6498, for the H atom and H^+ affinities of $c\text{-}C_5H_4^-\cdot$.

[14] $HA(O^-\cdot)$ = 110.1 kcal mol^{-1};[15] $PA(O^-\cdot)$ = 382.1 ± 0.5 kcal mol^{-1}.[16]

[15] Rosenstock, H. M.; Draxl, K.; Steiner, B. W.; Herron, J. T. *J. Phys. Chem. Ref. Data, Suppl.* **1977**, *6*. $\Delta H_f°(O^-\cdot)$ = 25.2 kcal mol^{-1}; $\Delta H_f°(HO^-)$ = −32.8 kcal mol^{-1}.

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

[17] Dawson and Nibbering (Dawson, J. H. J.; Nibbering, N. M. M. *Int. J. Mass. Spectrom. Ion Phys.* **1980**, *33*, 3–19) examined the reactions of $O^-\cdot$ with various saturated and unsaturated aliphatic nitriles.

[18] McDonald, R. N.; Chowdhury, A. K.; Setser, D. W. *J. Am. Chem. Soc.* **1981**, *103*, 6599–6603. $PA(PhN^-\cdot)$ = 372 ± 2 kcal mol^{-1}, $D°(PhN^--H)$ = 91.3 ± 2 kcal mol^{-1}, and $H_f°(PhN^-\cdot)$ = 60 ± 2 kcal mol^{-1}.

[19] $HA(S^-\cdot)$ = 89.1 kcal mol^{-1};[20] $PA(S^-\cdot)$ = 351.2 kcal mol^{-1}.[21]

[20] Reference 15; $\Delta H_f°(S^-\cdot)$ = 18 kcal mol^{-1}; $\Delta H_f°(HS^-)$ = −19 kcal mol^{-1}.

[21] Benson, S. W. "Thermochemical Kinetics", 2nd ed.; Wiley-Interscience: New York, 1976; $\Delta H_f°(HS\cdot)$ = 34 kcal mol^{-1}.

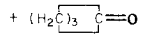
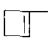
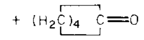
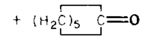
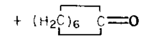
[22] Cox, J. D.; Pilcher, G. "Thermochemistry of Organic and Organometallic Compounds"; Academic Press: New York, 1970; $\Delta H_f°(CH_3Br)$ = −9.1 ± 0.3 kcal mol^{-1}; $\Delta H_f°(CH_3Cl)$ = −20.55 ± 0.10 kcal mol^{-1}.

[23] $\Delta H_f°(X^-)$ is calculated from the $\Delta H_f°(X\cdot)$[21] and $EA(X\cdot)$;[24] $\Delta H_f°(Br^-)$ = −50.8 kcal mol^{-1}, and $\Delta H_f°(Cl^-)$ = −54.4 kcal mol^{-1}.

[24] Janousek, B. K.; Brauman, J. I. In "Gas Phase Ion Chemistry"; Bowers, M. T., Ed.; Academic Press: New York, 1979; Vol. 2, Chapter 10.

[25] O'Neal, H. E.; Benson, S. W. In "Free Radicals"; Kochi, J. K., Ed.; Wiley: New York, 1973; Vol. 2, Chapter 17. $\Delta H_f°(PhNCH_3\cdot)$ = 53.5 kcal mol^{-1}, and $\Delta H_f°(PhNH\cdot)$ = 55.0 kcal mol^{-1}.

Table I. Summary of Kinetic and Product Data for the Ion-Molecule Reactions of Phenylnitrene Anion Radical ($PhN^{-}\cdot$) with Carbonyl-Containing Molecules

reaction	ion + neutral reactants	products [assumed neutral]	fraction of product ion signal	k_{total},[a] cm^3 molecule^{-1} s^{-1}	k_{ADO},[b] cm^3 molecule^{-1} s^{-1}
1	$PhN^{-}\cdot + CH_3Br$	Br^{-} [+ $PhNCH_3\cdot$]	1.00	$(1.8 \pm 0.1) \times 10^{-11}$	1.3×10^{-9}
2	$PhN^{-}\cdot + CH_3Cl$	no reaction		$\leqslant 10^{-13}$	1.7×10^{-9}
3a	$PhN^{-}\cdot + CH_3CHO$	$PhNCHO^{-}$ [+ $\cdot CH_3$]	0.31	$(7.7 \pm 0.4) \times 10^{-11}$	2.0×10^{-9}
3b		$PhNCOCH_3^{-}$ [+ $\cdot H$]	0.59		
3c		H_2CCHO^{-} [+ $PhNH\cdot$]	0.10		
4a	$PhN^{-}\cdot + C_2H_5CHO$	$PhNCHO^{-}$ [+ $\cdot C_2H_5$]	0.75	$(1.8 \pm 0.2) \times 10^{-10}$	1.8×10^{-9}
4b		$PhNCOC_2H_5^{-}$ [+ $\cdot H$]	0.23		
4c		CH_3CHCHO^{-} [+ $PhNH\cdot$]	0.02		
5a	$PhN^{-}\cdot + (CH_3)_3CCHO$	$PhNCHO^{-}$ [+ $\cdot C(CH_3)_3$]	0.98	$(3.9 \pm 0.1) \times 10^{-10}$	
5b		$PhNCOC(CH_3)_3^{-}$ [+ $\cdot H$]	0.02		
6a	$PhN^{-}\cdot + CH_3COCH_3$	$PhNCOCH_3^{-}$ [+ $\cdot CH_3$]	0.91	$(6.3 \pm 0.4) \times 10^{-12}$	2.0×10^{-9}
6b		$H_3CCOCH_2^{-}$ [+ $PhNH\cdot$]	0.08		
6c		$PhNC(O)(CH_3)_2^{-}\cdot$	0.01		
7a	$PhN^{-}\cdot + CH_3COC_2H_5$	$PhNCOCH_3^{-}$ [+ $\cdot C_2H_5$]	0.85	$(2.3 \pm 0.2) \times 10^{-11}$	1.1×10^{-9} [c]
7b		$PhNCOC_2H_5^{-}$ [+ $\cdot CH_3$]	0.10		
7c		$C_2H_5COCH_2^{-}$ [+ $PhNH\cdot$]	0.03		
7d		$PhNC(O)(CH_3)C_2H_5^{-}\cdot$	0.02		
8a	$PhN^{-}\cdot + CF_3COCH_3$	$PhNCOCF_3^{-}$ [+ $\cdot CH_3$]	0.36	$(9.1 \pm 0.8) \times 10^{-10}$	1.1×10^{-9} [c]
8b		$PhNCOCH_3^{-}$ [+ $\cdot CF_3$]	0.15		
8c		$CF_3COCH_2^{-}$ [+ $PhNH\cdot$]	0.49		
9a	$PhN^{-}\cdot + CF_3COCF_3$	$PhNCOCF_3^{-}$ [+ $\cdot CF_3$]	0.96	$(4.9 \pm 0.1) \times 10^{-10}$	1.2×10^{-9}
9b		$(CF_3)_2CO^{-}\cdot$ [+ PhN]	0.02		
9c		$PhNCO(CF_3)_2^{-}\cdot$	0.02		
10a	$PhN^{-}\cdot\ CH_3COCOCH_3$	$PhNCOCH_3^{-}$ [+ $CO + \cdot CH_3$]	0.98	$(6.4 \pm 0.5) \times 10^{-10}$	1.0×10^{-9}
10b		$CH_3COCOCH_2^{-}$ [+ $PhNH\cdot$]	0.02		
11a	$PhN^{-}\cdot$ + 	$PhNCOCH_2^{-}\cdot$ [+ C_2H_4]	0.93	$(6.6 \pm 0.3) \times 10^{-11}$	2.0×10^{-9}
11b		 [+ $PhNH\cdot$]	0.04		
11c		$PhNCO(CH_2)_3^{-}\cdot$	0.03		
12	$PhN^{-}\cdot$ + 	$PhNCO(CH_2)_4^{-}\cdot$	1.00	*e*	
13	$PhN^{-}\cdot$ + 	$PhNCO(CH_2)_5^{-}\cdot$	1.00	*e*	
14	$PhN^{-}\cdot$ + 	$PhNCO(CH_2)_6^{-}\cdot$	1.00	*e*	
15a	$PhN^{-}\cdot + HCO_2CH_3$	$PhNCHO^{-}$ [+ $\cdot OCH_3$]	0.84	$(1.6 \pm 0.1) \times 10^{-12}$	1.5×10^{-9}
15b		CH_3O^{-} ($HOCH_3$)	0.13		
15c		CH_3O^{-} ($(HOCH_3)_2$)	0.03		
16a	$PhN^{-}\cdot + CH_3CO_2CH_3$	$PhNCOCH_3^{-}$ [+ $\cdot OCH_3$]	0.88	1.5×10^{-13} [f]	1.4×10^{-9}
16b		$CH_3CO_2CH_2^{-}$ [+ $PhNH\cdot$]	0.12		
17	$PhN^{-}\cdot + C_6H_5CO_2CH_3$	$PhNCOC_6H_5^{-}$ [+ $\cdot OCH_3$]	1.00	*e*	
18a	$PhN^{-}\cdot + CF_3CO_2CH_3$	$PhNCOCF_3^{-}$ [+ $\cdot OCH_3$]	0.99	$(9.1 \pm 0.3) \times 10^{-10}$	1.6×10^{-9}
18b		$PhNCO_2CH_3^{-}$ [+ $\cdot CF_3$]	0.01		
19a	$PhN^{-}\cdot + CF_3CO_2C_2H_5$	$PhNCOCF_3^{-}$ [+ $\cdot OC_2H_5$]	0.99	$(7.9 \pm 0.4) \times 10^{-10}$	1.6×10^{-9} [d]
19b		$PhNCO_2C_2H_5^{-}$ [+ $\cdot CF_3$]	0.01		
20	$PhN^{-}\cdot + CF_3COSC_2H_5$	$PhNCOCF_3^{-}$ [+ $\cdot SC_2H_5$]	1.00	$(7.6 \pm 0.2) \times 10^{-10}$	
21	$PhN^{-}\cdot + CH_3COCl$	Cl^{-} [+ $PhNCOCH_3\cdot$]	1.00	$(7.5 \pm 0.4) \times 10^{-10}$	1.8×10^{-9}
22a	$PhN^{-}\cdot + CH_3COCO_2CH_3$	$PhNCOCH_3^{-}$ [+ $\cdot CO_2CH_3$]	0.83	$(6.7 \pm 0.4) \times 10^{-10}$	1.1×10^{-9} [c]
22b		$PhNCOCO_2CH_3^{-}$ [+ $\cdot CH_3$]	0.03		
22c		$PhNCO_2CH_3^{-}$ [+ $\cdot COCH_3$]	0.08		
22d		$PhNCOCOCH_3^{-}$ [+ $\cdot OCH_3$]	0.04		
22e		$CH_2COCO_2CH_3^{-}$ [+ $PhNH\cdot$]	0.02		
23	$PhN^{-}\cdot + CO_2$	$PhNCO_2^{-}\cdot$	1.00	$(1.4 \pm 0.2) \times 10^{-10}$	7.0×10^{-10}
24a	$PhN^{-}\cdot + COS$	$S^{-}\cdot$ [+ $PhNCO$]	variable[g]	$(2.1 \pm 0.1) \times 10^{-10}$	1.0×10^{-9}
24b		$S_2^{-}\cdot$ [+ CO from $S^{-}\cdot + COS$]	variable		
24c		$PhNS^{-}\cdot$ [+ CO]	0.15		
25a	$PhN^{-}\cdot + CS_2$	$S^{-}\cdot$ [+ $PhNCS$]	0.32	$(1.3 \pm 0.1) \times 10^{-10}$	1.1×10^{-9}
25b		$S_2^{-}\cdot$ [+ $PhNC$]	0.33		
25c		$PhNCS_2^{-}\cdot$	0.19		
25d		$PhNS^{-}\cdot$ [+ CS]	0.16		
26a	$PhN^{-}\cdot + O_2$	NO_2^{-} [+ $\cdot C_6H_5$]	0.58	$(5.9 \pm 0.7) \times 10^{-12}$	6.1×10^{-10}
26b		$PhNO_2^{-}\cdot$	0.35		
26c		PhO^{-} [+ NO]	0.07		

