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Are the Elusive Ions $^-CH_2SH$, $^-CH_2OH$, and $^-CH_2NH_2$ Detectable in the Gas Phase? A Joint ab Initio/Experimental Approach

Kevin M. Downard,[1a] John C. Sheldon,[1a] John H. Bowie,*,[1a] David E. Lewis,[1b] and Roger N. Hayes[1c]

Contribution from the Departments of Chemistry, The University of Adelaide, Adelaide, South Australia, 5001 Australia, and University of Nebraska, Lincoln, Nebraska 68588-0362. Received October 4, 1988

Abstract: Ab initio calculations at the MP4SDTQ/6-311^{++}G**//6-311^{++}G** level indicate the electron affinities of $^{\bullet}CH_2SH$, $^{\bullet}CH_2OH$, and $^{\bullet}CH_2NH_2$ to be +5.6, −8.8, and −16.2 kcal mol^{-1}; thus $^-CH_2OH$ and $^-CH_2NH_2$ should be unstable with respect to their radicals. In accord with these predictions, $^-CH_2SH$ may be observed experimentally; neither $^-CH_2OH$ nor $^-CH_2NH_2$ is observed directly in our experiments but their participation in intermediate and transient ion complexes in particular reactions may be inferred. The ΔH°_{acid} values for $C\mathit{H}_3SH$, $C\mathit{H}_3OH$, and $C\mathit{H}_3NH_2$ are calculated to be 399, 413.5, and 418 kcal mol^{-1}, making $^-CH_2NH_2$ and $^-CH_2OH$, at least theoretically, among the most powerful of all gas-phase bases.

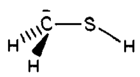
The ΔH°_{acid} values of $\mathrm{MeS}\mathit{H}$, $\mathrm{MeO}\mathit{H}$, and $\mathrm{MeN}\mathit{H}_2$ are 357,[2] 381,[2] and 403[3] kcal mol^{-1}, respectively; thus deprotonation leads to MeS^-, MeO^-, and $MeNH^-$. The isomeric ions $^-CH_2SH$, $^-CH_2OH$, and $^-CH_2NH_2$ are of much theoretical interest. They have been shown to be stable (i.e., lie in potential wells) by ab initio calculations,[4] and it has been suggested that $^-CH_2OH$ could transform to the more stable MeO^- over a barrier of some 46 kcal mol^{-1}.[5] Yet none of these ions have been reported in gas-phase studies, and the possibility must be considered that they are unstable with respect to their corresponding radicals (i.e., the electron affinities of the radicals may be negative).[6] If that is so, then it follows that the anions, theoretically at least, must be among the strongest of all gas-phase bases.[7]

In this paper we report the use of ab initio calculations to estimate (i) the electron affinities of $^{\bullet}CH_2SH$, $^{\bullet}CH_2OH$, and $^{\bullet}CH_2NH_2$ and (ii) the ΔH°_{acid} values for $C\mathit{H}_3SH$, $C\mathit{H}_3OH$, and $C\mathit{H}_3NH_2$. In addition, we describe experimental procedures planned to detect the formation of the three anions.

Experimental Section

Negative ion chemical ionization mass spectra and collisional activation (CA) and charge reversal (CR) mass spectra were measured with an MM VG ZAB 2HF mass spectrometer. The chemical ionization slit was used in the ion source: ionizing energy, 70 eV (tungsten filament); ion source temperature, 150 °C; and accelerating voltage, −8 kV. All slits were fully open to obtain maximum sensitivity and to minimize energy-resolution effects.[8] The reagent ions NH_2^-, MeO^-, and EtO^- were formed from NH_3, MeONO,[9] and EtONO,[9] respectively. The indicated source pressure of NH_3 (or RONO) was 5×10^{-4} Torr. All liquid substrates were introduced through the septum inlet at 150 °C. The substrate pressure was typically 5×10^{-7} Torr. The estimated total pressure in the ion source was 10^{-1} Torr. The pressure of He in the second collision cell (for CA mass spectra) was 2×10^{-7} Torr, measured by an ion gauge situated between the collision cell and the electric sector. This produced a decrease in the main beam signal of ca. 10% corresponding to essentially single collision conditions. Similar conditions were

