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Gas-Phase Ion Chemistry of Azides. The Generation of $CH_2{=}N^-$ and $CH_2{=}NCH_2^-$

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(Trimethylsilyl)methyl azide has been found to be a convenient source for generating the methanimine anion ($CH_2{=}N^-$) in a flowing afterglow device. The acidity (388 ± 5 kcal/mol) and electron affinity (0.5 ± 0.1 eV) were established and compared to those of a theoretical prediction. Ion-molecule reactions of the anion were explored and it was found to transfer a hydride to oxygen, nitrous oxide, carbon dioxide, carbonyl sulfide, and carbon disulfide and to undergo sulfur atom transfer with the last two reagents. Methanimine anion also reacts with ethylene oxide to produce the novel 2-azallyl anion ($CH_2{=}NCH_2^-$) which was briefly investigated with respect to its acidity (388 ± 5 kcal/mol), electron affinity (0.8 ± 0.3 eV), and reactivity. In the process of carrying out this study it was found that azide ion, which is typically considered to be inert, reacts with carbon disulfide with a rate constant of 3.8×10^{-11} cm^3 molecule^{-1} s^{-1} to generate the thiocyanate anion.

Phenyl azide was first prepared in 1866 by Peter Griess[1] and since then azides, both organic and inorganic, have been widely used in synthesis[2,3] and as precursors to highly reactive intermediates.[4] However the gas phase ion-molecule chemistry of these compounds has largely been restricted to studies of the azide ion itself and to the generation of nitrene radical anions.[5-11] Since azides are such energy-rich molecules, they should be highly reactive species whose chemistry might be further exploited to generate new and interesting ions. In this paper we show how the M − 1 anion from methyl azide (**1**) may be used to form the methanimine anion (**2**) and describe further reactions of this novel species.

Experimental Section

All of our experiments were carried out in a flowing afterglow apparatus which has previously been described.[12] In brief, the system consists of a 100 × 7.6 cm i.d. cylindrical stainless steel reaction vessel through which purified helium is passed. Typical operating pressures of approximately 0.4 torr, which corresponds to a helium flow of 200 STP cm^3 s^{-1} and a velocity of 8000 cm s^{-1}, were employed. Small amounts (≤1 STP cm^3 s^{-1}) of reagent gases were added upstream such that they pass an electron gun resulting in ionization and the production of the initial reactant ions. For example, introduction of ammonia leads to the generation of amide while hydroxide is formed from a mixture of methane and nitrous oxide. Additional compounds were added either through fixed inlets further down the tube or through a moveable inlet in order to carry out the reactions of interest. The resulting ions were analyzed by a quadrupole mass filter and detected with an electron multiplier.

All of the reagents used in this study were commercially available except for the (trimethylsilyl)methyl azide which was generously given to us by Professor R. Damrauer.

Table I. Products and Thermochemistry (in kcal mol^{-1}) of the Reactions of the Methanimine Anion

reagent	products	thermochemistry
N_2O	$HN_2O^- + HCN$	$\Delta H_f°(HN_2O^-) \le 31$
CO_2	$HCO_2^- + HCN$	$\Delta H° = -30$
CS_2	$HCS_2^- + HCN$	$\Delta H° = -44$
	$CH_2{=}NS^- + CS$	$\Delta H_f°(CH_2{=}NS^-) \le 16$
OCS	$HCOS^- + HCN$	$\Delta H° = -44$
	$CH_2{=}NS^- + CO$	
	$NCO^- + CH_2S$	$\Delta H° = -39$
O_2	$CN^- + H_2O_2$	$\Delta H° = -60$
$\overline{CH_2CH_2O}$	$CH_2{=}NCH_2^- + CH_2O$	$\Delta H° = -20$
CO_2	$CH_2{=}NCH_2CO_2^-$	
N_2O	$CH_2{=}NCH_2N_2O^-$	