[a] k's are estimated to be accurate to ±30%. Errors given are standard deviations from multiple determinations. [b] Calculated collision rate constants using the average dipole orientation theory; ref 32. [c] Calculated Langevin collision rate constant[32] since the dipole moment of the neutral is unknown. [d] Assumes the same k_{ADO} as that for the methyl ester. [e] Rate constant not determined due to the low vapor pressure of the neutral. [f] This k measured at $P_{He} = 1.1$ torr, $\bar{v} = 30$ m s^{-1}. [g] See text.

with CH_3Cl) require that sizeable barriers exists on the potential energy surfaces of these reactions.[7-9] Thus, the kinetic nucleophilicity of $PhN^{-}\cdot$ must be considered to be *low* toward S_N2 displacement at sp^3 carbon of the methyl haldies (similar to Cl^{-}, CN^{-}, $C_2^{-}\cdot$, and $S_2^{-}\cdot$).[7] The slow rate constant for the reaction of $PhN^{-}\cdot$ with CH_3Br has also been observed at low pressure in an

Table II. Summary of Kinetic and Product Data for the Ion-Molecule Reactions of Sulfur Anion Radical ($S^{-}\cdot$)

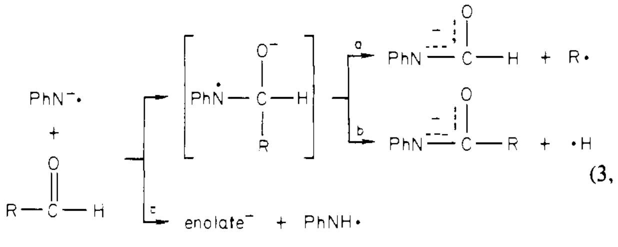
reaction	ion + neutral reactants	products [assumed neutral]	fraction of product ion signal	k_{total},[a] cm^3 $molecule^{-1}$ s^{-1}	k_{ADO},[b] cm^3 $molecule^{-1}$ s^{-1}
27	$S^{-}\cdot + CH_3Br$	Br^- [+ $\cdot SCH_3$]	1.00	$(4.2 \pm 0.5) \times 10^{-10}$	1.8×10^{-9}
28	$S^{-}\cdot + CH_3Cl$	Cl^- [+ $\cdot SCH_3$]	1.00	(3.0×10^{-11})	1.9×10^{-9}
29	$S^{-}\cdot + CH_3CHO$	HS^- [+ $CH_3CO\cdot$]	1.00	$(3.1 \pm 0.3) \times 10^{-11}$	2.5×10^{-9}
30	$S^{-}\cdot + CF_3COCH_3$	$CF_3COCH_2^-$ [+ $\cdot SH$]	1.00	1.1×10^{-9} [e]	1.5×10^{-9} [c]
31a	$S^{-}\cdot + CF_3COCF_3$	CF_3COS^- [+ $\cdot CF_3$]	0.96	$(7.3 \pm 0.6) \times 10^{-10}$	1.7×10^{-9}
31b		$(CF_3)_2CO(S)^{-}\cdot$	0.04		
32a	$S^{-}\cdot + CF_3CO_2CH_3$	CF_3COS^- [+ $\cdot OCH_3$]	0.35	$(1.2 \pm 0.1) \times 10^{-9}$	2.3×10^{-9}
32b		$CF_3CO_2^-$ [+ $\cdot SCH_3$]	0.65		
33a	$S^{-}\cdot + CF_3CO_2C_2H_5$	CF_3COS^- [+ $\cdot OC_2H_5$]	0.96	$(1.1 \pm 0.1) \times 10^{-9}$	2.3×10^{-9} [d]
33b		$CF_3CO_2^-$ [+ $\cdot SC_2H_5$]	0.04		

[a-d] Same description as footnotes *a-d* in Table I. [e] A single determination.

ion cyclotron resonance (ICR) spectrometer ($k = (1.9 \pm 0.3) \times 10^{-11}$ cm^3 $molecule^{-1}$ s^{-1}).[26]

Bohme et al.[7] have reported the rate constants for the reactions of $S^{-}\cdot$ with CH_3Br ($k = 4.6 \times 10^{-10}$ cm^3 $molecule^{-1}$ s^{-1}) and CH_3Cl ($k = 3.0 \times 10^{-11}$ cm^3 $molecule^{-1}$ s^{-1}) in an FA at 297 K. We repeated the reaction with CH_3Br and obtained the same value (Table II). These reactions are exothermic by 31 and 24 kcal mol^{-1},[7] respectively. On the basis of these data, $S^{-}\cdot$ was considered to be kinetically of *medium* nucleophilicity toward sp^3 carbon of the methyl halides.[7]

Reactions of $PhN^{-}\cdot$ and $S^{-}\cdot$ with Aldehydes. The reactions of $PhN^{-}\cdot$ with CH_3CHO and C_2H_5CHO (reactions 3 and 4) occurred mainly by carbonyl addition followed by radical β fragmentation (channels a and b) with a small amount of proton transfer (channel c). However, the qualitative similarity shown in eq 3,4 is shattered when we consider that the fragmentation ratio a/b changes from 0.5 for $R = CH_3$ to 3.0 for $R = C_2H_5$. For $R = CH_3$, channel a has $\Delta H° = -16.4$ kcal mol^{-1} [27] and channel b has $\Delta H° = -7.6$ kcal mol^{-1},[28] and $\delta\Delta H° = -8.8$ kcal mol^{-1}; for $R = C_2H_5$, channel a has $\Delta H° = -18.4$ kcal mol^{-1} [27] and channel b has $\Delta H° = -9.8$ kcal mol^{-1},[28] and $\delta\Delta H° = -8.6$ kcal mol^{-1}. Thus, thermochemistry favors fragmentation channel a over that of channel b. This agrees with the observed a/b ratio from C_2H_5CHO (reaction 4) but is in obvious disagreement with the inverted a/b ratio observed from CH_3CHO (reaction 3). We would also expect no difference in the exothermicity of the addition of $PhN^{-}\cdot$ to RCHO to give the tetrahedral intermediate $PhNCH(O^-)R$ where $R = CH_3$ vs. C_2H_5.



(3, 4)

These same reactions have been examined in the trapped ion cell of an ICR spectrometer.[26] Although the minor H^+-transfer channels (c) were not observed, the a/b fragmentation ratio from $PhN^{-}\cdot$ with C_2H_5CHO was 3.0, the same as the FA ratio, with a somewhat smaller rate constant ($k = (7.0 \pm 0.7) \times 10^{-11}$ cm^3 $molecule^{-1}$ s^{-1}). For the analogous reaction of $PhN^{-}\cdot$ with CH_3CHO, "H-atom displacement (was) the major pathway" (a/b < 1), but no rate constant was reported. The somewhat larger rate constant measured for the reaction of $PhN^{-}\cdot$ with C_2H_5CHO in the FA compared to that in the ICR could be due to a P_{He} dependency on the reaction. No change in the rate constant or production distribution was observed when P_{He} was varied from 0.4 to 1.1 torr in the FA. Since this difference is small ($k_{FA}/k_{ICR} = 2.6$), it may simply reflect an error in the ICR rate constant. This latter conclusion is reinforced when we note that the fragmentation ratio a/b is the *same* from both techniques.[29]

For the reaction of $PhN^{-}\cdot$ with $(CH_3)_3CCHO$, channel a has $\Delta H° = -23.7$ kcal mol^{-1}, while channel b has $\Delta H° = -11.8$ kcal mol^{-1}.[27,30] As expected, loss of the $(CH_3)_3C\cdot$ from the tetrahedral intermediate formed in this reaction is the major product-forming channel (98%). The preferred loss of the larger alkyl radical vs. hydrogen is, therefore, observed in the reactions of $PhN^{-}\cdot$ with C_2H_5CHO and $(CH_3)_3CCHO$ but *not* in the reaction of $PhN^{-}\cdot$ with CH_3CHO.