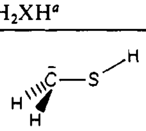
Table I. Ab Initio Calculations on Ions $^-CH_2XH^a$



1

C_s (plane of symmetry)
(i) −437.08427
(ii) −437.42700
(iii) 0.0382

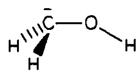
CS	1.8104 Å
SH	1.3586 Å
CH	1.0909 Å
CSH	109.18°
HCS	109.40°
HCSH	59.93°



2

C_s symmetry
(i) −437.08333
(ii) −437.42543
(iii) 0.03310

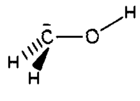
CS	1.8455 Å
SH	1.3362 Å
CH	1.0917 Å
CSH	101.70°
HCS	105.79°
HCSH	122.80°



3

C_s symmetry
(i) −114.38721
(ii) −114.79451
(iii) 0.03740

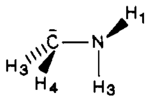
CO	1.4827 Å
OH	0.9402 Å
CH	1.1076 Å
COH	107.46°
HCO	106.34°
HCOH	55.97°



4

C_s symmetry
(i) −114.39323
(ii) −114.80102
(iii) 0.03800

CO	1.4884 Å
OH	0.9332 Å
CH	1.1022 Å
COH	104.16°
HCO	104.89°
HCOH	124.97°



5

C_1 symmetry (gauche)
(i) −94.55100
(ii) −94.94758
(iii) 0.05086

CN	1.4981 Å	CH_4	1.1053 Å	H_4CN	110.37°
NH_1	0.9981 Å	CNH_1	109.69°	H_3CNH_4	115.73°
NH_2	1.0072 Å	CNH_2	114.12°	H_1NCH_2	119.39°
CH_3	1.0981 Å	H_3CN	107.67°	H_2NCH_4	29.71°

[a] Geometries HF/6-311^{++}G**//6-311^{++}G** (Å, deg). Energies: (i) HF/6-311^{++}G**//6-311^{++}G** (au) hartrees, (ii) MP4SDTQ/6-311^{++}G**//6-311^{++}G**; (iii) zero-point vibrational energy (MP4SDTQ/6-311^{++}G**//6-311^{++}G**).

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(1) (a) University of Adelaide. (b) On leave at University of Adelaide from Baylor University, Waco, TX. (c) University of Nebraska.

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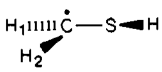
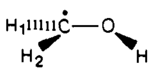
Table II. Ab Initio Calculations on Radicals $^{\bullet}CH_2XH^a$

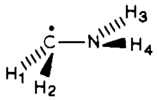


6



7

6		7	
C_1 symmetry ($\mathrm{C}H_2$ lies 24° below plane of H_1CSH)		C_1 symmetry ($\mathrm{C}H_2$ lies ca. 30° below plane of H_1COH)	
(i) −437.11331		(i) −114.45353	
(ii) −437.41869		(ii) −114.81642	
(iii) 0.03347		(iii) 0.03917	
CS	1.7468 Å	CO	1.3556 Å
SH	1.3299 Å	OH	0.9402 Å
CH_1	1.0728 Å	CH_1	1.0731 Å
CH_2	1.0728 Å	CH_2	1.0776 Å
CSH	98.25°	COH	110.75°
H_1CS	115.98°	H_1CO	113.34°
H_2CS	120.30°	H_2CO	117.94°
H_1CSH	177.85°	H_1COH	182.05°
H_2CSH	−24.05°	H_2COH	−31.11°



