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Gas-Phase Synthesis and Reactions of Nitrogen- and Sulfur-Containing Anions

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The flowing afterglow and selected ion-flow tube techniques have been used to study the reactions of H_2N^- with N_2O, CO_2, CS_2, SO_2, and OCS in the gas phase. Thermal energy rate coefficients and product branching ratios have been determined and are discussed in terms of detailed reaction mechanisms. With use of the SIFT–drift technique, the product distribution for the reaction of H_2N^- with N_2O was measured as a function of the center of mass kinetic energy in the range of thermal energy to $\sim$15 kcal mol^{-1}. Qualitative studies were made of the reactions of HO^-, CH_3O^-, and $(CH_3)_2N^-$ with N_2O, CO_2, CS_2, SO_2, and OCS, and the reactions of a variety of other ions with OCS were also examined. These reactions provide efficient synthetic routes for the gas-phase preparation of a variety of interesting negative ions containing nitrogen and sulfur. The basicities and heats of formation of three of these anions, H_2NS^-, NSO^-, and NCS^-, have been bracketed by proton-transfer reactions. The nucleophilicities of these three anions, as well as of H_2N^-, HO^-, HO_2^-, F^-, HS^-, CN^-, NCO^-, N_3^-, Cl^-, and Br^- toward CH_3I, have been measured.

Introduction

Gas-phase positive ions can usually be produced in abundance by electron impact on appropriate neutral precursors, but only a few types of anions are accessible by this method. In general, anions must be formed by ion–molecule reactions, most commonly by proton or electron transfer. The flowing afterglow system has proven to be especially suited to the study of anions in the gas phase for several reasons. First, under typical experimental conditions many exothermic bimolecular processes are rapid, and thus the synthesis of ions that require several sequential reactions can be carried out easily. Moreover, the flow nature of the technique allows spatial separation of the region of initial ion formation and subsequent ion reaction. This allows generation and study of highly reactive species. For example, electron impact on NH_3 with downstream addition of N_2O allows study of the reaction of H_2N^- with N_2O. In contrast, if both NH_3 and N_2O are present in the ionization region, HO^- (from production of O^- and reaction with NH_3) emerges as the dominant species.

In earlier work we showed how a variety of anions can be generated in the gas phase by reaction of suitable trimethylsilyl derivatives with F^-.[1] In this paper we report a synthetic method for the production of a number of simple inorganic, nitrogen-containing ions, N_3^-, NCO^-, NCS^-, and NSO^-.[2] In addition, a general method for the production of thiol anions, most of them new to gas-phase ion studies, has been developed.[3] The approximate proton affinities of some of these anions have been determined. In addition, their gas-phase nucleophilicities toward CH_3I have been measured and compared to those of other common gas-phase anions.

Experimental Section

Most of these experiments were performed at 298 K in a flowing afterglow system,[4] which has been described previously. Some of the studies of H_2N^- were carried out in a selected ion-flow tube (SIFT)[5] in which the reactant ion is formed in a low-pressure ion source, mass selected, and injected into the flow tube; this system also incorporates a drift tube[6] in which the kinetic energy of the ions can be varied. H_2N^- was generated by electron impact on NH_3, and HO^- was formed by dissociative electron attachment to N_2O followed by rapid hydrogen atom abstraction from CH_4. CH_3O^- was produced by an elimination reaction of H_2N^- with $CH_3OCH_2CH_2OCH_3$. CH_3NH^-, $(CH_3)_2N^-$, $C_6H_5^-$, $(CH_3)_3SiCH_2^-$, $C_3H_5^-$, and CH_2CN^- were formed by proton abstraction from their parent neutrals with H_2N^-. Typical helium pressures and flow rates were 0.3–0.4 torr and 140–190 STP cm^3 s^{-1}, respectively. All neutral reactants were obtained from commercial suppliers, and their flow rates were determined by monitoring the pressure increase with time in a calibrated volume. Rate coefficients were measured by following reactant ion counts as a function of reaction time. Product distributions were determined by extrapolating product ion percentages to zero flow of the neutral reagents.