Generally, for stable molecules, $D°(C-H) > D°(C-CH_3)$ by 10–18 kcal mol^{-1}, $D°(C-CH_3) \geq D°(C-C_2H_5)$ by 0–4 kcal mol^{-1}, and $D°(C-C_2H_5) > D°(C-C(CH_3)_3)$ by 5–10 kcal mol^{-1}.[31] The following considerations are noted to develop an explanation for the apparent reversal of the CH_3 vs. H radical fragmentation order in the reaction of $PhN^{-}\cdot$ with CH_3CHO: (a) collisional stabilization was not a factor since similar rate constants and product ratios were obtained at low (~10^6 torr, ICR) and moderate (0.5 torr, FA) pressures, (b) the product acylanilide anions are closely related to one another so no special effect is seen in the reaction products, and (c) the structural similarities of the starting aldehydes disallows the idea of a change in mechanism in this series of reactions. Therefore, we direct our attention to the structure of the tetrahedral intermediate $Ph\dot{N}CHR(O^-)$. The results suggest that the $D°(C-H)$ is unusually small in these structures. Although we cannot exclude the effect of the oxy anion in this structure, we believe that the major influence on the special weakening of the C–H bond is its coupling with the β-radical center on the anilino nitrogen. We suggest that this may be due to a radical hyperconjugative effect. Not only would this account for the data but this effect would explain why signals for the intermediate adducts are observed in the reactions of $PhN^{-}\cdot$ with $(CH_3)_2C{=}O$ and $CH_3COC_2H_5$ (next section) but not with these three aldehydes.

The reaction of $S^{-}\cdot$ with CH_3CHO (reaction 29) proceeded exclusively by H-atom transfer. This result requires that the H atom affinity of $S^{-}\cdot$ is greater than that of $PhN^{-}\cdot$[18,19] and means that the $HA(S^{-}\cdot)$ in ref 19 is low by several kcal mol^{-1}.

Reactions of $PhN^{-}\cdot$ and $S^{-}\cdot$ with Acyclic Ketones. The reaction of $PhN^{-}\cdot$ with acetone (reaction 6) occurred primarily by addi-

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(26) Pellerite, M.; Brauman, J. I. *J. Am. Chem. Soc.* **1981**, *103*, 676–677.

(27) $\Delta H°$'s calculated on the basis of the following data: $\Delta H_f°(PhN^{-}\cdot) = 60$ kcal mol^{-1};[18] $\Delta H_f°(PhNCHO^-) = 30.4$ kcal mol^{-1} on the basis of $\Delta H_f°(PhNHCHO) = -13.2$ kcal mol^{-1} (calcd)[21] and estimated $\Delta H°_{acid}(PhNHCHO) = 350$ kcal mol^{-1}; and $\Delta H_f°$'s of $\cdot CH_3$ and $\cdot C_2H_5$ from ref 21.

(28) $\Delta H°$'s calculated on the basis of the following data: $\Delta H_f°(PhN^{-}\cdot) = 60$ kcal mol^{-1};[18] $\Delta H_f°(PhNCOCH_3^-) = -45.2$ kcal mol^{-1} on the basis of $\Delta H_f°(PhNHCOCH_3) = -45.2$ kcal mol^{-1} [21] and $\Delta H°_{acid}(PhNHCOCH_3) = 352.8$ kcal mol^{-1};[16] $\Delta H_f°(PhNCOC_2H_5^-) = -47.4$ kcal mol^{-1} on the basis of $\Delta H_f°(PhNHCOC_2H_5) = -32.2$ kcal mol^{-1} and estimated $\Delta H°_{acid}(PhNHCOC_2H_5) = 352$ kcal mol^{-1}; and $\Delta H_f°$'s of CH_3CHO and C_2H_5CHO.[22]

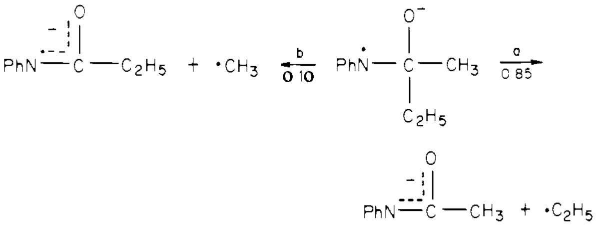
(29) It is generally agreed that rate constants measured by the FA method are more accurate than those obtained in the ICR technique. However, branching ratios are easily measured by both methods.

(30) $\Delta H_f°(PhNCOC(CH_3)_3^-) = -62.2$ kcal mol^{-1} on the basis of $\Delta H_f°(PhNHCOC(CH_3)_3) = -46.0$ kcal mol^{-1} (calcd)[21] and estimated $\Delta H°_{acid}(PhNHCOC(CH_3)_3) = 351$ kcal mol^{-1}; $\Delta H_f°$'s of $(CH_3)_3C\cdot$ from ref 20 and $(CH_3)_3CCHO$ from ref 22.

(31) Benson, S. W. *J. Chem. Ed.* **1965**, *42*, 502–518.

tion/fragmentation to yield $PhN{=}C(O^-)CH_3$ (*m/z* 134) with a minor amount of H^+ transfer producing the enolate anion $CH_3C(O^-){=}CH_2$ (*m/z* 57). In this reaction, 1% of the product ion signals was *m/z* 149 and was considered to be the tetrahedral anion radical intermediate $Ph\dot{N}C(O^-)(CH_3)_2$.

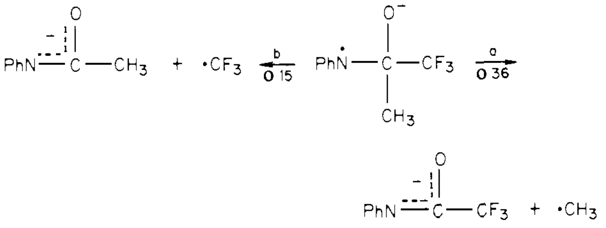
The overall results of the reaction of $PhN^{-}\cdot$ with $CH_3COC_2H_5$ (reaction 7) were similar to those of acetone, and, here also, a



(7)

small amount of the product ion signal *m/z* 161 was attributed to the tetrahedral intermediate $Ph\dot{N}C(O^-)(CH_3)C_2H_5$. However, in this example, the tetrahedral intermediate formed by carbonyl addition can fragment in two directions with loss of $\cdot CH_3$ or $\cdot C_2H_5$. The ratio (reaction 7a)/(reaction 7b) = 8.5, favoring loss of the $\cdot C_2H_5$ is in agreement with a tenant of mass spectrometry that loss of the larger radical is preferred in fragmentation of various cation radicals. This is similar to the addition/fragmentation channels for the reaction of $PhN^{-}\cdot$ with C_2H_5CHO and $(CH_3)_3CCHO$ but not with CH_3CHO.

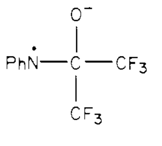
While the above two reactions are rather inefficient (efficiency = k_{total}/k_{ADO}[32]), the reaction of $PhN^{-}\cdot$ with CF_3COCH_3 occurred at nearly the collision limit. The major single reaction channel (reaction 8c) is H^+ transfer expected because of the high acidity ($\Delta H^\circ_{acid}(CF_3COCH_3) = 350.3 \pm 2$ kcal mol^{-1})[16] of this ketone. However, it is interesting that the addition/fragmentation channels (reactions 8, a and b) comprise the principal (51%) pathway of



(8)

reaction. In this example, we see that fragmentation of the tetrahedral, anion radical intermediate prefers loss of $\cdot CH_3$ over loss of $\cdot CF_3$ by a factor of 2.4. This is in qualitative agreement with the overall thermochemistry of the two channels; for channel 8a, $\Delta H^\circ = -27.8$ kcal mol^{-1}, and for channel 8b, $\Delta H^\circ = -22.4$ kcal mol^{-1}.[28,33a]

The reaction of $PhN^{-}\cdot$ with CF_3COCF_3 (reaction 9) was also fast, and the exclusive reaction channel was addition/fragmentation ($\Delta H^\circ = -30.9$ kcal mol^{-1}).[28,33] The rate constant for this reaction was the same as that for the sum of the two addition/fragmentation channels (reactions 8a and 8b) in the reaction of $PhN^{-}\cdot$ with CF_3COCH_3. Thus, the expected stabilizing influence of an additional CF_3 group on the tetrahedral intermediate **1**



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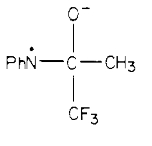


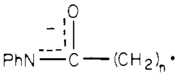
2

compared to that of **2** was not felt in their overall rate constants ($\Delta H^\circ_{acid}(CF_3CH(CH_3)OH = 364 \pm 4$ kcal mol^{-1} and $\Delta H^\circ_{acid}((CF_3)_2CHOH) < 351$ kcal mol^{-1}).[16] However, these two rate constants are approaching those of their collision limits.

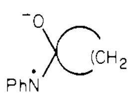
The reaction of $PhN^{-}\cdot$ with the α-diketone biacetyl (reaction 10) occurred with a rate constant 100 times greater than the corresponding reaction of $PhN^{-}\cdot$ with acetone. Addition/fragmentation was the major reaction channel along with 2% H^+ transfer. Since the trans conformation of biacetyl has no dipole moment, the factors contributing to this large rate acceleration for the biacetyl reaction include (a) greater polarizability of the neutral molecule, and (b) a decreased bond strength of the C_2–C_3 bond in the tetrahedral anion radical intermediate concomitant with a lower barrier to radical fragmentation. It is conceivable that trans biacetyl undergoes rotation about its C_2–C_3 bond in the collision complex and reacts with $PhN^{-}\cdot$ in the dipolar cis conformation.

The reaction of $S^{-}\cdot$ with CF_3COCH_3 proceeded by exclusive H^+ transfer at nearly the collision limit (reaction 30). The related reaction of $PhN^{-}\cdot$ with CF_3COCH_3 produced addition/fragmentation along with H^+ transfer. These results require that $PA(S^{-}\cdot) > PA(PhN^{-}\cdot)$ and that the value listed in ref 19 is low by >20 kcal mol^{-1}. When the H^+-transfer channel was removed as a possibility, as in the reaction of $S^{-}\cdot$ with CF_3COCF_3, a fast addition reaction was observed (reaction 31). Although addition/fragmentation was the principle process in the latter reaction, a small amount of the anion *m/z* 257, assumed to be the addition adduct, was observed. In this reaction of $S^{-}\cdot$ with CF_3COCF_3, a small signal for an anion *m/z* 289 was observed with the concomitant small decrease in the $S_2^{-}\cdot$ signal present as a byproduct signal in the preparation of $S^{-}\cdot$. We consider the structure of the *m/z* 289 product ion to be that of the addition adduct of $S_2^{-}\cdot$ with CF_3COCF_3.

