The Thiomethyl Anion: Formation, Reactivity, and Thermodynamic Properties

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The thiomethyl anion (**1**) has been generated by fluorodesilylation of trimethylsilyl-methanethiol in a variable-temperature flowing afterglow device. The proton affinity ($1649 \pm 12 \text{ kJ mol}^{-1}$) and electron affinity ($0.67 \pm 0.13 \text{ eV}$) were determined and compared to a previously reported molecular orbital calculation. Isomerization via a 1,2-proton shift does not take place between -40° and 100°C despite a 156 kJ mol^{-1} driving force. Ion-molecule reactions of **1** were examined with a number of reagents including N_2O , O_2 , CS_2 , COS , and CO_2 . Hydride ion transfer was observed in every case, along with other products, and thermodynamic information has been derived. (*J Am Soc Mass Spectrom* 1990, 1, 366–371)

Anions that are thermodynamically labile can isomerize to more stable ions, at least in principle, via unimolecular rearrangements. Many examples of this type of ion have been reported in recent years, including several in which a 1,2-proton shift would lead to significant stabilization [1]. For instance, deprotonation of trimethylsilane produces an α -silyl carbanion, which does not isomerize to the corresponding silyl anion (eq 1) despite a $\sim 42 \text{ kJ mol}^{-1}$ driving force [1a]. Observations such as this indicate that there is a significant barrier for 1,2-proton shifts.

They are also in accord with the general structural integrity of anions and the fact that this particular process is forbidden by orbital symmetry considerations [2]. Nonetheless, the formation of thermodynamically labile ions such as the α -silyl carbanion is often difficult, and only a few have been thoroughly examined.

It is well known that second-row elements such as silicon, phosphorous, and sulfur can stabilize a carbanion when they are adjacent to the charge [1a, 3]. As a result, dimethylsulfide ($(\text{CH}_3)_2\text{S}$) is readily deprotonated by a number of different bases and is approximately 98 kJ mol^{-1} more acidic than methane [3c]. Given the stability of the α -thiocarbanion and its ease of formation, one might infer that the thiomethyl anion (**1**) would also be a viable species. Indeed, during the preparation of this manuscript Downard et al. [4] reported the existence of **1** in a double-sector mass spectrometer, and predicted some of its characteristics with the aid of *ab initio* molecular orbital calculations.

We report herein our experimental studies, carried out with a variable temperature flowing afterglow apparatus, on the formation, reactivity, and thermodynamic properties of **1**.

Experimental

Among the various techniques for examining gas phase ion-molecule reactions, the flowing afterglow device has proved to be especially valuable. A number of reviews of this method have appeared in the literature, including a recent and comprehensive one by Graul and Squires [5]. Our apparatus was modeled after the Boulder selected ion flow tube [6] and is illustrated schematically in Figure 1. It consists of three separate regions: ion source, reaction tube, and detector, and can currently be operated over a temperature range of $\sim -193^\circ$ to 400°C .

Ions are produced by passing a small amount of an appropriate precursor by a thoriated iridium filament (Electron Technology Co.) biased at -20 to -30 V relative to a grounded accelerating grid and operated in a constant emission current mode ($\sim 0.025 \text{ mA}$ to 0.5 mA). The resulting ions are carried down a 106-cm long $\times 7.3\text{-cm}$ i.d. flow tube by a constant flow ($100\text{--}250 \text{ STP cm}^3 \text{ s}^{-1}$) of a fast-moving ($v \approx 9000 \text{ cm s}^{-1}$) inert buffer gas, typically helium. System pressures of 27 to 173 Pa are measured with an MKS Baratron capacitance manometer and are maintained with a Kinney model MB1600/TOC150 booster pumping system (547 L s^{-1} for air at 53 Pa). Under these conditions the ions undergo rapid collisional relaxation, and thermal equilibration with the walls of the instrument is established. In situ multistep syntheses are conveniently carried out by adding neutral reagents at successive points along the flow tube, and converting ions from one to another. Likewise, the measurement of rate constants is extremely facile because distance is linearly related to time. As a result, rate constants can be obtained by introducing a constant flow of a neu-

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Figure 1. Variable temperature flowing afterglow apparatus.