Results

Reaction of H_2N^- with N_2O, CO_2, CS_2, and SO_2. The products and branching ratios for the reactions of H_2N^- with N_2O, CO_2, CS_2, SO_2, and OCS are summarized in Table I as eq 1–5. The reactions of OCS will be described in a separate section. H_2N^- reacts rapidly with N_2O to form N_3^- and H_2O and also the conjugate acid–base pair, HO^- and HN_3; this reaction therefore provides a convenient gas-phase synthesis for the azide, obviating the necessity of working with hydrazoic acid or organic azides. The reaction of H_2N^- with N_2O was also examined in the SIFT–drift apparatus; the branching ratio of the products as a function of the center of mass kinetic energy is shown in Figure 1. H_2N^- reacts with CO_2, CS_2, and SO_2 to generate NCO^-, NCS^-, and NSO^-, respectively. The reactions with CS_2 and SO_2 also produce conjugate acid–base pairs (HS^- + HNCS and HO^- + HNSO) while the reaction with SO_2 also proceeds by electron transfer (SO_2^- + H_2N). The mechanism and product distributions will be considered in detail in the Discussion section. The experimental rate coefficients and reaction efficiencies ($k_{\text{expt}}/k_{\text{ADO}}$)[7] for these processes are collected in Table I. Reaction occurs at or near the theoretical collision rate for all reactants except H_2N^- + N_2O, for which only one in four encounters leads to reaction. The measured rate coefficient for reaction of H_2N^- with CO_2 (9.3×10^{-10} cm^3 molecule^{-1} s^{-1}) is in good agreement with that determined by Wight and Beauchamp[8] in ICR experiments (8.6×10^{-10} cm^3 molecule^{-1} s^{-1}).

The proton affinity of N_3^- (344 ± 2 kcal mol^{-1}) has recently been measured by Pellerite et al.,[9] and the proton affinity of NCO^- (344.7 ± 2 kcal mol^{-1}) has been determined by Wight and Beauchamp.[8] We have measured relative basicities, and thereby

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TABLE I: Branching Ratios, Rate Coefficients, and Enthalpies for Reactions of H_2N^-

	branching ratio[a]	$10^{10}k_{expt}$, cm^3 $molecule^{-1}$ s^{-1}	reacn efficiency[b]	ΔH,[c] kcal mol^{-1}
(1a) $H_2N^- + N_2O \rightarrow N_3^- + H_2O$	72	2.9	0.24	−56
(1b) $\rightarrow HO^- + HN_3$	28			−9
(2a) $H_2N^- + CO_2 \rightarrow NCO^- + H_2O$	100	9.3	0.84	−42
(2b) $\rightarrow HO^- + HNCO$	0			+4
(3a) $H_2N^- + CS_2 \rightarrow NCS^- + H_2S$	54	18	0.95	−70
(3b) $\rightarrow HS^- + HNCS$	46			−42
(4a) $H_2N^- + SO_2 \rightarrow NSO^- + H_2O$	26	29	1.4	$\leqslant -46$
(4b) $\rightarrow HO^- + HNSO$	8			$\leqslant 0$
(4c) $\rightarrow SO_2^- + H_2N$	66			−7
(5a) $H_2N^- + OCS \rightarrow NCO^- + H_2S$	6	19	1.0	−50
(5b) $\rightarrow HS^- + HNCO$	42			−41
(5c) $\rightarrow NCS^- + H_2O$	0			−62
(5d) $\rightarrow HO^- + HNCS$	0			+3
(5e) $\rightarrow H_2NS^- + CO$	52			$\leqslant 0$

[a] For reactions of N_2O, CO_2, and SO_2, product distributions were measured in the selected ion-flow tube; mass discrimination was measured, and corrections were applied to the branching ratios. For reactions of CS_2 and OCS, product distributions were measured in the flowing afterglow; mass discrimination was minimized by carrying out the measurements at low resolution. [b] Reaction efficiency = k_{expt}/k_{ADO}, where k_{ADO} is calculated by the method of Su and Bowers.[7] [c] Enthalpies calculated from the data in Table II.

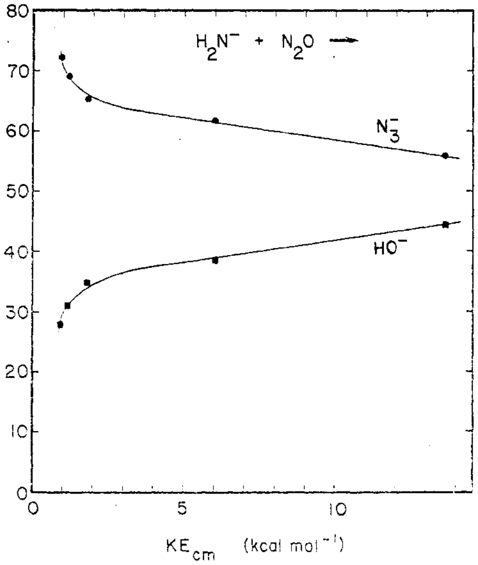

Figure 1. Product distribution for the reaction of H_2N^- with N_2O plotted as a function of the center of mass kinetic energy of the ion. Helium was used as the buffer gas. Mass discrimination was measured as a function of kinetic energy and corrections were applied to the branching ratio.