Reactions of $PhN^{-}\cdot$ with Cyclic Ketones. If we apply the idea of carbonyl addition followed by radical β fragmentation to the reactions of $PhN^{-}\cdot$ with cyclic ketones, a new type of anion radical structure **3** will result. In structure **3**, the anion portion of the



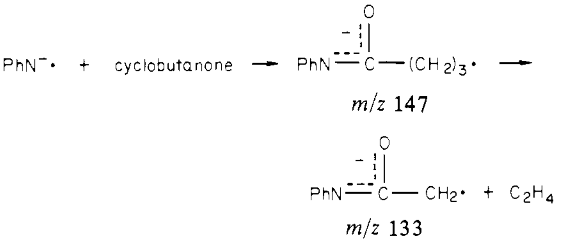
3



4

molecule is delocalized at one end as an acyl anilide anion unit with a reactive alkyl free radical unit at the other end. Our interest in anion radicals with these structural features is that they should allow free radical chemistry to be studied by using the ion dipole and ion induced dipole attractive forces between neutral substrates and the relatively unreactive anion end of the species to produce long-lived, ion–molecule collision complexes.

The question of whether the acyclic structure **3** or cyclic structure **4** represents such species appears to be answered in the reaction of $PhN^{-}\cdot$ with cyclobutanone (reaction 11). If the small



(11a,c)

amount of H^+ transfer is ignored (reaction 11b), the product ions are *m/z* 147 and 133. We rationalize these data by initial formation of the anion radical *m/z* 147, which is produced vibrationally hot due to the exothermic addition reaction and from release of the strain energy of the four-membered ring ($E_s = 22.6$ kcal mol^{-1}).[21] While a small number of *m/z* 147 ions are stabilized by collisions with the buffer gas, most of these ions suffer fragmentation and loss of C_2H_4 to yield the anion radical *m/z* 133. The relief of the four-membered-ring strain energy in the radical fragmentation of the addition adduct to ion radical *m/z* 147 offsets

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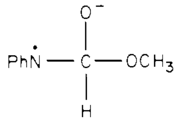
[32] Collision limit rate constants, k_{ADO}, are calculated by the average dipole orientation theory: Su, T.; Bowers, M. T. *J. Chem. Phys.* **1973**, *58*, 3027–3037; *Int. J. Mass Spectrom. Ion Phys.* **1973**, *12*, 347–356.

[33] (a) $\Delta H_f^\circ(PhNCOCF_3^-) = -196$ kcal mol^{-1} on the basis of $\Delta H_f^\circ(PhNHCOCF_3) = -168.8$ kcal mol^{-1} (calcd)[21] and estimated $\Delta H^\circ_{acid}(PhNHCOCF_3) = 340$ kcal mol^{-1} and ΔH_f°'s of CF_3COCH_3,[16] $\cdot CH_3$,[21] and $\cdot CF_3$.[21] (b) $\Delta H_f^\circ(CF_3COCF_3) = -336.2$ kcal mol^{-1} (calcd).[21]

the endothermic loss of C_2H_4 from the alkyl radical. With the reaction $CH_3CH_2CH_2\cdot \rightarrow \cdot CH_3 + C_2H_4$ as a model for this process, $\Delta H° = +25.8$ kcal mol^{-1}.[34]

The reactions of $PhN^{-}\cdot$ with cyclopentanone, cyclohexanone, and cycloheptanone (reactions 12–14) were found to give exclusively the product anion radicals with m/z values equal to the sum of the masses of $PhN^{-}\cdot$ and cyclic ketone. Due to the rather high boiling points of these ketones, the vapor of each was inletted directly to the flow from small reservoirs of the liquid attached to the flow tube. We consider the structures of the product anion radicals to be **3** with n = 4, 5, and 6, respectively, rather than those of the corresponding addition adducts **4**.

Reactions of $PhN^{-}\cdot$ and $S^{-}\cdot$ with Esters. The slow reaction of $PhN^{-}\cdot$ and HCO_2CH_3 yielded three product anions, $PhNCHO^{-}$ (m/z 120, 84%), $CH_3O^{-}(HOCH_3)$ (m/z 63, 13%), and $CH_3O^{-}(HOCH_3)_2$ (m/z 95, 3%) (reaction 15). $PhNCHO^{-}$ was the expected product of the addition/fragmentation channel, with loss of $\cdot OCH_3$ from the tetrahedral intermediate **5**; $\Delta H° = -6.1$ kcal mol^{-1} for this reaction.[27,35] Anionic fragmentation of **5** to yield CH_3O^{-} and $PhNCHO\cdot$ is considered unlikely since EA($PhNCHO\cdot$) should be significantly greater than EA($CH_3O\cdot$) (36.2 ± 0.5 kcal mol^{-1}),[36] and the overall reaction would be endothermic. Further, the much stronger base CH_3O^{-} would be generated (δPA = 29 kcal mol^{-1}),[16,27] and no other examples of reactions of $PhN^{-}\cdot$ with esters to produce naked alkoxide anions are known. Therefore, we consider the source of the two cluster ions $CH_3O^{-}(HOCH_3)$ and $CH_3O^{-}(HOCH_3)_2$ to be a Riveros reaction[37] where $PhN^{-}\cdot$ removes the formyl hydrogen of HCO_2CH_3 as a proton to yield the unobserved complex $CH_3O^{-}(\cdot NHPh)$ (eq IV). This complex, which is probably weakly bound, would be



$$PhN^{\bullet}-\overset{O^{-}}{\underset{H}{C}}-OCH_3$$

5

$$PhN^{-}\cdot + HCO_2CH_3 \rightarrow CH_3O^{-}(\cdot NHPh) + CO \quad \text{(IV)}$$

expected to undergo a fast Riveros reaction with a large excess of HCO_2CH_3 to produce the two observed clusters. Although the tertiary reaction in eq 15c has not been reported in ICR experiments, it was readily observed in the FA apparatus when CH_3O^{-}, generated by dissociative electron attachment with CH_3ONO, and the reaction of CH_3O^{-} with HCO_2CH_3 was examined (k_{15b} = (6.5 ± 0.3) × 10^{-10} cm^3 molecule^{-1} s^{-1}; k_{15c} = (1.2 ± 0.1) × 10^{-11} cm^3 molecule^{-1} s^{-1}).

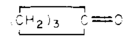
$$CH_3O^{-}(\cdot NHPh) + HCO_2CH_3 \rightarrow CH_3O^{-}(HOCH_3) + CO + PhNH\cdot \quad \text{(15b)}$$

$$CH_3O^{-}(HOCH_3) + HCO_2CH_3 \rightarrow CH_3O^{-}(HOCH_3)_2 + CO \quad \text{(15c)}$$

The reaction of $PhN^{-}\cdot$ with $CH_3CO_2CH_3$ was extremely slow (reaction 16). To measure the rate constant for this reaction, we had to reduce $\bar{v}$ to 36 m s^{-1} to increase the ion and neutral residence time in the ion–molecule reaction region. Under these conditions, three data points varying the $CH_3CO_2CH_3$ concentration were obtained to yield the rate constant and product distribution listed in Table I. As expected, addition/fragmentation producing $PhNCOCH_3^{-}$ (m/z 134) was the major reaction channel along with a small amount (12%) of H^+ transfer.

Due to the high boiling point of $PhCO_2CH_3$, the vapors of the liquid ester were added directly to the helium flow containing $PhN^{-}\cdot$. The only observed product was $PhNCOPh^{-}$ (m/z 196).

Table III. Relative Rate Constants for the Addition/Fragmentation Reactions of $PhN^{-}\cdot$ with Carbonyl Compounds

compound	$k_{rel}^{C=O\ a}$	$\Delta H°$,^{b} kcal mol^{-1}
CH_3COCH_3	1	−19.0
$CH_3COC_2H_5$	4	−21.7
CF_3COCH_3	80	−22.4
CF_3COCF_3	83	−30.9
	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
CH_3COCl	129	−63.3

[a] These relative rate constants are k_{total} × (sum of the fractions of those channels yielding addition adducts and/or acyl anilide anions) from Table I relative to that of acetone. [b] $\Delta H°$'s are for the major addition/fragmentation channel in those reactions involving more than one such channel. Most of these values are given in the text; the others are calculated with data in ref 16, 18, 21, 22, 27, and 28.

The reactions of $PhN^{-}\cdot$ with the methyl and ethyl esters of CF_3CO_2H (reactions 18 and 19) were of interest since these reactions allow a direct comparison of the nucleophilicity of $PhN^{-}\cdot$ in carbonyl addition vs. S_N2 displacement at the alkyl group with a good leaving anion group $CF_3CO_2^{-}$.[8,38] Both reactions occurred with the same rate constant (within error limits) and gave the same product distribution formed *exclusively* by the addition/fragmentation mechanism. The related reaction of $PhN^{-}\cdot$ with $CF_3C(O)SC_2H_5$ (reaction 20) also occurred with essentially the same rate constant as determined with CF_3CO_2R (above), and $PhNCOCF_3^{-}$ (m/z 188) was the only product anion.

It is obvious from these results that the rate constant for carbonyl addition (followed by fragmentation) must be 50–100 times greater than the rate constant for S_N2 displacement. This occurs in spite of the fact that the S_N2 displacement reaction (eq V) is considerably more exothermic than that of addition/fragmentation (eq 18a).[25,33a,35,39] We consider this to be evidence for a three-minimum-potential surface in the addition/fragmentation mechanism (to be discussed).

$$PhN^{-}\cdot + CF_3CO_2CH_3 \rightarrow CF_3CO_2^{-} + PhNCH_3\cdot \quad \text{(V)}$$

$$\Delta H° = -55.8 \text{ kcal mol}^{-1}$$

$$PhN^{-}\cdot + CF_3CO_2CH_3 \rightarrow PhNCOCF_3^{-} + \cdot OCH_3 \quad \text{(18a)}$$

$$\Delta H° = -14.6 \text{ kcal mol}^{-1}$$

The reaction of $PhN^{-}\cdot$ with CH_3COCl (reaction 21) was fast, and Cl^{-} was the only observed anion product. We favor a mechanism of carbonyl addition by $PhN^{-}\cdot$ followed by anionic fragmentation from the tetrahedral intermediate. However, we cannot exclude the possibility of $PhN^{-}\cdot$ functioning as a base to effect an E2 elimination from CH_3COCl to produce $PhNH\cdot + CH_2{=}C{=}O + Cl^{-}$ ($\Delta H° = -15.2$ kcal mol^{-1}).[23,25,40]

The results of the reactions of $PhN^{-}\cdot$ with $(CH_3)_2CO$ and $CH_3CO_2CH_3$ demonstrated a larger rate constant for addition/fragmentation at the ketone C=O compared to that of the ester group. The reaction of $PhN^{-}\cdot$ with $CH_3COCO_2CH_3$ was investigated (reaction 22) to see if a similar selectivity of addition/fragmentation would be observed with the two types of carbonyl groups in a more complex structure. The α-dicarbonyl

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(34) The $\Delta H_f°$'s of n-$C_3H_7\cdot$, $\cdot CH_3$, and C_2H_4 are from ref 21.