Results and Discussion

Methyl azide, while easy to prepare, is toxic and explosive; no doubt this accounts in part for the lack of study of its ion chemistry. (Trimethylsilyl)methyl azide (**3**) is also readily prepared[13,14] and in common with other trimethylsilyl derivatives (e.g., (trimethylsilyl)diazomethane) is much more stable. It reacts rapidly with a variety of bases (F^-, NH_2^-, HO^-, CH_3O^-) to form, not the anion from methyl azide as might be expected, but an anion of *m/z* 28 to which we assign the structure of the methanimine anion (**2**). Large amounts of cyanide ion are also produced as well as smaller amounts of azide and trimethylsilyl anion. The ratio of products formed is very much dependent upon the base which is used. For the generation of the maximum amount of **2**, amide ion appears to be best; a representative distribution of product ions is given in eq 1. We propose that the anion **2** is formed by the pathway

$$\underset{3}{(CH_3)_3SiCH_2N{=}N{=}N} + NH_2^- \xrightarrow{47\%} CH_2{=}N^- \quad (1a)$$
$$\xrightarrow{33\%} CN^- \quad (1b)$$
$$\xrightarrow{8\%} N_3^- \quad (1c)$$
$$\xrightarrow{12\%} (CH_3)_3Si^- \quad (1d)$$

given in eq 2. Reaction with base at the silicon atom first produces the expected anion **1a**, based on previous studies or ours[15] which have shown that alkyl silanes react with a variety of bases to produce the corresponding anions as examplified in eq 3. Anion **1a** has a resonance structure

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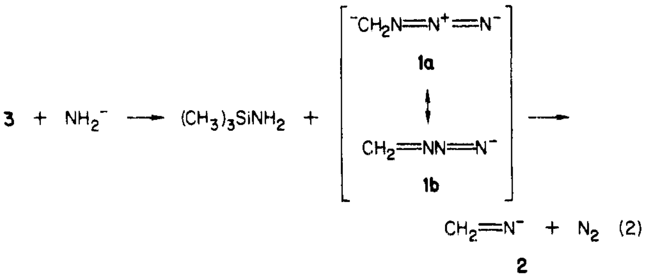

$$Me_3SiC{\equiv}CCH_3 + F^- \rightarrow CH_3C{\equiv}C^- + (CH_3)_3SiF \quad (3a)$$

$$Me_3SiCH_2C{\equiv}CH + F^- \rightarrow {}^-CH_2C{\equiv}CH + (CH_3)_3SiF \quad (3b)$$

1b which shows it to be an imide anion. Loss of nitrogen from this labile anion gives **2**. Cyanide may result from further decomposition of **2**, driven by the overall exothermicity of the reaction (eq 4). We have previously

$$H_2C{=}N^- \rightarrow H_2 + CN^- \quad (4)$$

$$\Delta H° = -27 \text{ kcal mol}^{-1}$$

noted the loss of H_2 from anions formed in highly exothermic nucleophilic reactions.[16] The azide ion presumably arises by substitution, while the trimethylsilyl anion (eq 1d) could arise from loss of nitrogen from the ion obtained by proton abstraction from **3** (eq 5). Some (or all) of the cyanide ion may also be produced in this way, by the thermodynamically favorable proton transfer from HCN to $(CH_3)_3Si^-$.

$$[(CH_3)_3SiCH^-N{=}N{=}N] \rightarrow [(CH_3)_3SiCH{=}N^-] + N_2 \rightarrow (CH_3)_3Si^- + HCN \quad (5)$$

Methanimine (**4**), the simplest imine and its corresponding radical (**5**) and cation (**6**) have been observed in interstellar space[17,18] and are of considerable current interest; they have been investigated both experimentally[19-26]

$$\underset{\textbf{5}}{CH_2{=}N} \quad \underset{\textbf{6}}{CH_2{=}N^+}$$

and theoretically.[27-31] The corresponding anion (**2**) has been the subject of several calculations[27,29,31] but has not previously been observed. One reason, undoubtedly, is that methanimine itself is highly unstable,[19] decomposing rapidly in solution at temperatures above −80 °C, and thus is not a particularly attractive precursor. Our new synthesis from **3** makes this ion easy to prepare and has allowed us to examine its physical properties and chemical reactions.