tral reagent at several points along the flow tube and monitoring the ion intensity. A movable inlet along with sixteen fixed inlets at eight different locations are available. The bulk of the material passing down the flow tube is exhausted by the pumping system, but a small fraction of the ions is sampled through a 0.5-mm molybdenum orifice located at the blunted end of a 120° stainless steel nose cone. The detection region is differentially pumped with two Varian oil diffusion pumps, an M6 and an M4, and is maintained at a pressure between 10^{-4} and 10^{-5} Pa. The ions are focused with a three-element Einzel Co., lens, separated with a flange-mounted 5/8" Extrel quadrupole mass filter (1-450 u, Model 7-270-9), and detected with a conversion dynode electron multiplier. The resulting pulses are fed into a Modern Instrumentation Technology preamplifier-discriminator (20 ns pulse-pair resolution, Model F-100T), and are counted either with the same company's PRM-100 ratemeter or a Teknivent Co. data system interfaced to a Zenith 248 PC. In this way real-time mass spectra can be obtained manually or under computer control.

The temperature of the system can be varied by heating or cooling the helium buffer gas, the neutral reagents (if desired), and the entire flow tube. This is accomplished by thermally isolating the ion source and reaction region with a vacuum box, and using heaters and cooling coils. The pressure in the box is typically maintained at $\sim 10^{-3}$ Pa with a 2" diffusion pump backed with a 2020A Alcatel mechanical pump (7.1 L s^{-1}). An Omega CN5001 temperature controller is used to maintain a constant temperature, and four type J thermocouples are used as monitors. Subambient temperatures are achieved with liquid nitrogen or a Neslab Co. Cryocool CC-100 refrigeration system rated to -100°C . Resistive tubular heaters with a maximum sheath temperature of 870°C (Chromalox TRI-5212) are used for elevated temperatures. Overall, the currently accessible temperature range is $\sim -193^\circ$ to 400°C .

In these experiments electron impact on NF_3 or perfluoropropylene afforded large signals of F^- (m/z 19). Trimethylsilylmethanethiol was prepared and purified

as described by Block et al. [7]. The deuterated reagent (SD) was obtained by hydrogen-deuterium exchange with deuterium oxide. All of the other materials used in this investigation were obtained from commercial suppliers. Liquid samples were subjected to several freeze-pump-thaw cycles to remove any noncondensable impurities, and gaseous materials were used as supplied. Gas purities (minimum) and sources were as follows: He (Air Products, 99.995%), NF_3 (Air Products, 99.0%), perfluoropropylene (Matheson, 99.5%), CO_2 (Matheson, 99.8%), COS (Matheson, 97.5%), $(\text{CH}_3)_2\text{NH}$ (Scott, 99.0%), N_2O (Air Products, 99.99%), O_2 (Matheson, 99.6%), and SO_2 (Linde, 99.9%).

Results and Discussion

Trimethylsilylmethanethiol (2) reacts with F^- in our flowing afterglow apparatus at low conversions to afford three product ions in a $\sim 75:20:5$ ratio (eq 2). Proton transfer is the major pathway (ion 3 has previously

been prepared [8]), a significant fraction proceeds via attack at the silicon center leading to fluorodesilylation and the formation of the thiomethyl anion (1), and a minor amount of methylthiolate (4) is also produced. The latter two species are isomeric but can readily be distinguished because 1 is much more reactive than 4. For example, D_2O , N_2O , and O_2 all react rapidly with the thiomethyl anion but are inert to the thiolate ion. The relative amount of the two isomers was therefore determined by difference—that is, the initial signal at m/z 47 due to both ions was compared to the intensity at the same mass after reacting away 1, using all three reagents.

The products of the reaction of the thiomethyl anion with D_2O ($\Delta H_{\text{acid}} = 1640 \text{ kJ mol}^{-1}$) [9] are OD^- and an m/z 48 ion. The formation of both of these anions is illustrated in Scheme I and is reminiscent of the behavior of the acetyl anion (CH_3CO^-) [1c]. Less acidic reagents such as $(\text{CH}_3)_2\text{NH}$ and NH_3 , $\Delta H_{\text{acid}} = 1658$ and 1689 kJ mol^{-1} , respectively [9], catalyze the isomerization of 1 to 4, but do not appear to be strong enough to protonate it since their conjugate bases are not observed. Therefore, we conclude that the proton affinity of 1 is between the values for OD^- and $(\text{CH}_3)_2\text{N}^-$ and assign it a value of $1649 \pm 12 \text{ kJ mol}^{-1}$. This result is in reasonable accord with Downard et al.'s [4] ab initio molecular orbital value of 1669 kJ mol^{-1} obtained at the MP4/6-311++G**//6-311++G** level.