TABLE II: Heats of Formation

species	$\Delta H_f{}^\circ{}_{298}$, kcal mol^{-1}	ref	species	$\Delta H_f{}^\circ{}_{298}$, kcal mol^{-1}	ref
N_2O	+19.6	11	HS^-	−18.5	10
CO_2	−94.1	12	HN_3	+70.3	11
CS_2	+28.0	12	N_3^-	+47.1	9
SO_2	−70.9	12	HNCO	−30.0	11
OCS	−33.1	12	NCO^-	−52.5	8
CO	−26.4	12	HNCS	+30.0	11
H^+	+367.2	12	NCS^-	−12	this work
H_2N^-	+25.4	10	HNSO	$\leqslant -11$	this work
H_2O	−57.8	12	NSO^-	$\leqslant -34$	this work
HO^-	−34.4	12	H_3NS	$\leqslant 26$	this work
H_2S	−4.8	11	H_2NS^-	$\leqslant 19$	this work

TABLE III: Rate Coefficients for the Reaction $X^- + CH_3I$[a]

X^-	$PA(X^-)$,[b] kcal mol^{-1}	$10^{10}k_{expt}$,[c] cm^3 $molecule^{-1}$ s^{-1}	reacn efficiency[d]
H_2N^-	403.6 ± 1	31	1.3
HO^-	390.8 ± 0.4	30	1.3
HO_2^-	374.8 ± 0.7[e]	22	1.3
F^-	371.5 ± 0.7	26	1.2
H_2NS^-	360 ± 3[c]	13	0.88
HS^-	353.4 ± 2	8.9	0.52
CN^-	353.1 ± 2	1.8	0.096
NCO^-	344.7 ± 2[f]	0.13	0.0084
N_3^-	344 ± 2[g]	1.3	0.084
NSO^-	344 ± 5[c]	0.28	0.021
Cl^-	333.3 ± 0.3	2.1	0.13
NCS^-	325 ± 5[c]	<0.002	<0.00015
Br^-	323.6 ± 0.3	0.33	0.027

[a] Reaction proceeds primarily by nucleophilic displacement; for the most basic anions, there is also a small product channel arising by proton transfer. [b] Reference 10, unless otherwise noted. [c] This work. [d] Reaction efficiency = k_{expt}/k_{ADO} is calculated by the method of Su and Bowers.[7] [e] Reference 13. [f] Reference 8. [g] Reference 9.

approximate proton affinities, of NCS^- and NSO^- by the bracketing technique. In this method the anion is allowed to react with an acid, HA, of known gas-phase acidity.[10]

$$X^- + HA \rightarrow A^- + HX \qquad (6)$$

Rapid appearance of A^- indicates that the reactant anion has a higher proton affinity than A^-. Lack of formation of A^- suggests that the proton affinity of A^- exceeds that of the reactant anion, but this result must be treated with caution; occasionally even simple exothermic processes are slow. However, proton transfer between relatively localized ions is usually a facile reaction in the exothermic direction.

NSO^- does not react with CH_3COOH (PA = 349 kcal mol^{-1}); it reacts slowly with HCOOH (PA = 345 kcal mol^{-1}), moderately with $ClCH_2CH_2COOH$ (PA = 341 kcal mol^{-1}), and rapidly with HCl (PA = 333 kcal mol^{-1}).[10] We therefore conclude that the gas-phase proton affinity of NSO^- is 344 ± 5 kcal mol^{-1}. NCS^- is a considerably less basic anion. It does not react with HCl (PA = 333 kcal mol^{-1}) or CF_2HCOOH (PA = 330 kcal mol^{-1}) but does react with CF_3COOH (PA = 323 kcal mol^{-1}) and with HBr (PA = 324 kcal mol^{-1}). We therefore assign the gas-phase proton affinity of NCS^- as 325 ± 5 kcal mol^{-1}.[10]

By combining these gas-phase proton affinities with other thermochemical data from the literature, we have estimated enthalpy changes for the reactions of H_2N^- with N_2O, CO_2, CS_2,

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(10) The relative gas-phase acidity of HA and HX (or the relative basicity of A^- and X^-) is defined as the free energy change for reaction 6. The relative proton affinity of A^- and X^- is the enthalpy change for this process. Our experiments directly provide information only on the free energy change. However, for these proton-transfer reactions the entropy change is small and we will assume that relative basicity equals relative proton affinity. Bartmess, J. E.; McIver, R. T., Jr. In "Gas Phase Ion Chemistry", Bowers, M. T., Ed; Academic Press: New York, 1979; Vol. 2, pp 87–121.