8

C_s symmetry
(i) −94.62358
(ii) −94.97572
(iii) 0.05313

CN	1.3985 Å	CNH_4	114.42°
NH_4	0.9968 Å	H_1CN	116.19°
CH_1	1.0752 Å	H_1CNH_2	145.10°
		H_4NCH_3	129.00°

^{a}Geometries UHF/6-311^{++}G**//6-311^{++}G** (Å, deg). Energies: (i) UHF/6-311^{++}G**//6-311^{++}G** (au) hartrees, and (ii) MP4SDTQ/6-311^{++}G**//6-311^{++}G**]; (iii) zero-point vibrational energy (MP4SDTQ/6-311^{++}G**//6-311^{++}G**).

used for charge reversal spectra[10] except that the polarity of the electric sector voltage was reversed.

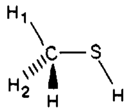
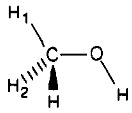
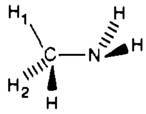
Samples were commercially available except for R_3SiCH_2SH,[11] R_3SiCH_2OH,[12] and $R_3SiCH_2NH_2$[13] (R = Me and Et) which were prepared by reported procedures. The labeled compounds Me_3SiCH_2SD, Me_3SiCH_2OH, $(DSCH_2)_2$, and $(DOCH_2)_2$ were made by exchange of the appropriate neutral with D_2O at 20 °C for 1 h. Incorporation (D_1 or D_2 as appropriate) was greater than 90% in all cases as shown by ^1H NMR and positive ion mass spectrometry.

Results and Discussion

A. Ab Initio Calculations. Ab initio calculations were performed using GAUSSIAN 86.[14] Geometries and energies of anions, radicals, and neutrals are shown in Tables I–III. The conformers adopted by the negative ions (assumed singlet states) and radicals (assumed doublet states) were identified from a number of conformational starting points, and then fully optimized by the Berny routine at the UHF/6-311^{++}G** level. All structures were confirmed as proper potential energy local minima with respect to force constants and to constraints on the wave function, by harmonic frequency analysis and standard tests of wave-function stability. A final single-point correlation-corrected energy was computed for each conformer by fourth-order Moller–Plesset theory (MP4SDTQ/6-311^{++}G**//6-311^{++}G**).

The related ions $^-CH_2SH$ and $^-CH_2OH$ each give "syn" [**1** and **3** (Table I)] and "anti" (**2** and **4** (Table I)] conformers. Both anti conformers have low torsional force constants around the central single bond. The syn conformer **1** of $^-CH_2SH$ is more stable than the anti form by 1.1 kcal mol^{-1},[15] whereas the anti conformer **4** of $^-CH_2OH$ is more stable than the syn form by 3.9 kcal mol^{-1}; cf. ref 4. The ion $^-CH_2NH_2$ adopts only the gauche (C_1) form **5** (Table I).[16] The radicals $^{\bullet}CH_2SH$ and $^{\bullet}CH_2OH$ each adopt a single and similar low-energy C_1 conformer: an almost planar trans HCXH arrangement with the other CH bond some 30° out of plane. The radical $^{\bullet}CH_2NH_2$ adopts an anti (C_s) conformer of lowest energy.

Table III. Ab Initio Calculations on Neutrals CH_3XH^a

					
C_s symmetry		C_s symmetry		C_s symmetry	
(i) −437.74149		(i) −115.08051		(i) −95.24617	
(ii) −438.07924		(ii) −115.47645		(ii) −95.63103	
(iii) 0.04889		(iii) 0.05477		(iii) 0.06804	
CS	1.8183 Å	CO	1.4003 Å	CN	1.4541 Å
SH	1.3306 Å	OH	0.9398 Å	NH	0.9994 Å
CH_1	1.0819 Å	CH_1	1.0817 Å	CH_1	1.0907 Å
CH_2	1.0811 Å	CH_2	1.0877 Å	CH_2	1.0847 Å
H_1CS	106.46°	H_1CO	107.24°	H_1CN	114.45°
H_2CS	111.12°	H_2CO	111.78°	H_2CN	109.34°
CSH	97.98°	COH	110.02°	CNH	111.33°
H_2CSH_1	±118.45°	H_2COH_1	118.78°	H_2CNH_1	121.38°
				$HNCH_1$	60.01°