Several pathways can account for the formation of methylthiolate ion in the reaction of F^- with 2. A particularly appealing one, in accord with the data presented above, is the isomerization of 1 to 4 brought about by trimethylsilylmethanethiol. Consistent with this explanation is our observation that when the reac-

Scheme I

Scheme II

tion is run to higher conversions the 1 : 4 ratio, and the total amount of these two ions, decreases. This scheme can account for all of the thiolate ion, but we cannot entirely rule out a contribution from a direct pathway (Scheme II). On the basis of previous results [1c, 10], the absence of an m/z 91 ion, and the tendency for carbon acids to undergo slow proton transfers [11], it seems unlikely that the process in Scheme II is occurring to any significant extent.

An alternative explanation for the formation of 4 that needs to be considered is a unimolecular rearrangement. The driving force for such a reaction is 156 kJ mol⁻¹. Despite this unusually large thermodynamic impetus, the thiomethyl anion does not isomerize at thermal energies in the millisecond time frame of our experiment (eq 3). In an attempt to induce the proton shift, we generated 1 at several temperatures between

~40 ° and 100 °C, but this had no effect on the 1 : 4 ratio. A dramatic change would have been expected if a unimolecular rearrangement was occurring. Clearly there is a significant activation energy for this process in accord with the Woodward-Hoffmann rules [2].

The electron affinity (EA) of the thiomethyl radical, $\cdot\text{CH}_2\text{SH}$, is related to the carbon-hydrogen bond dissociation energy (BDE) of methanethiol (CH_3SH , 5), the ionization potential (IP) of atomic hydrogen, and the proton affinity (PA) of the thiomethyl anion by the thermodynamic cycle shown in eqs 4-7. We have measured PA(1), and both the IP(H $\cdot$) and the

EA($\cdot\text{CH}_2\text{SH}$)

$$= \text{BDE}(\text{H}-\text{CH}_2\text{SH}) + \text{IP}(\text{H} \cdot) - \text{PA}(^-\text{CH}_2\text{SH}) \quad (8)$$

C-H BDE of 5, 1312 and 402 ± 4 kJ mol⁻¹, respectively, have been reported [9, 12]. Substitution into eq. 8 leads to an electron affinity for the thiomethyl radical of 65 ± 13 kJ mol⁻¹ (0.67 ± .13 eV), which is in accord with our observation that 1 undergoes electron transfer to SO₂ (EA = 1.11 eV) [9] and does not appear to do so with O₂ (EA = 0.451 eV) [13]. Many additional compounds with electron affinities between those for oxygen and sulfur dioxide are known and could be used to refine the bracketed value [14]. However, it has been our experience that many of these reagents are not very volatile and almost all of them contain acidic hydrogens. As a result, basic ions such as 1 often undergo uninformative proton transfer reactions. This is exactly what happens with biacetyl ($\text{CH}_3\text{COCOCH}_3$, EA = 0.69 eV) [9]; 1 readily deprotonates it and no electron transfer is observed. Consequently, nothing can reliably be concluded about the electron affinities in this instance. In addition, bracketing experiments are unlikely to provide a more precise EA than was obtained from the thermodynamic cycle (eqs 4-7); therefore, further experiments were not carried out. These results do provide excellent support for the contention made by Grabowski et al. [15] that the observed electron transfer between CH_3S^- and SO₂ in an ion cyclotron resonance spectrometer was due to thiomethyl anion contamination. On the other hand, a recent molecular orbital calculation predicted an electron affinity for 1 of 0.243 eV [4]. We believe that this value is too small and that given the difficulty in accurately computing electron affinities, this discrepancy is not surprising.