(35) The $\Delta H_f°(HCO_2CH_3)$ is from ref 21, and $\Delta H_f°(\cdot OCH_3)$ from ref 36.

(36) Engelking, P. C.; Ellison, G. B.; Lineberger, W. C. *J. Chem. Phys.* **1978**, *69*, 1826–1832.

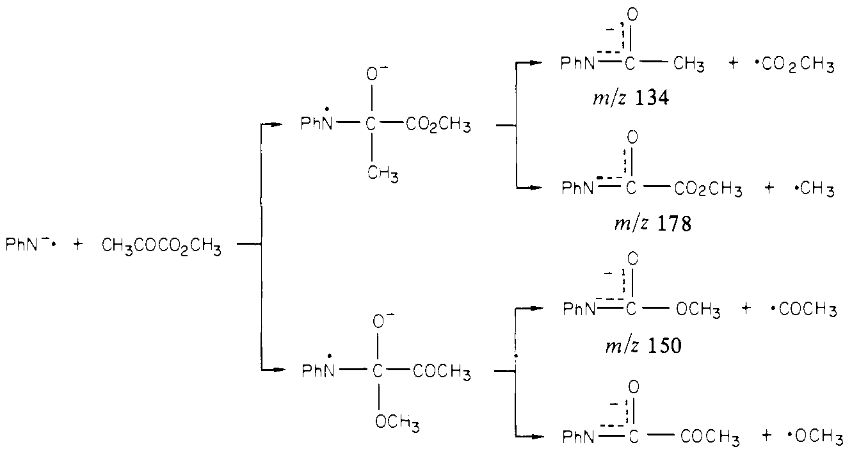
(37) (a) Faigle, J. F. G.; Isolani, P. C.; Riveros, J. M. *J. Am. Chem. Soc.* **1976**, *98*, 2049–2052. (b) Isolani, P. C.; Riveros, J. M. *Chem. Phys. Lett.* **1975**, *33*, 362–364. (c) Blair, L. K.; Isolani, P. C.; Riveros, J. M. *J. Am. Chem. Soc.* **1973**, *95*, 1057–1060.

(38) (a) McDonald, R. N.; Chowdhury, A. K. *J. Am. Chem. Soc.* **1982**, *104*, 901–902. (b) Comisarow, M. *Can. J. Chem.* **1977**, *55*, 171–173.

(39) $\Delta H_f°(CF_3CO_2CH_3) = -240.7$ kcal mol^{-1} (calcd)[21] and $\Delta H_f°(CF_3CO_2^{-}) = -290$ kcal mol^{-1}.[16]

(40) $\Delta H_f°$'s of CH_3COCl and $CH_2{=}C{=}O$ are from ref 22.

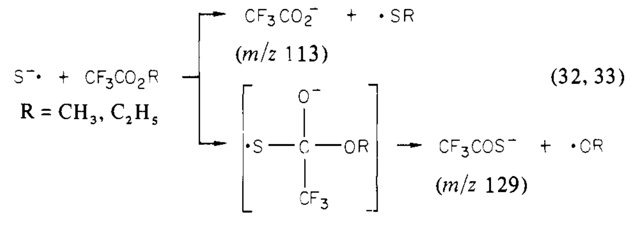
(41) Streitweiser, A. "Solvolytic Displacement Reactions"; McGraw-Hill: New York, 1962; pp 11–13.



(21a) (21b) (21c) (21d)

groupings of this pyruvate ester and biacetyl suggested that similar overall rate constants should be observed for these two reactions, and this was observed. The anion products were *m/z* 134 ($PhNCOCH_3^-$, 83%), *m/z* 178 ($PhNCOCO_2CH_3^-$, 3%), *m/z* 150 ($PhNCO_2CH_3^-$, 8%), and *m/z* 162 ($PhNCOCOCH_3^-$, 4%), along with *m/z* 101 ($CH_2COCO_2CH_3^-$, 2%) formed by H^+ transfer. The structure and mechanism of formation of the first four product anions are shown in eq 21, a–d. On the basis of this interpretation, the addition/fragmentation reaction of $PhN^-\cdot$ to the ketone carbonyl of $CH_3COCO_2CH_3$ is favored by a factor of 7 over that of addition/fragmentation to ester carbonyl group.

The reactions of $PhN^-\cdot$ with $CF_3CO_2CH_3$, $CF_3CO_2C_2H_5$, and $CF_3C(O)SC_2H_5$ occurred exclusively by the addition/fragmentation mechanism. However, the greater nucleophilicity of $S^-\cdot$ toward saturated carbon (S_N2 mechanism) with methyl halides suggested that both processes might be observed in its reactions with the methyl and ethyl esters, CF_3CO_2R. Both reactions occurred at essentially the collision limit (reactions 32 and 33)



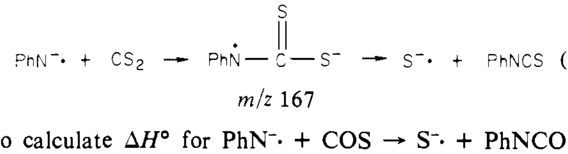
(32, 33)

but produced quite different branching ratios. The reaction of $S^-\cdot$ with $CF_3CO_2CH_3$ gave a 65/35 ratio of (S_N2 displacement)/(addition/fragmentation), while $S^-\cdot$ with $CF_3CO_2C_2H_5$ yielded 4/96 for this ratio.

Assuming that the structure had no effect on the intrinsic reactivity of $S^-\cdot$ at the carbonyl groups of the two esters (previously established for reactions of $PhN^-\cdot$ with these esters), the large variations observed in this reactivity ratio are the result of the change of the alkyl group from CH_3 to C_2H_5 on the S_N2 reactivity. From these data, we calculate $k_{CH_3}/k_{C_2H_5} = 16$ (65/4) for the gas-phase S_N2 relative reactivity value for methyl and ethyl esters. This is the first relative reactivity value for methyl and ethyl derivatives for the gas-phase S_N2 mechanism. This value of 16 is one-half the average relative reactivity (30) for nucleophilic displacement reactions with RX molecules ($R = CH_3$, C_2H_5) determined in solution[40] and is in agreement with the idea that an increased steric problem is encountered by the nucleophile displacing at C_α of C_2H_5 relative to that at CH_3.[38a]

Reactions of $PhN^-\cdot$ with CO_2, COS, CS_2, and O_2. The fast reaction of $PhN^-\cdot$ with CO_2 produced only the adduct $PhNCO_2^-\cdot$ (*m/z* 135) (reaction 23). We assume that the structure of the adduct is that derived from nucleophilic addition of $PhN^-\cdot$ to carbon of the CO_2 molecule. The C–O bond orders of 1.5 in the carboxylate anion adduct must be too strong to undergo fragmentation to yield PhNCO and $O^-\cdot$ (see below).

The fast reactions of $PhN^-\cdot$ with both COS and CS_2 produced significant quantities of $S^-\cdot$ and $S_2^-\cdot$ along with lesser amounts of other products (reactions 24 and 25). Although we are unable



$$PhN^-\cdot + CS_2 \rightarrow \overset{\bullet}{Ph N}-\overset{S}{\overset{\|}{C}}-S^- \rightarrow S^-\cdot + PhNCS$$

m/z 167

(25a,c)

to calculate $\Delta H°$ for $PhN^-\cdot + COS \rightarrow S^-\cdot + PhNCO$, it is probably similar to that of reaction 25a where $\Delta H° = -17.9$ kcal mol^{-1};[42] $PhNCS_2^-\cdot$ (*m/z* 167) and $S^-\cdot$ are major product ions. $PhNCS_2^-\cdot$ is considered to have the structure of the adduct formed by nucleophilic addition of $PhN^-\cdot$ to carbon of CS_2. Some of this adduct undergoes collisional stabilization with the helium buffer gas, but most of the excited *m/z* 167 ions suffer fragmentation to produce $S^-\cdot$ (eq 25a) and $S^-\cdot$ (see below). The formation of $PhNS^-\cdot$ (*m/z* 123) in both reactions 24 and 25 is considered to involve direct sulfur abstraction from the neutral by $PhN^-\cdot$.[44]

The source of the diatomic anion radical $S_2^-\cdot$ in both reactions 24 and 25 is interesting and involves different mechanisms. In the reaction of $PhN^-\cdot$ with COS, it is obvious that formation of $S_2^-\cdot$ must involve sequential steps with two COS molecules. The relative amount of the signal of $S^-\cdot$ in reaction 24 goes through an early maximum and then decays in the plot of log ion signal vs. added [COS] as the signal for $S_2^-\cdot$ continues to grow in magnitude. The sequence suggested for generation of $S_2^-\cdot$ in reaction 24 is that the primary product ion $S^-\cdot$ abstracts S from COS in the flow to yield $S_2^-\cdot$ and CO, $\Delta H° = -18.9$ kcal mol^{-1}.[42,45]

A similar sequence leading to $S_2^-\cdot$ from reaction 25 is unlikely due to its thermochemistry ($S^-\cdot + CS_2 \rightarrow S_2^-\cdot + CS$, $\Delta H° = +0.6 \pm 5$ kcal mol^{-1}).[42,43] This reaction can only contribute a small amount of $S_2^-\cdot$ as seen in this log ion signal vs. added [CS_2] plot. This plot shows very little change in the $S^-\cdot/S_2^-\cdot$ ratio as a function of added CS_2. An alternate pathway not involving a second CS_2 molecule must be sought. For this pathway, we suggest that the excited adduct $PhNCS_2^-\cdot*$ may yield products by three separate channels, eq 25a–c.

$$PhN^-\cdot + CS_2 \rightarrow [PhNCS_2^-\cdot*] \rightarrow S^-\cdot + PhNCS \quad (25a)$$

$$PhN^-\cdot + CS_2 \rightarrow [PhNCS_2^-\cdot*] \rightarrow S_2^-\cdot + PhNC \quad (25b)$$

$$PhN^-\cdot + CS_2 \rightarrow [PhNCS_2^-\cdot*] \xrightarrow{He} PhNCS_2^-\cdot \quad (25c)$$

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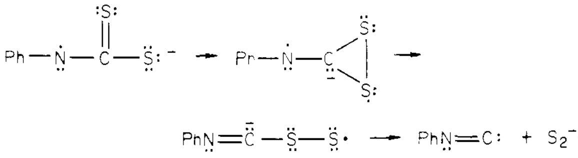
[42] $\Delta H°$ calculated on the basis of the following data: $\Delta H_f°(PhN^-\cdot)$;[18] $H_f°(S^-\cdot) = 18.8$ kcal mol from the $\Delta H_f°(S) = 66.7$ kcal mol^{-1} [21] and EA(S) = 2.077 eV,[24] $\Delta H_f°(CS)$[22] and $\Delta H_f°(PhNCS)$[43] from standard references.