We first examined the basicity of **2**. It rapidly generates methoxide ions in the presence of methanol but reacts only slowly with D_2O to produce DO^-. No H/D exchange is observed in competition with neutralization. Based on these observations we judge **2** to be slightly more acidic than water, and assign $\Delta H_{acid} = 388 \pm 5$ kcal/mol to its conjugate acid. This value is in good agreement with the calculated value of 393 kcal/mol by Lohr and Ponas.[27] The electron affinity of the methanimine anion was bracketted at the upper end by observing electron transfer to cyclooctatetraene (EA = 0.58 eV)[32] but the lower bound could not be firmly established due to the high reactivity of **2** and the scarcity of suitable compounds with electron affinities below 0.58 eV. However since no O_2^- is observed in its reaction with O_2 (see below) it probably has an EA greater than 0.44 eV[33] and a range of 0.44 eV < EA (*2*) < 0.58 eV can be tentatively assigned. This spread for the EA is consistent with an unpublished value of 0.52 eV obtained from photoelectron spectroscopy[34] and is not far from a calculated value of 0.66 eV.[35]

As might be expected from its structure and basicity, **2** undergoes a wide variety of gas-phase ion molecule reactions which are summarized in Table I. The thermodynamic data which were used to calculate enthalpies of formation or reaction are listed in Table II. Foremost among the reactions of **2** is hydride ion transfer; this pathway is observed with N_2O, CO_2, CS_2, OCS, and O_2 and is illustrated for the first of these reagents in eq 6. Because this reaction proceeds as written, we can calculate an upper bound on the heat of formation ($\Delta H_f°$) of HN_2O^-. In the

$$\textbf{2} + N_2O \rightarrow HN_2O^- + HCN \quad (6)$$

$$\Delta H_f°(HN_2O^-) \le 31 \text{ kcal mol}^{-1}$$

reaction with O_2, CN^- (ΔH_{acid}(HCN) = 353 kcal/mol) is formed instead of HO_2^- ($\Delta H_{acid}(H_2O_2)$ = 376.4 kcal/mol)[45] due to proton transfer within the complex. Sulfur atom transfer to form the anion of the thiooxime of formaldehyde **7** is observed in the reactions of **2** with OCS and CS_2 (eq 7). This process has been reported previously[46,47]

$$CH_2{=}N^- + S{=}C{=}O \rightarrow \underset{\textbf{7}}{CH_2{=}NS^-} + CO \quad (7)$$

$$\Delta H_f°(\textbf{7}) \le 16 \text{ kcal mol}^{-1}$$

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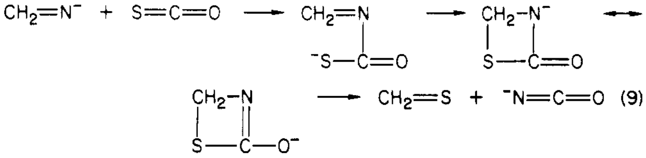
Table II. Heats of Formation

species	$\Delta H_f°_{298}$, kcal mol^{-1}	ref	species	$\Delta H_f°_{298}$	ref
$CH_2{=}NH$	22.6	36	$HCOS^-$	-65.7	40
$CH_2{=}N^-$	43.4	this work	CO	-26.42	37
N_2O	19.6	36	NCO^-	-52.5	41
HCN	32.3	37	CH_2S	24.3	42
HN_2O^-	≤31	this work	CN^-	16	37
CO_2	-94.1	37	H_2O_2	-32.5	37
HCO_2^-	-112.5	36	N_3^-	47.1	43
CS_2	28.04	37	NCS^-	-12.2	44
HCS_2^-	-4.6	this work[38]	N_2S	≤87	this work
$CH_2{=}NS^-$	≤16	this work	$\overline{CH_2CH_2O}$	-12.58	39
CS	55.0	37	CH_2O	-27.7	39
OCS	-33.08	37	$CH_2{=}NCH_3$	17.5	36
HCOSH	-43.49	39	$CH_2{=}NCH_2^-$	38.3	this work