^{a}Geometries RHF/6-31^{++}G**//6-311^{++}G**(Å, °). Energies: (i) RHF/6-311^{++}G** (au) hartrees, and (ii) MP4SDTQ/6-311^{++}G**//6-311^{++}G**; (iii) zero-point vibrational energy (MP4SDTQ/6-311^{++}-G**//6-311^{++}G**).

Table IV. Calculated Electron Affinities of $^{\bullet}CH_2XH$ and Gas-Phase Acidities of $\mathrm{C}H_3\mathrm{XH}$ (X = S, O, and NH)

CH_2XH	$EA(CH_2XH)$ (kcal mol^{-1})	$\Delta H^\circ_{acid}(\mathrm{C}H_3\mathrm{XH})$ (kcal mol^{-1})^a
CH_2SH	+5.6	399
CH_2OH	−8.8	413.5
CH_2NH_2	−16.2	418

^{a} ΔH°_{acid} ($\mathrm{C}H_3\mathrm{XH}$) = (total energy H^+ + $^-CH_2XH$ + zero-point energy correction) − (energy of CH_3XH + zero-point energy correction), e.g., $\Delta H^\circ_{acid}(\mathrm{C}H_3\mathrm{OH})$ = (0.0 − 114.80102 + 0.0 + 0.03800) − (−115.47645 + 0.05477) = 0.65866 au = 413.5 kcal mol^{-1}.

The data in Tables I and II may be used to determine the electron affinities of the three radicals. For example, the electron affinity of $^{\bullet}CH_2SH$ is the MP4/6-311^{++}G**//6-311^{++}G** energy of **6** (Table II, corrected for zero-point energy) minus the MP4/6-311^{++}G**//6-311^{++}G** energy of **1** (Table I, corrected for zero-point energy) = +5.6 kcal mol^{-1}. The electron affinities of $^{\bullet}CH_2OH$ and $^{\bullet}CH_2NH_2$ are −8.8 and −16.2 kcal mol^{-1} respectively. Thus the ab initio calculations predict that *$^-CH_2SH$ is stable (with respect to electron loss), whereas $^-CH_2OH$ and $^-CH_2NH_2$ are both unstable with respect to their respective radicals.*

The ΔH°_{acid} values for the reactions $CH_3XH \rightarrow H^+ + {}^-CH_2XH$ may be determined from MP4 SDTQ/6-311^{++}G**//6-311^{++}G** calculations of CH_3XH and $^-CH_2XH$ (see Table I for geometries and energies of anions, Table III for geometries and energies of neutrals, and Table IV for the ΔH°_{acid} values).[17] The ΔH°_{acid} values for $\mathrm{C}H_3\mathrm{NH}_2$ and $\mathrm{C}H_3\mathrm{OH}$ (418 and 413.5 kcal mol^{-1}, respectively) predict that $^-CH_2NH_2$ and $^-CH_2OH$ are among the strongest of gas-phase bases (cf. Et^-, $\Delta H^\circ_{acid}(C_2H_6)$ estimated at 421 kcal mol^{-1}).[7] Even $^-CH_2SH$ is predicted to be only slightly less basic than NH_2^- (ΔH°_{acid} for $\mathrm{C}H_3\mathrm{SH}$ and NH_3 are 399 and 403.5[3] kcal mol^{-1}, respectively).

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(15) All energies designated in kcal mol^{-1} throughout this paper have been corrected for zero-point vibrational energies as given by the frequency analysis in the GAUSSIAN 86 program.