[43] Stull, D. R.; Westrum, E. F.; Sinke, G. C. "The Chemical Thermodynamics of Organic Compounds"; Wiley: New York, 1969.

[44] (a) DePuy, C. H.; Bierbaum, V. M. *Tetrahedron Lett.* **1981**, *22*, 5129–5130. (b) Beak, P.; Yamamoto, J.; Upton, C. J. *J. Org. Chem.* **1975**, *40*, 3052–3062.

[45] $\Delta H_f°(S_2^-\cdot) = -7.6$ kcal mol^{-1} from $\Delta H_f°(S_2) = 30.7$ kcal mol^{-1} [21] and $EA(S_2) = 1.66$ eV;[24] $\Delta H_f°$'s of COS,[22] CS_2,[22] and CS[21] are from standard references.

Equation 25a is the exoergic addition/fragmentation channel discussed above, and eq 25c represents collisional stabilization of the adduct by the helium buffer gas. We view channel 25b as forming $\mathrm{S_2^{-}\cdot}$ via an α-elimination reaction involving sequential S–S bond formation followed by fragmentation to yield $\mathrm{S_2^{-}\cdot}$ and PhNC. A possible mechanism for this sequence is shown in eq VI. Since the reaction of $\mathrm{PhN^{-}\cdot}$ with $\mathrm{CS_2}$ gave ion signals for $\mathrm{S^{-}\cdot}$ and $\mathrm{S_2^{-}\cdot}$ of about equal intensity with only small variations as a function of added $\mathrm{CS_2}$, this was the method of producing $\mathrm{S^{-}\cdot}$ used in the above gas-phase studies.


(VI)

The reaction of doublet $\mathrm{PhN^{-}\cdot}$ with triplet oxygen ($\mathrm{^3O_2}$, $\mathrm{X^3\Sigma_g^-}$) (reaction 26) was surprisingly slow. The major anion products were $\mathrm{NO_2^-}$ (m/z 46, 58%) and $\mathrm{PhNO_2^{-}\cdot}$ (m/z 123, 35%) along with some $\mathrm{PhO^-}$ (m/z 93, 7%). Since EA(PhN) = 33.3 ± 0.8 kcal mol^{-1},[46] electron transfer between these reactants to yield ($\mathrm{PhN + O_2^{-}\cdot}$) is not possible ($\mathrm{EA(O_2)} \simeq 12$ kcal mol^{-1}).[24,47] The data can be rationalized by reaction of $\mathrm{PhN^{-}\cdot}$ with $\mathrm{^3O_2}$ to yield a linear doublet adduct that rearranges to $\mathrm{PhNO_2^{-}\cdot}$ and $\mathrm{PhONO^{-}\cdot}$. Formation of $\mathrm{RO^-}$ by dissociative electron attachment to RONO is well known ($\Delta H° = -78.9$ kcal mol^{-1} for reaction 26c).[48] Assuming that the reaction producing $\mathrm{PhNO_2^{-}\cdot}$ is reasonably exothermic, this exothermicity may be sufficient to overcome the barrier for dissociation of excited $\mathrm{[PhNO_2^{-}\cdot]^* \rightarrow NO_2^- + \cdot Ph}$. The overall reaction (eq 26a) of $\mathrm{PhN^{-}\cdot}$ with $\mathrm{O_2}$ is exothermic ($\Delta H° = -26.6$ kcal mol^{-1}).[48]

$$\mathrm{PhN^{-}\cdot + O_2 \rightarrow NO_2^- + \cdot Ph} \qquad (26a)$$

Relative Reactivities of Carbonyl-Containing Compounds. The relative reactivity of dipolar carbonyl groups of molecules in different steric and electronic environments has long been of interest.[11] For such a comparison of gas-phase reactivities, we will use the more extensive data set for the reactions of $\mathrm{PhN^{-}\cdot}$ listed in Table I. To generate the set of $k_{\mathrm{rel}}^{\mathrm{C=O}}$, k_{total} was multiplied by the sum of the percentages of only those channels involving addition and/or addition/fragmentation in each reaction; $\mathrm{H^+}$-transfer channels were excluded. These $k_{\mathrm{rel}}^{\mathrm{C=O}}$ values are listed in Table III.

Several interesting points emerge from the $k_{\mathrm{rel}}^{\mathrm{C=O}}$ values: (a) all of the rate constants are less than the ADO or Langevin collision limits for gas-phase ion–molecule reactions;[32] (b) a range of 7850 in $k_{\mathrm{rel}}^{\mathrm{C=O}}$ is observed; (c) the gas-phase relative reactivities of these carbonyl reactants with $\mathrm{PhN^{-}\cdot}$ are those observed or expected for nucleophilic addition reactions with these carbonyl reagents in solution; (d) the reaction channel of lower overall exothermicity is sometimes the major product forming channel; and (e) a general correlation between $k_{\mathrm{rel}}^{\mathrm{C=O}}$ and the exothermicity of the major product channel of the addition/fragmentation reaction is absent. The fact that the rate constants for these ion–molecule reactions are less than those calculated by collision theory means that a degree of selectivity is assured as to which of several possible reaction channels will be followed on the ion–molecule potential surface. The relative reactivity range of 7850 for this series of reactions in Table III is unusual for gas-phase ion–molecule reactions that frequently occur at or near the collision limit.

From the $k_{\mathrm{rel}}^{\mathrm{C=O}}$ data in Table III, the relative reactivities of the C=O unit in different functional groups can be compared in the series $\mathrm{CH_3COX}$ molecules, where X = H, $\mathrm{CH_3}$, $\mathrm{OCH_3}$, Cl.

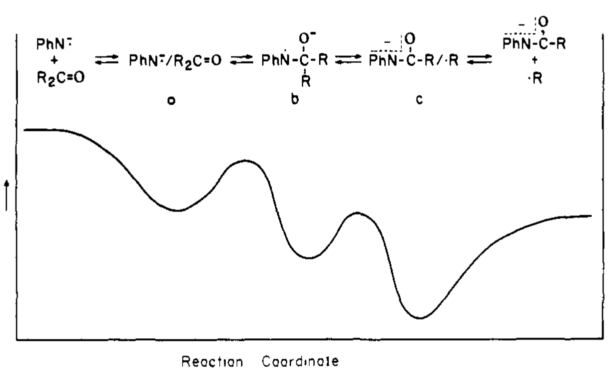


Figure 1. Reaction coordinate vs. energy diagram for the addition/fragmentation reaction of $\mathrm{PhN^{-}\cdot}$ with a carbonyl-containing molecule.

The gas-phase reactivity order for the ion–molecule reactions with $\mathrm{PhN^{-}\cdot}$ is $\mathrm{CH_3CO_2CH_3 < (CH_3)_2CO < CH_3CHO < CH_3COCl}$. This is the same relative order observed or expected for nucleophilic addition reactions with the carbonyl-containing molecules in solution.[11] Brown et al.[49] determined the rate constants for the reduction of varous aldehydes and ketones using $\mathrm{NaBH_4}$ in isopropanol, e.g., $k\mathrm{(PhCHO)}/k\mathrm{(PhCOCH_3)} = 400$.[49a] The relative rate of reduction of cyclobutanone compared to that of acetone was 17.5[49a,b] in good agreement with our value of 11. The gas-phase reactions of $\mathrm{PhN^{-}\cdot}$ with $\mathrm{CH_3COC_2H_5}$ and $\mathrm{(CH_3)_2CO}$ exhibited a larger rate constant (factor of 4) for the higher molecular weight ketone; in solution, the rate constant for reduction of $\mathrm{CH_3COC_2H_5}$ was two-fifths of that for the reduction of $\mathrm{(CH_3)_2CO}$.[49d] This latter difference in the relative rate constants for reactions at these two carbonyl centers probably reflects an increased importance of polarizability effects of alkyl groups and somewhat reduced steric effects in gas-phase reactions compared to related solution reactions.

The large increase in the rate constants by replacing the $\mathrm{CH_3}$ group by the $\mathrm{CF_3}$ group is demonstrated with the ketones, $\mathrm{(CH_3)_2CO}$ and $\mathrm{CF_3COCH_3}$ or $\mathrm{(CF_3)_2CO}$, and the esters, $\mathrm{CH_3CO_2CH_3}$ and $\mathrm{CF_3CO_2CH_3}$. We were somewhat surprised to find that $k_{\mathrm{rel}}^{\mathrm{C=O}}$ for the reactions of $\mathrm{PhN^{-}\cdot}$ with $\mathrm{CF_3COCH_3}$ and $\mathrm{(CF_3)_2CO}$ were the same value within experimental error; however, both rate constants are close to their ADO collision limits. A better test of substituent group additivity effects should involve rate constants that differ from their collision limits by larger factors. The large values of $k_{\mathrm{rel}}^{\mathrm{C=O}}$ for the reactions of $\mathrm{CF_3CO_2CH_3}$ and $\mathrm{CH_3COCl}$ are in keeping with the fast hydrolysis of these species in solution.