SO_2, and OCS; Table I summarizes these results. The data used in these calculations are collected in Table II.[8-13]

We have characterized the ions generated in this study by their reactivity toward carbon as well as toward hydrogen, and in Table III we report their rates of nucleophilic substitution. Because some of these ions are such poor nucleophiles, they do not in general react with CH_3Br, CH_3Cl, or CH_3F, the three substrates for which gas-phase nucleophilicities have been reported earlier.[14] We have therefore determined S_N2 rates with CH_3I for these new ions as well as for other common anionic nucleophiles.

Reactions of HO^- with N_2O, CO_2, CS_2, and SO_2. HO^- is known to add to CO_2 to form the bicarbonate ion in a termolecular process, with the reaction exothermicity being removed by collision with helium ($k = 2.5 \times 10^{-28}$ cm^6 molecule^{-2} s^{-1}).[15] Similarly, the reaction of HO^- with SO_2 leads to adduct formation. In contrast, we have observed that the reaction of HO^- with N_2O is immeasurably slow, while the reaction of HO^- with CS_2 proceeds by a rapid bimolecular pathway ($k = 1.5 \times 10^{-9}$ cm^3 molecule^{-1} s^{-1}):

$$HO^- + CS_2 \rightarrow HS^- + OCS \tag{7}$$

Reaction of CH_3O^- with N_2O, CO_2, CS_2, and SO_2. CH_3O^- does not react with N_2O. With CO_2, CS_2, and SO_2, addition and reduction by hydride transfer occur competitively.

Reaction of $(CH_3)_2N^-$ with N_2O, CO_2, CS_2, and SO_2. $(CH_3)_2N^-$ reacts with N_2O and CO_2 predominantly by adduct formation. Reaction with CS_2 occurs by hydride transfer, and reaction with SO_2 proceeds both by electron and hydride transfer.

Reactions of H_2N^- and Other Anions with OCS. The gas-phase ion chemistry of OCS is intriguing, as was first noted by Dillard and Franklin.[16] The products, branching ratio, and rate coefficient for reaction of H_2N^- with OCS are summarized in Table I. In analogy to the reactions of H_2N^- with CO_2 and CS_2, NCO^- and HS^- are generated; however, in contrast to the reaction of CS_2, a channel leading to formation of NCS^- was not detected. Instead, an ion of m/z 48 is observed which Dillard and Franklin identified as H_2NS^-. We concur in this assignment, based on the isotope peak at m/z 50 (^{34}S = 4.2%), the occurrence of two hydrogen–deuterium exchanges with CF_3CH_2OD, and the detection of analogous products with other reactant bases. The nucleophilicity and approximate proton affinity of H_2NS^- are reported in Table III. H_2NS^- was found to be unreactive toward CF_3CH_2OH (PA = 364 kcal mol^{-1}), moderately reactive with CH_3SH (PA = 359 kcal mol^{-1}), and highly reactive with H_2S (PA = 353 kcal mol^{-1}).[10] The gas-phase proton affinity of H_2NS^- was therefore deduced to be 360 ± 3 kcal mol^{-1}.

Numerous other highly basic ions react analogously with OCS to transfer a sulfur atom, although these are sometimes minor channels:

$$HO^- + OCS \rightarrow HOS^- + CO \tag{8a}$$

$$\rightarrow HS^- + CO_2 \tag{8b}$$

$$CH_2{=}CHCH_2^- + OCS \rightarrow CH_2{=}CHCH_2S^- + CO \tag{9a}$$

$$\xrightarrow{He} CH_2{=}CHCH_2COS^- \tag{9b}$$

Other anions for which these reactions occur include CH_3NH^-, $(CH_3)_2N^-$, $C_6H_5^-$, and $^-CH_2CN$. For the M-1 anion of $C_6H_5CH_3$, only addition and no sulfur atom transfer was observed. The reaction of the M-1 anion of $(CH_3)_4Si$ proceeds by two major channels:

$$(CH_3)_3SiCH_2^- + OCS \rightarrow (CH_3)_3SiCH_2S^- + CO \tag{10a}$$

$$\rightarrow (CH_3)_3SiS^- + CH_2CO \tag{10b}$$

CH_3O^- reacts with OCS both by addition and by hydride transfer:

$$CH_3O^- + OCS \xrightarrow{He} CH_3OCOS^- \tag{11a}$$

$$\rightarrow HCOS^- + CH_2O \tag{11b}$$

Discussion

For some of these reactions, consideration of the thermochemistry can facilitate an understanding of the mechanisms involved and of the products generated. The enthalpy changes for the reactions of H_2N^- with N_2O, CO_2, CS_2, SO_2, and OCS are summarized in Table I, and Table II collects the data used in these calculations. For several of the reactions (for example, eq 3b), the heats of formation of all reactants and all products are available from the literature so that the heat of reaction is easily calculated. In contrast, for reaction 3a the heat of formation of one of the species, NCS^-, is not known. However, this value can be deduced from our measured proton affinity of NCS^- (325 ± 5 kcal mol^{-1}) and known heats of formation of HNCS and H^+:

$$HNCS \rightarrow H^+ + NCS^- \tag{12}$$

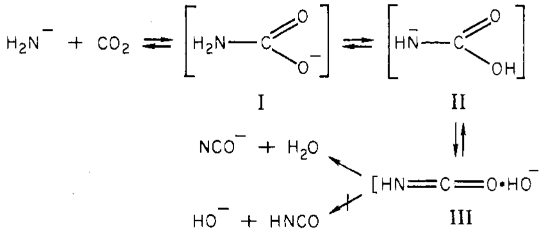
$$\Delta H^\circ_{acid}(HNCS) = \Delta H_f^\circ(H^+) + \Delta H_f^\circ(NCS^-) - \Delta H_f^\circ(HNCS) \tag{13}$$

In this way we calculate $\Delta H_f^\circ(NCS^-) = -12$ kcal mol^{-1} and thereby ΔH(eq 3a) = -70 kcal mol^{-1}.

The enthalpy change for reaction 4b cannot be calculated since ΔH_f°(HNSO) is not known. However, since this reaction is observed to proceed, ΔH(eq 4b) ≤ 0 and thus $\Delta H_f^\circ(HNSO) \leq -11$ kcal mol^{-1}. Using $\Delta H^\circ_{acid}(HNSO) = 344 \pm 5$ kcal mol^{-1}, determined in this work, yields $\Delta H_f^\circ(NSO^-) \leq -34$ kcal mol^{-1}. This in turn allows us to place a limit on the enthalpy change of reaction 4a; ΔH(eq 4a) ≤ -46 kcal mol^{-1}. Similarly, the occurrence of reaction 5e indicates that ΔH(eq 5e) ≤ 0 and $\Delta H_f^\circ(H_2NS^-) \leq 19$ kcal mol^{-1}. Combining this with our measured proton affinity of H_2NS^- (360 ± 3 kcal mol^{-1}) allows us to deduce that $\Delta H_f^\circ(H_3NS) \leq 26$ kcal mol^{-1}. Similar considerations were employed in obtaining the other results summarized in Tables I and II.

One calculation, however, deserves further comment. The enthalpy change for reaction 4c is simply the difference in electron affinities of H_2N and SO_2. Using the commonly accepted values[17] of EA(H_2N) = 18.0 kcal mol^{-1} and EA(SO_2) = 25.3 kcal mol^{-1} gives ΔH(eq 4c) $\simeq -7$ kcal mol^{-1} as indicated in Table I. However, Fukuda and McIver[18] have recently reported a new determination of the electron affinity of SO_2, namely 50.7 kcal mol^{-1}; this value leads to an exothermicity of ~33 kcal mol^{-1} for electron transfer from H_2N^- to SO_2.

H_2N^- reacts with CO_2 at essentially the collision rate to form exclusively NCO^-. We picture the reaction proceeding as shown in eq 14. The anion and neutral are attracted to one another



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by long-range ion-induced dipole forces. The initially formed adduct, I, contains about 30 kcal mol^{-1} excess energy since the formation of the nitrogen–carbon bond and the generation of a stable anion more than compensates for the breaking of the carbon–oxygen double bond. If not stabilized by further reaction or loss of energy by collision, this adduct will redissociate to H_2N^- and CO_2. Intramolecular proton transfer from nitrogen to oxygen generates II; this reaction would normally be endothermic, but there is sufficient energy in the complex to accomplish it. Loss of HO^- generates a new complex, III, which dissociates after proton transfer to form NCO^- and H_2O; NCO^- is the only ionic product observed. As indicated in Table I, dissociation to HO^- and HNCO would be about 4 kcal mol^{-1} endothermic.

The key feature of this reaction is the intramolecular proton transfer by which I is transformed to II. Although protons transfer easily in gaseous cations, such processes are rare in anions. However, the high exothermicity of the addition together with the great mobility of protons bound to nitrogen and oxygen probably accounts for the result. It is also possible that the sp^2 hybridization of the carbonyl carbon plays an essential rôle. Further experiments which might elucidate the important factors that facilitate this proton transfer are planned.