for the reaction of strong bases with OCS, and we have also observed it with CS_2. The thiooxime anion **7** abstracts a proton from acetic acid (ΔH_{acid} = 348.5 kcal/mol) but not from H_2S (ΔH_{acid} = 353.4 kcal/mol)[47] so we have assigned its conjugate acid ΔH_{acid} = 351 ± 3 kcal/mol. The analogous ion H_2NS^- has been generated from the reaction of amide ion with OCS; its conjugate acid was determined to have ΔH_{acid} = 363 ± 3 kcal/mol.[44] Thus resonance of the type shown in eq 8 stabilizes **7** by approximately 10 kcal/mol.

$$CH_2{=}NS^- \leftrightarrow {}^-CH_2{=}N{=}S \qquad (8)$$

The methanimine anion reacts with OCS in still a third way, forming cyanate ion; we propose the pathway shown in eq 9 for this reaction.



(9)

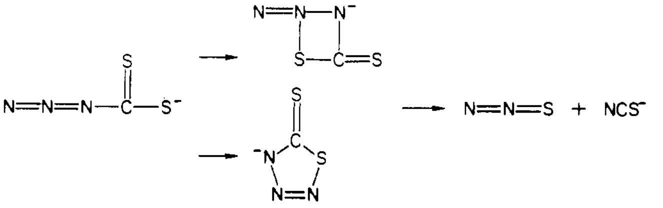
$\Delta H°$ = -39 kcal mol^{-1}

Although cyanate has the same mass (42) as azide, an ion already present in the flow tube as a byproduct of the initial formation reactions, there is a large enough increase in the signal at this mass when OCS is added to make us reasonably certain that reaction 9 occurs. An analogous reaction may occur with CO_2, but the increase in intensity of the *m/z* 42 peak is quite small. We looked for a similar reaction to produce NCS^-, upon reaction of **2** with CS_2. This ion was formed, but we noticed that at the same time the azide ion disappeared from the spectrum. We generated N_3^- separately in two different ways, from NH_2^- and N_2O and from trimethylsilyl azide and F^-, and studied its reaction with CS_2. The thiocyanate ion is the exclusive product (eq 10).

$$N_3^- + CS_2 \rightarrow NCS^- + N_2S \qquad (10)$$

$$\Delta H_f°(N_2S) \leq 87 \text{ kcal mol}^{-1}$$

A mechanism for its formation which is analogous to that proposed above can be written for this reaction, but it cannot be distinguished from one involving a five rather than a four-membered ring (eq 11).



(11)

The rate constant for this perhaps rather surprising reaction was found to be (3.8 ± 0.4) × 10^{-11} cm^3 molecule^{-1} s^{-1}, giving a reaction efficiency of 0.029.[48] The neutral product predicted to be formed in this process, N_2S, is a compound of considerable interest at the present time, but is as yet unknown.[49-53] Our mechanism predicts that N_2S is NNS rather than NSN. Making the usual assumption that gas-phase ion-molecule reactions which occur are exothermic allows us to calculate $\Delta H_f°(N_2S) \leq$ 87.3 kcal mol^{-1}. This result is consistent with the work of Sensarma and Turner[49] who calculated, using the MNDO method, $\Delta H_f°$(NNS) = 47.6 kcal mol^{-1} which is lower in energy than NSN by approximately 164 kcal mol^{-1}. The reaction of sodium azide with CS_2 suggests itself as a possible method for the preparation of N_2S. In any event, since SCN^- is formed in this reaction, we cannot be sure whether or not it is also a product of the reaction of **2** with CS_2.