Mechanism of Formation of Acyl Anilide Anions from the Reactions of $\mathrm{PhN^{-}\cdot}$ and $\mathrm{S^{-}\cdot}$ with Carbonyl-Containing Molecules. The carbonyl addition followed by radical β-fragmentation mechanism for formation of acyl anilide anions from the reactions of $\mathrm{PhN^{-}\cdot}$ with carbonyl-containing molecules has been described.[1,26] Briefly, it involves the triple-minimum potential energy surface shown in Figure 1. The first and third minima are the loose collision complexes $\mathrm{PhN^{-}\cdot/R_2CO}$ and $\mathrm{PhNCOR^-/\cdot R}$, respectively, and the central minimum is the tetrahedral intermediate $\mathrm{Ph\dot{N}C(O^-)R_2}$. This mechanism is supported by the present results in that small ion signals of anion radicals representing the adducts of $\mathrm{PhN^{-}\cdot}$ with the ketones $\mathrm{(CH_3)_2CO}$, $\mathrm{CH_3COC_2H_5}$, and $\mathrm{(CF_3)_2CO}$ and of $\mathrm{S^{-}\cdot}$ with $\mathrm{(CF_3)_2CO}$ are observed. Further, the signals of these adduct anion radicals increase (1.5–2-fold) in these reactions when the P_{He} is doubled with no change (outside of experimental error) in the rate constants for $\mathrm{PhN^{-}\cdot}$ or $\mathrm{S^{-}\cdot}$ decay. In the reaction of $\mathrm{PhN^{-}\cdot}$ with $\mathrm{CH_3COC_2H_5}$, the ratio of channels

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[46] Private communication from J. Brauman.

[47] Schmitt et al. (Schmitt, R. J.; Bierbaum, V. M.; DePuy, C. H. *J. Am. Chem. Soc.* **1979**, *101*, 6443–6445) consider electron transfer possible between $\mathrm{R^-}$ and $\mathrm{^3O_2}$ if EA(R·) ≤ 20 kcal mol^{-1}.

[48] $\Delta H°$ calculated on the basis of the following data: $\Delta H_f°(\mathrm{PhN^{-}\cdot})$[18]; $\Delta H_f°(\mathrm{NO_2^-}) = 45.1$ kcal mol^{-1} assuming $\mathrm{EA(NO_2)} = 53.0$ kcal mol^{-1} (2.3 eV)[24] with $\Delta H_f°(\mathrm{NO_2}) = 7.9$ kcal mol^{-1};[21] $\Delta H_f°(\mathrm{\cdot Ph}) = 78.5$ kcal mol^{-1}.[21]

[49] (a) Brown, H. C.; Wheeler, O. H.; Ichikawa, K. *Tetrahedron* **1957**, *1*, 214–220. (b) Brown, H. C.; Ichikawa, K. *Ibid.* **1957**, *1*, 221–230. (c) Brown, H. C.; Ichikawa, K. *J. Am. Chem. Soc.* **1961**, *83*, 4372–4374. (d) Brown, H. C.; Ichikawa, K. *Ibid.* **1962**, *84*, 373–376.

[50] $\Delta H_f°(\mathrm{PhN{=}C(O^-)OCH_3}) = -81$ kcal mol^{-1} from $\Delta H_f°(\mathrm{PhNHCO_2CH_3}) = -61.8$ kcal mol^{-1} (calcd using the group value CO(N)(O) = -25 kcal mol^{-1})[21] and the estimated $\Delta H°_{\mathrm{acid}}(\mathrm{PhNHCO_2CH_3}) = 348$ kcal mol^{-1}.

7a and 7b remains constant (±2%) as does the amount of H^+ transfer (reaction 7c). Therefore, some collisional stabilization of the adduct anion radical by the helium buffer gas occurred without significant effects on the fragmentation ratio of the addition adduct.

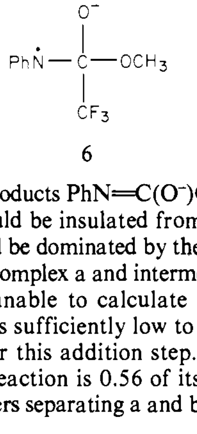
In Table III, no general correlation between $\Delta H°$ of the major addition/fragmentation reaction channel and $k_{rel}^{C=O}$ was observed for the reactions of $PhN^{-}\cdot$ and $R_1R_2C{=}O$. While the calculated $\Delta H°$'s within a class of carbonyl-containing molecules (aldehydes, ketones, and esters) may describe the small changes observed in $k_{rel}^{C=O}$ in that class, correlation of the $\Delta H°$'s between these classes of substrates fails; e.g., compare acetone ($k_{rel}^{C=O} = 1$, $\Delta H° = -19$ kcal mol^{-1}) and $CF_3CO_2CH_3$ ($k_{rel}^{C=O} = 157$, $\Delta H° = -14.6$ kcal mol^{-1}). This suggests that the overall exothermicity of the reaction channel has little to do with the values of $k_{rel}^{C=O}$.

As already pointed out, $PhN^{-}\cdot$ is a poor nucleophile in the S_N2 displacement reactions with CH_3Br (reaction 1) and CH_3Cl (reaction 2). The fast reaction of $PhN^{-}\cdot$ with $CF_3CO_2CH_3$ yielded the products from the addition/fragmentation channels 18a ($\Delta H° = -14.6$ kcal mol^{-1}) and 18b ($\Delta H° = -11.4$ kcal mol^{-1})[33,39] even though the overall exothermicities for these two channels are much smaller than that for S_N2 displacement (eq V, $\Delta H° = -55.8$ kcal mol^{-1}). These results must be kinetic in origin since $PhN^{-}\cdot$ has a large, thermodynamic methyl cation affinity, 268.5 kcal mol^{-1} (defined as $-\Delta H°$ for the reaction $PhN^{-}\cdot + H_3C^+ \rightarrow PhNCH_3\cdot$). This is very similar to the H_3C^+ affinity of $^-OCH_3$ (270 kcal mol^{-1}),[16] which reacts rapidly ($k = 1 \times 10^{-9}$ cm^3 molecule^{-1} s^{-1}) with $CF_3CO_2CH_3$ principally by an S_N2 ($B_{AL}2$) mechanism (eq VIII).[9,38] $PhN^{-}\cdot$ is a poorer nucleophile than $PhCH_2^-$ in the S_N2

$$CH_3O^- + CF_3CO_2CH_3 \rightarrow CF_3CO_2^- + CH_3OCH_3 \qquad \text{(VII)}$$

displacement reaction with CH_3Cl (for $PhCH_2^- + CH_3Cl$, $k = 1.5 \times 10^{-11}$ cm^3 molecule^{-1} s^{-1};[2] compare to reaction 2) where the slow rate constant for the $PhCH_2^-$ reaction was attributed to delocalization of the charge in the nucleophile.[2]

In the fast reaction of $PhN^{-}\cdot$ with $CF_3CO_2CH_3$, let us make the simplifying assumption that formation of the tetrahedral intermediate **6** is rate limiting, followed by fast radical β fragmentation to yield the products $PhN{=}C(O^-)CF_3$ and $\cdot OCH_3$. The rate of the reaction would be insulated from the overall reaction exothermicity and would be dominated by the height of the barrier separating the collision complex a and intermediate b (**6**) in Figure 1. Although we are unable to calculate $\Delta H_f°(\mathbf{6})$, it appears unlikely that $\Delta H_f°(\mathbf{6})$ is sufficiently low to give $-\Delta H°$ in excess of 20 kcal mol^{-1} [26,51] for this addition step. Since the observed rate constant for this reaction is 0.56 of its calculated collision limit (k_{ADO}),[32] the barriers separating a and b, and b and c (Figure 1) must be small.



$$Ph\dot{N}-\overset{O^-}{\underset{CF_3}{C}}-OCH_3$$

6

The considerations discussed above for the reaction of $PhN^{-}\cdot$ with $CF_3CO_2CH_3$ should also apply to the reaction of $S^{-}\cdot$ with $CF_3CO_2CH_3$. However, we are unable to calculate $\Delta H°$ for the addition/fragmentation channel 32a since $\Delta H°_{acid}(CF_3C(O)SH)$ is unknown,[52] while $\Delta H° = -34.8$ kcal mol^{-1} for channel 32b.[20,21,39] Figure 2 illustrates the potential energy surface considered to describe the two separate mechanisms involved in the reaction of $S^{-}\cdot$ with the esters CF_3CO_2R (reactions 32 and 33). Formation of the common ion–molecule collision complex a is followed by selection of one or the other of the two outlet channels, which is highly dependent on the nature of R in the ester. The barriers separating a and b, and a and c must be small in these reactions to account for the fact that both rate constants are about 50% of the calculated collision rate constant.[32]

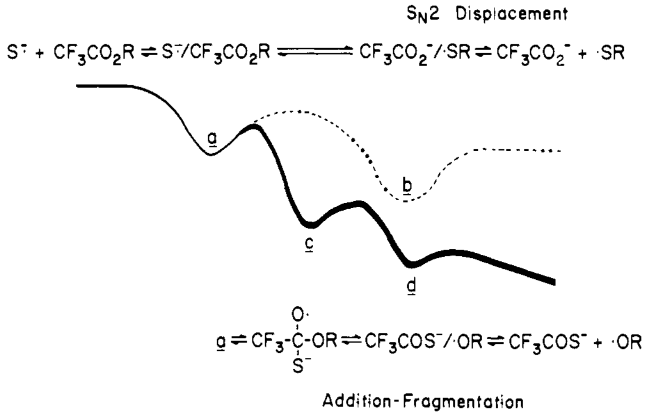


Figure 2. Mechanism and three-dimensional potential energy surface for the reactions of $S^{-}\cdot$ with CF_3CO_2R ($R = CH_3$ and C_2H_5).