Reaction of H_2N^- with CS_2 takes a similar course, with addition, proton transfer, and loss of HS^- leading to complex IV.

$$[\underset{\text{IV}}{HN{=}C{=}S\cdot HS^-}] \rightarrow NCS^- + H_2S \qquad (15a)$$

$$\rightarrow HS^- + HNCS \qquad (15b)$$

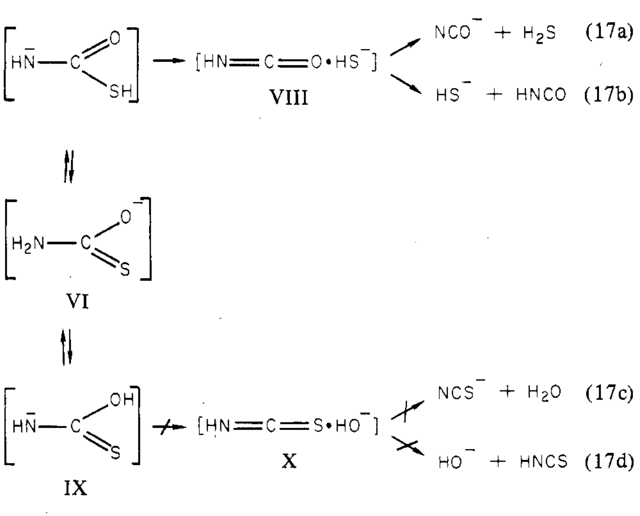
Despite the fact that HS^- is 28 kcal mol^{-1} more basic than NCS^-, a nearly equal mixture of the two ions is formed. Thus, extensive but not complete equilibration of the proton within the complex occurs before separation of the ion and neutral. Similarly, the reaction of H_2N^- with SO_2 leads to a complex that also decomposes by two pathways:

$$[\underset{\text{V}}{HN{=}S{=}O\cdot HO^-}] \rightarrow NSO^- + H_2O \qquad (16a)$$

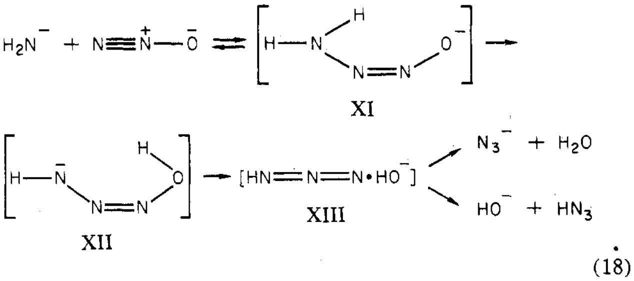
$$\rightarrow HO^- + HNSO \qquad (16b)$$

In this case, HO^- is approximately 47 kcal mol^{-1} more basic than NSO^- and still dissociation of complex V produces some HO^-. Therefore, while the proton-transfer process is more nearly complete in reaction 16 than in 15, total equilibration is still not observed. Reaction of H_2N^- with SO_2 proceeds primarily by electron transfer, however, since $EA(SO_2) > EA(H_2N)$.

The reaction of H_2N^- with OCS is intriguing. The initial adduct VI could in principle decompose by two major channels, eq 17a,b or 17c,d. Only the former pathway is in fact observed, although the latter is more exothermic. The product-controlling step is undoubtedly the formation of complex VIII, which is about 44 kcal mol^{-1} more exothermic than formation of X. Dissociation of complex VIII leads to mainly HS^- and little of the less basic anion NCO^-. Although HNCO and H_2S differ in acidity by 9 kcal mol^{-1}, there is little proton transfer within complex VIII.



H_2N^- also reacts with N_2O, forming $N_3^- + H_2O$ and $HO^- + HN_3$. The reaction is significantly slower than those of CO_2, CS_2, SO_2, and OCS, and this may reflect the lower stability of the initial adduct; i.e., dissociation of complex XI to reactants may compete efficiently with intramolecular proton transfer and reaction to form products. It is also possible, however, that formation of the initial adduct is rate determining; these two possibilities cannot be distinguished from the present data.



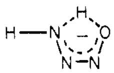
This reaction was also studied as a function of ion kinetic energy in the SIFT-drift system. Figure 1 shows the branching ratios of the product channels as a function of center of mass collision energy. For these experiments, the mobility of H_2N^- in helium was not measured but was assumed to be equal to that of O^- in helium;[6] any error in this approximation would require slight adjustment of the absolute energy scale. Nevertheless, it is interesting to note that as the collision energy is increased, the HO^- channel increases relative to the N_3^- channel. In comparing the two sets of products, it is clear that formation of HO^- is the less exothermic pathway as well as the product which arises earlier during the chemical transformation. Therefore, the increase in the HO^- product channel with energy may reflect either a more statistical distribution of products or a shorter lifetime of complex XIII due to its higher energy content. Further studies of product distributions as a function of kinetic energy should provide valuable insight into these processes as well as into the lifetimes of the intermediates.