(16) The effect of the substituent R on the stability of ions $^-CH_2R$ has been discussed in full previously.[4,5]

(17) For a recent description of the method, see: Siggel, M. R. F.; Thomas, T. D.; Saethre, L. J. *J. Am. Chem. Soc.* **1988**, *110*, 91.

Table V. CA Mass Spectra

precursor ion[a]	*m/z* (loss) abundance %
$HSCH_2CH_2S^-$	92 ($H^\bullet$) 12, 91 (H_2) 3, 60 ($HS^\bullet$) 1, 59 (H_2S) 4, 58 $H_2S + H^\bullet$) 3, 47 (CH_2S) 2, 46 ($CH_2S + H^\bullet$) 3, 33 (C_2H_4S) 100.
$DSCH_2CH_2S^-$	93 ($H^\bullet$) 15, 92 (H_2, D) 8, 61 ($HS^\bullet$) 8, 60 (H_2S, $DS^\bullet$) 12, 59 (HDS) 9, 58 (H_2DS) 7, 48 (CH_2S) 6, 46 ($CH_2S + D^\bullet$) 7, 34 (C_2H_4S) 100, 33 (C_2H_3DS) 56.
$HSCH_2CO_2^-$	90 ($H^\bullet$) 100, 89 (H_2) 15, 75 (O) 78, 73 (H_2O) 54, 47 (CO_2) 63, 46 ($HCO_2^\bullet$) 12, 45 ($CO_2 + H_2$) 84.
$HOCH_2CH_2O^-$	59 (H_2) 100, 31 (CH_2O) 5, 29 ($CH_2O + H_2$) 1.
$HOCH_2CO_2^-$	74 ($H^\bullet$) 100, 73 (H_2) 18, 57 (H_2O) 6, 47 (CO) 61, 45 (CO + H_2) 15, 17 ($C_2H_2O_2$).
$NH_2CH_2CH_2NH^-$	58 ($H^\bullet$) 100, 57 (H_2) 61, 42 (NH_3) 46, 26 (CH_7N).
$NH_2CH_2CO_2^-$	73 ($H^\bullet$) 100, 72 (H_2) 12, 56 (H_2O) 4, 46 (CO) 8, 45 ($HCO_2^\bullet$) 9.

[a] Prepared from the appropriate neutral by reaction with NH_2^-.

Table VI. CA and Charge Reversal (CR) Mass Spectra of MeS^-, $^-CH_2SH$, and MeO^-

precursor ion	spectrum type	[*m/z* (abundance %)]
MeS^- [a]	CA	46 (100), 45 (29), 33 (3) and 32 (92)
	CR	see Figure 1
$^-CH_2SH$ (from $HSCH_2CO_2^-$)	CA[24]	46 (81), 45 (63), 33 (30), 32 (100)
	CR	see Figure 1
MeO^- [b]	CA	30 (5), 29 (100) and 16 (0.6)[5]
	CR	31 (18), 29 (100), 28 (16), 17 (1), 16 (2), 15 (9), 14 (3), 13 (2), and 12 (1)

[a] Formed by the reaction between NH_2^- and dimethyl disulfide. [b] Formed by the reaction between NH_2^- and methanol.

B. Experimental Approach. The calculations outlined above predict that $^-CH_2SH$ should be directly observable whereas $^-CH_2OH$ and $^-CH_2NH_2$ should not. Three experimental procedures were used for the attempted formation of each of the three anions: viz. (i) collision-induced dissociation of the bis-substituted ethane derivative (eq 1, X = S, O, or NH as appropriate), (ii) collision-induced dissociation of the appropriate carboxylate anion[18] (eq 2), and (iii) the S_N2 (Si) reaction of the appropriately substituted trimethylsilyl derivative (eq 3).[19]