Finally, we have found that **2** reacts with ethylene oxide to produce the 2-azallyl anion (**8**), as shown in eq 12.

$$CH_2{=}N^- + \overline{CH_2CH_2O} \rightarrow [CH_2{=}NCH_2CH_2O^-] \rightarrow CH_2{=}NCH_2^- + CH_2O \qquad (12)$$

$$\Delta H° = -20 \text{ kcal mol}^{-1}$$

Although this ion has the same mass as azide, it can readily be distinguished from the latter by its chemical reactions. For example, it exchanges up to four hydrogens for deuterium with D_2O and adds CO_2 and N_2O (eq 13).

$$\begin{aligned} CH_2{=}NCH_2^- &\xrightarrow{D_2O} CD_2{=}NCD_2^- \\ &\xrightarrow{CO_2} CH_2{=}NCH_2CO_2^- \qquad (13) \\ &\xrightarrow{N_2O} CH_2{=}NCH_2N_2O^- \end{aligned}$$

None of these reactions is observed for azide. Ion **8** is less basic than allyl ion. Propylene (ΔH_{acid} = 390.8 kcal/mol) is similar in acidity to water (ΔH_{acid} = 391 kcal/mol)[47] and the allyl anion reacts with D_2O to give DO^- in competition with exchange. DO^- is not seen in the reaction of **8** with D_2O. It reacts rapidly with methanol (ΔH_{acid} = 379.2 kcal/mol)[47] to form methoxide ion, which suggests a value of 385 ± 5 kcal/mol for the acidity of *N*-methylmethan-

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imine. Since **8** does not transfer an electron to cyclooctatetraene and does do so to SO_2 we tentatively assign EA(**8**) = 0.8 ± 0.3 eV.[54] Allyl anion[55] has EA = 0.357 eV; therefore, as expected, the nitrogen atom in **8** stabilizes the anion more than it stabilizes the radical. It would be interesting to know the EA more precisely and we hope to do this in the future.

Conclusion

In summary, we have shown that the methanimine anion (**2**) can readily be generated from (trimethylsilyl)methyl azide in the gas phase presumably through the azidomethide ion. Ion **2** was found to have an acidity of 388 ± 5 kcal/mol and an electron affinity of approximately 0.5 ± 0.1 eV, both of which are in accord with a recent calculation. The methanimine anion was also found to react with a variety of reagents. In particular, it is a reasonably efficient hydride donor, undergoes sulfur atom transfer with CS_2 or OCS to produce a resonance stabilized thiooxime anion, and reacts with ethylene oxide to produce the novel 2-azallyl anion. Furthermore, in the study of these reactions it was found that the azide ion is not completely inert and that it reacts with CS_2 to generate the thiocyanate ion.

The 2-azallyl anion was briefly examined and found to have ΔH_{acid} = 385 ± 5 kcal/mol and EA = 0.8 ± 0.3 eV. It thus has a slightly larger proton and electron affinity than the allyl anion.

Acknowledgment. We thank G. B. Ellison, J. Filley, and V. Bierbaum for several helpful discussions as well as aid in preparing this paper. We also thank B. Damrauer for supplying us with (trimethylsilyl)methyl azide. This work was supported by the U.S. Army Research office [Contract No. DAAG29-82-K-0025]. S.K. was also supported by the Army Research office [Contract No. DAAG29-81-K-0169].