The reactivity of the thiomethyl anion was examined with a variety of reagents including N₂O, O₂, CS₂, COS, CO₂, and SO₂. The results of these reactions along with some thermodynamic data are summarized in Table 1. Heats of formation used in this study are given in Table 2. In every case hydride ion transfer is observed, which is consistent with the small hydride ion binding energy of 1 (eq 9). Nitrous oxide,

for example, reacts readily with the thiomethyl anion to afford HN₂O⁻ (m/z 45) as the major product (eq 10). Smaller amounts of OH⁻ and SH⁻ (m/z 17

Table 1. Products, relative amounts, and thermochemistry derived from the reactions of the thiomethyl anion (1)^a

Reagent	Products	Relative amounts ^b	Thermochemistry (kJ mol ⁻¹)
N ₂ O	HN ₂ O ⁻ + CH ₂ S	~ 70%	ΔH _f [°] (HN ₂ O ⁻) ≤ 73
	OH ⁻ + CH ₂ S + N ₂	20%	ΔH [°] = - 210
	SH ⁻ + (CH ₂ N ₂ O)	10%	
O ₂	HCOS ⁻ + H ₂ O	~ 66%	ΔH [°] = - 613
	HO ₂ ⁻ + CH ₂ S	33%	ΔH [°] = - 85
CS ₂	HCS ₂ ⁻ + CH ₂ S	~ 95%	ΔH [°] = - 127
	SH ⁻ + (C ₂ H ₂ S ₂)	5%	
	⁻ S-CH=C=S + H ₂ S	trace	ΔH _f [°] (⁻ S-CH=C=S) ≤ 234
COS	SH ⁻ + CH ₂ S + CO	~ 85%	ΔH [°] = - 41
	⁻ S-CH=C=O + H ₂ S	10%	ΔH _f [°] (⁻ S-CH=C=O) ≤ - 25
	HCOS ⁻ + CH ₂ S	5%	ΔH [°] = - 124
CO ₂	HSCH ₂ CO ₂ ⁻	~ 85%	
	HCO ₂ ⁻ + CH ₂ S	15%	ΔH [°] = - 61
SO ₂	SO ₂ ⁻ + CH ₂ SH	~ 70%	EA(CH ₂ SH) ≤ 1.11 eV
	HSO ₂ ⁻ + CH ₂ S	20%	ΔH [°] = - 109
	HSCH ₂ SO ₂ ⁻	10%	

^aThe neutral products from these reactions are inferred on the basis of reasonable mechanisms that have previously been put forth in the literature; they are not observed in these experiments.

^bThe relative amounts of the product ions were not obtained by extrapolating to zero flow of the neutral reagent and therefore are only a guide to the behavior of these reactions.

Table 2. Heats of formation (in kJ mol⁻¹)

Species	ΔH _f [°]	Reference	Species	ΔH _f [°]	Reference
⁻ CH ₂ SH	96	This work	CS ₂	117	[9]
CH ₃ SH	- 23	[9]	HCS ₂ ⁻	- 19	[17]
H ⁺	1530	[9]	SH ⁻	- 81	[9]
CH ₃ S ⁻	- 60	[9]	H ₂ S	- 21	[9]
H ⁻	145	[9]	⁻ S-CH=C=S	≤ 234	This work
CH ₂ S	105	[9]	CO	- 110.53	[9]
HN ₂ O ⁻	≤ 73	This work	⁻ S-CH=C=O	≤ - 25	This work
	(lit. ≤ 130 [17])				
N ₂ O	82.1	[9]	COS	- 142	[9]
OH ⁻	- 137	[9]	HCOS ⁻	- 275	[17]
H ₂ O ₂	- 136.3	[9]	CO ₂	- 393.51	[9]
CH ₃ O ⁻	- 139	[9]	HCO ₂ ⁻	- 464	[9]
CH ₂ O	- 108.7	[9]	SO ₂	- 296.8	[9]
H ₂ O	- 242	[9]	HSO ₂ ⁻	- 415	[9]
HO ₂ ⁻	- 94	[9]	CS	268	[9]

and 33, respectively) are also produced and can be accounted for by the mechanism illustrated in Scheme III. (It is worth noting that although there are no examples of thermal proton rearrangements, many isomerizations of energetically excited adducts have been reported [16].) Consistent with this proposal is our observation that the reaction of ⁻CH₂SD, generated from deuterium-labeled trimethylsilylmethanethiol, yields DN₂O⁻, OD⁻, and SD⁻ (*m/z* 46, 18, and 34, respectively). The formation of the thioformyl anion, HCS⁻ (*m/z* 45), which has the same nominal mass as HN₂O⁻, is inconsistent with the labeling study. However, the deuterium-labeled thiomethyl anion was not isotopically pure (~75% D) and consequently some