An overview of the reactions of H_2N^- reveals that there is good correlation between the extent of proton equilibration in the complexes IV, V, VIII, and XIII and the driving force of the proton transfer, i.e., the relative proton affinity of the anions (ΔPA). In the reaction of OCS (complex VIII) where $\Delta PA \sim$ 9 kcal mol^{-1}, the more basic anion is formed in 7-fold excess. For CS_2 (complex IV) where $\Delta PA \sim$ 28 kcal mol^{-1}, the two anions are formed in approximately equal yields. Finally, for SO_2 (complex V) and N_2O (complex XIII) where $\Delta PA \sim$ 47 kcal mol^{-1}, the production of the less basic anion now exceeds that of the more basic species by about a factor of 3. Therefore, although proton equilibration is not achieved in any of these reactions, the extent of proton transfer increases as the basicity difference increases.

Proton transfer in N_2O adducts proceeds readily not only from nitrogen and oxygen but from carbon as well. For example, in analogy with the reaction of H_2N^-, the $CH_2{=}CH{-}CH_2^-$ anion reacts with N_2O to form the vinyldiazomethane anion.[2]

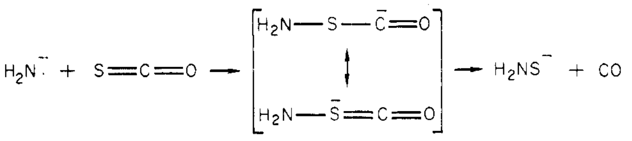
$$CH_2{=}CH{-}CH_2^- + N_2O \rightarrow CH_2{=}CH{-}\bar{C}{=}N{=}N + H_2O \qquad (19)$$

In view of these considerations, we formulate the proton transfer as a concerted Woodward–Hoffman-allowed 6-electron sigmatropic rearrangement



and believe analogous processes may occur in other, properly constructed systems.

H_2N^- reacts with OCS partly by the same pathway as does HO^-, namely by addition to carbon; however, the major product of the reaction is the ion H_2NS^- formed by attack on sulfur and extrusion of CO.



XIV

(20)

Other anions react analogously with OCS, giving a mixture of sulfur transfer and addition.

$$C_6H_5^- + OCS \rightarrow C_6H_5S^- + CO \tag{21a}$$

$$\xrightarrow{\text{He}} C_6H_5COS^- \tag{21b}$$

$$(CH_3)_3SiCH_2^- + OCS \rightarrow (CH_3)_3SiCH_2S^- + CO \tag{22a}$$

$$\rightarrow [(CH_3)_3SiCH_2COS^-] \rightarrow (CH_3)_3SiS^- + CH_2CO \tag{22b}$$

The $(CH_3)_3SiCH_2^-$ anion, prepared by reaction of $(CH_3)_4Si$ with H_2N^-, does not give a simple adduct with OCS but forms rather an anion of m/z 105, which we formulate as $(CH_3)_3SiS^-$ arising from further reaction of the adduct.

The sulfur-transfer reaction is a convenient source of thiol anions, one which does not involve working with mercaptans. It also allows the generation of anions such as H_2NS^- for which neutral precursors are not available. We believe the reaction occurs because of the ability of sulfur to stabilize an adjacent anion in the adduct (e.g., XIV) and because the carbon–sulfur double bond in OCS is exceedingly weak.

HO^- reacts with CO_2 and SO_2 by adduct formation:

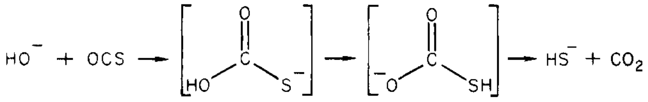
$$HO^- + CO_2 + He \rightarrow HOCO_2^- + He \tag{23}$$

$$HO^- + SO_2 + He \rightarrow HOSO_2^- + He \tag{24}$$

The product species are represented as bicarbonate ion and bisulfite ion, respectively, in which covalent bond formation has occurred, rather than simple clusters bound by ion–dipole forces. We estimate that these species are bound by 30 and 45 kcal mol^{-1}, respectively. In contrast, formation of an ion cluster or adduct between HO^- and N_2O occurs at such a slow rate that it cannot be reliably measured in our system.

$$HO^- + N_2O + He \nrightarrow HO^-(N_2O) + He \tag{25}$$

In the reaction of HO^- with the sulfur-containing compounds CS_2 and OCS, a mechanism similar to reaction 14 predicts formation of HS^-, which is indeed the sole product with CS_2. In the reaction of HO^- with OCS, a minor product, HOS^-, arises from direct attack on sulfur.