Registry No. **2**, 28892-56-0; **3**, 87576-94-1; **7**, 96761-35-2; **8**, 73859-26-4; NH_2^-, 17655-31-1; N_3^-, 14343-69-2; N_2O, 10024-97-2; CO_2, 124-38-9; CS_2, 75-15-0; OCS, 463-58-1; O_2, 7782-44-7; CH_2CH_2O, 75-21-8; HN_2O^-, 66833-68-9; HCO_2^-, 71-47-6; HCS_2^-, 37619-02-6; $HC(O)S^-$, 37619-01-5; NCO^-, 661-20-1; $CH_2{=}NCH_2CO_2^-$, 96761-36-3; $CH_2{=}NCH_2N_2O^-$, 96761-37-4; N_2S, 56400-02-3; NCS^-, 302-04-5; $CD_2{=}NCD_2^-$, 96761-38-5; D_2O, 7789-20-0.

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Mechanism of Fragmentation of Alkylidene-Meldrum's Acids. Carboxyketene, Vinylketene, and Methyleneketene Intermediates from 5-Cyclopentylidene-2,2-dimethyl-1,3-dioxane-4,6-dione

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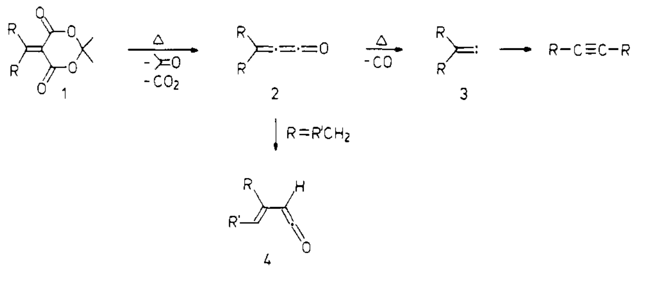
Three ketenes were successively observed on flash vacuum pyrolysis of 5-cyclopentylidene-2,2-dimethyl-1,3-dioxane-4,6-dione (**5**), viz., carboxycyclopentenylketene (**11**, 2126 cm^{-1}), cyclopentylideneketene (**12**, 2087 cm^{-1}), and cyclopentenylketene (**13**, 2110 cm^{-1}). **11** was thermally converted to **13** and probably also to **12**. **12** itself rearranged thermally to **13**. The three ketenes were trapped with methanol to give the esters **14**, **15**, and **16**. **14** was thermally unstable, rearranging at room temperature to methyl cyclopentylidenemalonate (**14a**) and decarboxylating at 150 °C, predominantly to **16**. A dimer of **12**, 2,4-bis(cyclopentylidene)cyclobutane-1,3-dione (**17**), was also isolated. 1-Cyclopentenyldiazomethane (**18**) was prepared and pyrolyzed to 1,3-cyclohexadiene and benzene. No evidence for the formation of cyclohexyne (**17**) was obtained in any of these experiments.

The thermal decomposition of 5-alkylidene-2,2-dimethyl-1,3-dioxane-4,6-diones (Meldrum's acid derivatives) **1** has been the subject of much investigation,[2] but little is known about the mechanism. It is generally believed that methyleneketenes **2** are the first-formed intermediates, and that these eliminate CO to give vinylidenes **3** and thence acetylenes, particularly when R = aryl,[2] or else isomerize to vinylketenes **4** when R = alkyl.[3]



We now wish to show that this sequence of events is not always followed, that the first step can lead to a vinylcarboxyketene, that this in a second step decarboxylates to a vinylketene, that a methyleneketene is also formed, and that at higher temperatures the methyleneketene also isomerizes to the vinylketene.

We chose the cyclopentylidene-Meldrum's acid **5** as a subject for a detailed investigation because the gas-phase pyrolysis of this compound had been previously reported to yield 1,3-cyclohexadiene (**9**) and benzene in a combined yield of 92%.[4] This was believed to occur via the vinylidene **6**, possibly in equilibrium with cyclohexyne (**7**) and the bicyclohexene **8**. Although the authors rightly point out that there was no evidence for the existence of cyclohexyne, the homologue cyclooctyne was isolated from the analogous pyrolysis of cycloheptylidene-Meldrum's acid.[4] It therefore appeared worthwhile to attempt the low-temperature isolation of **7** from the pyrolysis of **5**. As it turned

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