m/z 45 was produced. As a result, we cannot entirely rule out the formation of minor amounts ($\leq 10\%$) of HCS^- . Thermodynamic information derived from this reaction is given in Table 1. In particular, an upper bound for the heat of formation of HN_2O^- can be deduced if we assume that it is formed in an exothermic process. This seems reasonable since the reaction between 1 and N_2O is quite rapid. Our value, $\Delta H_f^\circ(\text{HN}_2\text{O}^-) \leq 73 \text{ kJ mol}^{-1}$, is in accord with a previous determination of $\Delta H_f^\circ(\text{HN}_2\text{O}^-) \leq 130 \text{ kJ mol}^{-1}$ [17]. In contrast to 1, methoxide does not react with N_2O [8] even though it binds hydride to only a slightly greater extent (eq 11). This lack of reactivity may reflect a kinetic barrier, or it may indicate that hydride

transfer is endothermic. If the latter explanation is correct, then a lower limit of 52 kJ mol^{-1} can be placed on the heat of formation of HN_2O^- .

Oxygen reacts readily with 1 to form two product ions, HCOS^- and HO_2^- (m/z 61 and 33, respectively), in approximately a 2:1 ratio. The hydroperoxy anion is the result of an exothermic hydride ion transfer, $\Delta H^\circ = -85 \text{ kJ mol}^{-1}$, while the thioformate anion presumably arises from addition followed by proton transfer and dehydration (eq 12). The latter pathway is driven by an unusually large reaction exothermicity of

613 kJ mol^{-1} . Both channels require a change in multiplicity because molecular oxygen is a ground-state triplet, but this obstacle can readily be overcome, as previously explained [18], by an initial electron transfer step.

Carbon disulfide, carbonyl sulfide, and carbon dioxide all react with 1 via hydride ion transfer, but the product ion distributions differ markedly. In particular, CS_2 is reduced to afford HCS_2^- almost exclusively, COS reacts to give SH^- as the dominant product ion, and CO_2 leads mainly to an adduct. The products all can be accounted for by a variety of pathways including: hydride ion transfer to carbon or sulfur, addition, addition followed by fragmentation, SH^- elimination, and sulfur atom transfer, all of which have previously been described [19]. The difference in behavior between CS_2 and COS , however, is worth commenting on. Both compounds have very similar hydride ion affinities (281 and 278 kJ mol^{-1}), yet COS reacts to give only a small amount of HCOS^- . The major product, SH^- , can be accounted for by sulfur atom transfer followed by elimination of thioformaldehyde. This product most likely results from the greater tendency for COS to lose CO ($\Delta H_f^\circ(\text{CO}) - \Delta H_f^\circ(\text{COS}) = 31.5 \text{ kJ mol}^{-1}$) than for CS_2 to lose CS ($\Delta H_f^\circ(\text{CS}) - \Delta H_f^\circ(\text{CS}_2) = 151 \text{ kJ mol}^{-1}$). In accord with this notion,

we and others have observed that COS often undergoes sulfur atom transfer under conditions in which CS_2 does not [8, 20].

In summary, we have shown that the thiomethyl anion can be prepared by fluorodesilylation of trimethylsilylmethanethiol in our variable temperature flowing afterglow apparatus. The anion has a proton affinity of $1649 \pm 12 \text{ kJ mol}^{-1}$, has an electron affinity of $0.67 \pm .13 \text{ eV}$, and is a potent hydride ion donor. It does not rearrange at temperatures up to 100°C despite a 156 kJ mol^{-1} driving force for a 1,2-proton shift. This is the result of a significant activation energy barrier, and is in accord with Woodward-Hoffmann rules [2]. Heats of formation for $^-\text{CH}_2\text{SH}$, HN_2O^- , $^-\text{S-CH=C=S}$, and $^-\text{S-CH=C=O}$ have been established, and the reactivity of 1 with a number of reagents has been explored.

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