(26)

We also examine briefly the reactions of CH_3O^- and of $(CH_3)_2N^-$ with N_2O, CO_2, CS_2, and SO_2, since in these adducts there would be no hydrogen on oxygen or nitrogen for intramolecular proton transfer. Simple addition competes with reduction via hydride transfer in these reactions. For example, reaction of CH_3O^- with CS_2 forms the dithioformate ion (eq 27a) as well as the adduct (eq 27b).

$$CH_3O^- + CS_2 \rightarrow HCS_2^- + CH_2O \tag{27a}$$

$$\xrightarrow{\text{He}} CH_3OCS_2^- \tag{27b}$$

Once having developed methods for the production of a number of ions new to the gas phase, we examined their basicity and nucleophilicity. The ion H_2NS^- is the most basic and most nucleophilic of these ions. The parent molecule is unknown; however, calculations suggest that protonation should occur on nitrogen to form $H_3N^+S^-$.[19] We find that the anion undergoes two H–D exchange reactions with CF_3CH_2OD. This confirms that protonation does indeed occur on nitrogen (eq 28a) although competitive protonation on sulfur (eq 28b), which would not lead to exchange, cannot be excluded. Protonation of the NCS^- anion probably occurs on nitrogen; ab initio calculations[20] indicate that HNCS is the most stable form of the neutral, lying 4.9 kcal mol^{-1} below the energy of the NCSH isomer. Unfortunately, there are no experimental or theoretical results on the site of protonation in NSO^-.

$$H_2NS^- + CF_3CH_2OD \rightleftarrows [DH_2NS{\cdot}CF_3CH_2O^-] \rightarrow DHNS^- + CF_3CH_2OH \tag{28a}$$

$$\rightleftarrows [H_2NSD{\cdot}CF_3CH_2O^-] \tag{28b}$$

In general, the nucleophilicities of the ions parallel their basicities with the exceptions that localized anions are generally more reactive than delocalized ones of similar or even higher basicity ($HS^- > CN^-$, $Cl^- > NCO^-$, $Br^- > NCS^-$). This trend has been noted earlier.[14] The much greater nucleophilicity of sulfur anions as compared to that of oxygen anions of the same basicity, which is observed in solution,[21] is not observed in the gas phase.

Conclusion

In summary, the reactions of a variety of negative ions with a series of triatomic neutrals, N_2O, CO_2, SO_2, CS_2, and OCS, were found to generate a host of novel anions containing nitrogen and sulfur. Our initial flowing afterglow and SIFT–drift studies of these processes reveal a rich and interesting chemistry and provide the first kinetic and thermodynamic data for many of these reactions.

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Registry No. H_2N^-, 17655-31-1; N_2O, 10024-97-2; CO_2, 124-38-9; CS_2, 75-15-0; SO_2, 7446-09-5; OCS, 463-58-1; NCS^-, 302-04-5; HNSO, 13817-04-4; NSO^-, 73439-98-2; H_3NS, 14097-00-8; H_2NS^-, 81649-96-9; HO^-, 14280-30-9; HO_2^-, 14691-59-9; F^-, 16984-48-8; HS^-, 15035-72-0; CN^-, 57-12-5; NCO^-, 661-20-1; N_3^-, 14343-69-2; Cl^-, 16887-00-6; Br^-, 24959-67-9; CH_3I, 74-88-4; CH_3O^-, 3315-60-4; $(CH_3)_2N^-$, 34285-60-4; $CH_2{=}CHCH_2^-$, 1724-46-5; CH_3NH^-, 54448-39-4; $C_6H_5^-$, 30922-78-2; CH_2CN^-, 21438-99-3; $C_6H_5CH_2^-$, 18860-15-6; $(CH_3)_3SiCH_2^-$, 88036-00-4; H_2O, 7732-18-5; HN_3, 7782-79-8; HNCO, 420-05-3; H_2S, 7783-06-4; HNCS, 463-56-9; SO_2^-, 12439-76-8; H_2N, 13770-40-6; CO, 630-08-0; HOS^-, 88657-56-1; $CH_2{=}CHCH_2S^-$, 81649-93-6; $CH_2{=}CHCH_2COS^-$, 81649-94-7; $(CH_3)_3SiCH_2S^-$, 88657-57-2; $(CH_3)_3SiS^-$, 88657-58-3; CH_2CO, 463-51-4; CH_3OCOS^-, 44204-01-5; $HCOS^-$, 37619-01-5; CH_2O, 50-00-0.

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