Reaction Site and Mechanism Selectivity in Certain Fast Ion–Molecule Reactions. A premise in the area of kinetics is that for a given mechanism, reaction site selectivity will be lower for fast reactions compared to the site selectivity (or specificity) observed in much slower reactions in a series. This premise implies that for reactions which occur at or near their collision limits, little or no reaction site selectivity should be observed. The reaction of $PhN^{-}\cdot$ with $CH_3COCO_2CH_3$ (reaction 22) occurred with a rate constant that was 61% of the calculated collision limit (essentially every collision led to reaction), and 98% of the product ions were formed by the addition/fragmentation mechanism. Seven times more of the product anions are considered to arise by addition/fragmentation at the keto carbonyl group than at the ester carbonyl group. This is the order of reactivity (selectivity) expected from the $k_{rel}^{C=O}$ values determined for the reactions of $PhN^{-}\cdot$ with monofunctional carbonyl-containing substrates in Table III. The precise magnitude of the difference in reactivity at the two carbonyl groups of $CH_3COCO_2CH_3$ cannot be determined at this time due to unknown factors in the coupling of the two carbonyl groups in the α-keto ester structure and whether the ester has the cis or trans dicarbonyl structure when it reacts with $PhN^{-}\cdot$ in the loose collision complex. The important point is that *reaction site selectivity is observed in the fast ion–molecule reaction of* $PhN^{-}\cdot$ *with* $CH_3COCO_2CH_3$ *where the same mechanism is involved.*

In the reactions of $S^{-}\cdot$ with $CF_3CO_2CH_3$ (reaction 32) and $CF_3CO_2C_2H_5$ (reaction 33), which occurred at 50% of the collision limit, two different mechanisms were considered to be involved in the product-forming channels: (a) S_N2 displacement at CH_3 and C_α of C_2H_5 to yield $CF_3CO_2^-$ and (b) carbonyl addition/fragmentation to product CF_3COS^-. The ratio of the two product ions ($CF_3CO_2^-/CF_3COS^-$) was quite different in the two experiments: 1.9 with $CF_3CO_2CH_3$ and 0.04 with $CF_3CO_2C_2H_5$. Since the same rate constant was obtained for the reactions of $PhN^{-}\cdot$ with these two esters where the carbonyl addition/fragmentation mechanism was exclusively observed, we assume that the barrier height and entropy for carbonyl addition/fragmentation for $S^{-}\cdot$ with these two esters also will be constant. On the basis of this assumption, the large change in the product ion distributions in these two reactions of $S^{-}\cdot$ with CF_3CO_2R is due to an increase in the height of the barrier (a → b, Figure 2) for the S_N2 displacement as R is changed from CH_3 to C_2H_5. Note that *both reaction site and reaction mechanism selectivity are preserved in these fast ion–molecule reactions.*

In these comparisons, $PhN^{-}\cdot$ and $S^{-}\cdot$ appear to have similar, good nucleophilicities in addition reactions to carbonyl groups

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(51) $\Delta H_f°(PhNHC(OH)(OCH_3)CF_3) = -204.5$ kcal mol^{-1} (calcd) assuming the group value equivalency, $C(O)_2(N)(C) = C(N)(C)_3$.[21] If we assume $D°$(N–H) in this alcohol is that of $D°(PhN(CH_3)\text{–}H) = 85$ kal mol^{-1} [25] and that $\Delta H°_{acid}(Ph\dot{N}C(OH)(OCH_3)CF_3) = 345$ kcal mol^{-1} (same as $\Delta H°_{acid}(HCO_2H)$), we calculate $\Delta H_f°(Ph\dot{N}C(O^-)(OCH_3)CF_3) = -193.8$ kcal mol^{-1}, which yields $\Delta H° = -13.1$ kcal mol^{-1} for the reaction of $PhN^{-}\cdot$ with $CF_3CO_2CH_3$ producing **6**.

(52) If we assume $\Delta H°_{acid}(CF_3C(O)SH) = \Delta H°_{acid}(CF_3CO_2H) = 322.7$ kcal mol^{-1},[16] we calculate $\Delta H° = -3.7$ kcal mol^{-1} using $\Delta H_f°(CF_3C(O)SH) = -185.4$ kcal mol^{-1} (calcd).[21] With the reasonable assumption that $\Delta H°_{acid}(CF_3C(O)SH) > \Delta H°_{acid}(CF_3CO_2H)$ by 10 kcal mol^{-1}, $\Delta H° = -13.7$ kcal mol^{-1} is calculated for the addition step.

($k_N^{C=O}(S^{-}\cdot) \sim k_N^{C=O}(PhN^{-}\cdot)$). However, they behave quite differently as nucleophiles in S_N2 displacement reactions at saturated carbon ($k_N^{sp^3}(S^{-}\cdot) > k_N^{sp^3}(PhN^{-}\cdot)$) with $S^{-}\cdot$ being the more potent. The two types of nucleophilic behavior manifest themselves when they are subject to potentially competitive processes within a given ion–molecule reaction.

Radical Group Fragmentation Order from the Tetrahedral Anion Radical Intermediates. From the data in Table I, the following radical group fragmentation order is established from the tetrahedral anion radical adducts formed in the reactions of $PhN^{-}\cdot$ with various carbonyl containing molecules: $CH_3CO > CO_2CH_3 > CH_3O > R\ (C_2H_5, (CH_3)_3C) > H$ and $CH_3 > CF_3$; exception, when R = CH_3, $H > CH_3$ was found by using CH_3CHO. From studies of the analogous reaction of $PhN^{-}\cdot$ with methyl vinyl ketone, the order $CH_3 > CH{=}CH_2$ was found.[1] Generally, the fragmentation orders reflect the bond dissociation energies of these groups to tertiary carbon[31] and the expected or known stabilities of the acyl anilide anion products. The major exception to this generalization was observed in the reaction of $PhN^{-}\cdot$ with CH_3CHO where the loss of $H\cdot$ was preferred (2:1) over loss of $\cdot CH_3$. Various considerations led us to speculate that this was due to a reduced $D°(C–H)$ in this tetrahedral anion radical intermediate, possibly the result of radical hyperconjugation.

It is the hope of the authors that the results of this gas-phase study and those of S_N2 displacement reactions will rekindle interest in understanding the various factors and their contribution to nucleophilic behavior in carbonyl addition and S_N2 displacement mechanisms. For example, are the factors involved in yielding similar $k_{rel}^{C=O}$ (for carbonyl additions) and $k_{CH_3}/k_{C_2H_5}$ (for S_N2 displacements) values in gas-phase and solution reactions the same in both circumstances or are they different? We believe that useful, transferable mechanistic information is obtained from related studies in both the gas and condensed phases. We must find out the degree to which this information can be transferred so that the special capabilities of each phase can be exploited.

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Registry No. $PhN^{-}\cdot$, 74586-02-0; CH_3Br, 74-83-9; CH_3Cl, 74-87-3; CH_3CHO, 75-07-0; C_2H_5CHO, 123-38-6; $(CH_3)_3CCHO$, 630-19-3; CH_3COCH_3, 67-64-1; $CH_3COC_2H_5$, 78-93-3; CF_3COCH_3, 421-50-1; CF_3COCF_3, 684-16-2; $CH_3COCOCH_3$, 431-03-8; *c*-$(H_2C)_3C{=}O$, 1191-95-3; *c*-$(H_2C)_4C{=}O$, 120-92-3; *c*-$(H_2C)_5C{=}O$, 108-94-1; *c*-$(H_2C)_6C{=}O$, 502-42-1; HCO_2CH_3, 107-31-3; $CH_3CO_2CH_3$, 79-20-9; $C_6H_5CO_2CH_3$, 93-58-3; $CF_3CO_2CH_3$, 431-47-0; $CF_3CO_2C_2H_5$, 383-63-1; $CF_3COSC_2H_5$, 383-64-2; CH_3COCl, 75-36-5; $CH_3COCO_2CH_3$, 600-22-6; CO_2, 124-38-9; COS, 463-58-1; CS_2, 75-15-0; O_2, 7782-44-7; $S^{-}\cdot$, 14337-03-2.

Reductive Electrochemistry of Iron–Carbene Porphyrins

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Abstract: The reductive electrochemistry of four types of iron–carbene porphyrins, vinylidene, thiocarbonyl, dichlorocarbene complexes, and the μ-carbido dimer, was investigated in aprotic solvents. The chemistry triggered by the successive injection of two electrons in the molecule essentially involves the carbene ligand. With the vinylidene and thiocarbonyl complexes, there is a $2e + H^+$ reduction of the liganding carbon leading to the corresponding vinyl and thioformyl complexes. In the latter case, a remarkable reversibility is observed: electrochemical reoxidation of the thioformyl complex regenerates the thiocarbonyl complex. With the μ-carbido dimer the followup reaction mainly involves the cleavage of the carbon–iron bonds while with the dichlorocarbene complex, fast reductive dehalogenation finally yields the μ-carbido dimer. With the exception of the dichlorocarbene complex for which reduction is facilitated by the extreme unstability of the one-electron intermediate, the energies required to introduce successively two electrons in the molecules are remarkably similar for the various complexes. The acido-basic properties of the first and second electron intermediates are more sensitive to the nature of the carbene ligand and can be rationalized in terms of charge delocalization. Electronic cis effects are described and discussed in the case of the vinylidene and thiocarbonyl complexes.

The reductive chemistry of the carbon–iron bond in porphyrin complexes has received recent active attention. This has concerned the synthesis, under reducing conditions, of complexes involving iron–carbon bond as well as the oxidoreduction properties of such compounds. Two main types of complexes have been investigated in this connection: iron–carbene and iron–σ-alkyl porphyrins. It has been shown that the latter complexes can be generated electrochemically, both under their Fe(III) and Fe(II) oxidation states by reaction of iron(I) porphyrins with the corresponding alkyl halides.[2a] The main electrochemical and spectral characteristics of these σ-alkyl complexes have been described.[2a] The same sort of approach was recently extended to the case of σ-aryl- and σ-vinyliron–porphyrin complexes.[2b] The formation of σ-alkyl complexes has also been shown to occur by coupling of alkyl radicals with iron(II) deuteroporphyrin[3a,b] under pulse radiolytic conditions, and upon reduction of some halogenated compounds, such as *p*-nitrobenzyl chloride[3c] and halothane, $CF_3CHClBr$,[3d] by iron(II) tetraphenylporphyrin in the presence of a reducing agent in excess.

On the other hand, several iron–carbene–porphyrin complexes have been recently synthesized by reaction of polyhalogenated compounds with the iron(II) porphyrins in the presence of an excess of a reducing agent (iron powder or sodium dithionite). The carbenes, CCl_2,[4a,b] CBr_2, CF_2, CFCl, CFBr,[4c] CClCN,[4d]

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