$$HXCH_2CH_2X^- \xrightarrow{CA} HXCH_2^- + CH_2X \qquad (1)$$

$$HXCH_2CO_2^- \xrightarrow{CA} HXCH_2^- + CO_2 \qquad (2)$$

$$Nu^- + Me_3SiCH_2XH \rightarrow HXCH_2^- + Me_3SiNu \qquad (3)$$

(a) Methylene Thiol Anion ($^-CH_2SH$). The CA mass spectra of $HS(CH_2)_2S^-$ and $HSCH_2CO_2^-$ are recorded in Table V. The spectrum of $HS(CH_2)_2S^-$ shows a small peak at *m/z* 47, while that of $DS(CH_2)_2S^-$ yields *m/z* 48 ($^-CH_2SD$). This confirms the operation of eq 1 in this case. The CA mass spectrum of the thioglycollate ion also shows a peak at *m/z* 47 (Table V). The MS/MS/MS spectrum[20] of this ion shows similarities to that of MeS^- (Table VI), but the CR (positive ion) spectra[10,20] of *m/z* 47 and MeS^- are quite different (see Figure 1). Ion MeS^- yields Me^+ and $S^{\bullet+}$, whereas *m/z* 47 from thioglycollate gives $CH_2^{\bullet+}$ and SH^+, *thus substantiating the formation of $^-CH_2SH$ by eq 2.*

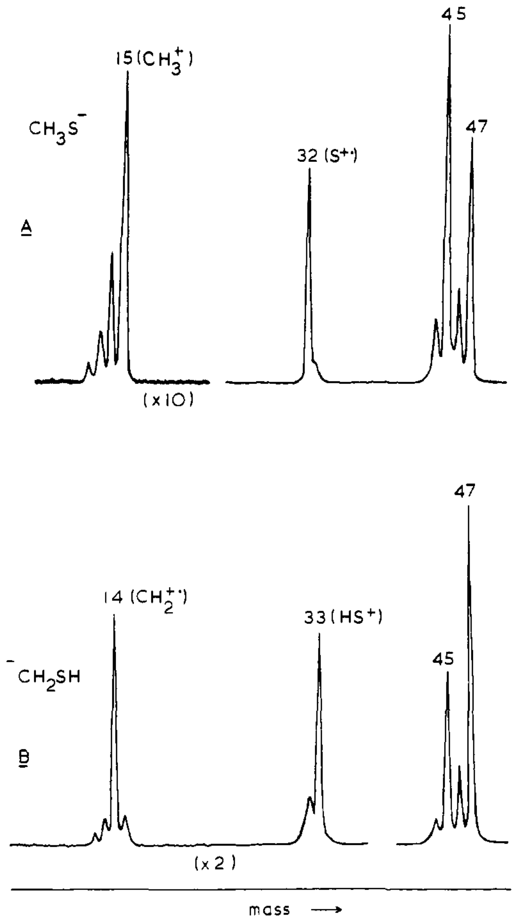

Figure 1. (a) Charge reversal spectrum of MeS^- [from $(MeS)_2$] (VG ZAB 2HF); for experimental details see Experimental Section. (b) Charge reversal spectrum of *m/z* 47 from $HSCH_2CO_2^-$ (Kratos MS 50 TA); for experimental details see ref 23.

The S_N2 (Si) reaction between Me_3SiCH_2SH and NH_2^- in the ion source of the mass spectrometer gives a *pronounced* peak at *m/z* 47. However, the CA and CR mass spectra of this ion identify it as MeS^-, not $^-CH_2SH$ (Table VI). Further, reaction between Me_3SiCH_2SD and NH_2^- yields *m/z* 47, not *m/z* 48. The corresponding reaction between MeO^- and Me_3SiCH_2SH also produces MeS^-. We suggest that these data are accommodated by reaction sequences 4 and 5. Consider, for example, sequence

$$NH_2^- + Me_3SiCH_2SH \rightarrow \underset{a}{[Me_3\overset{-}{Si}(NH_2)(CH_2SH)]} \rightarrow \underset{b}{[^-CH_2SH(Me_3SiNH_2)]} \rightarrow \underset{c}{[MeSH(Me_3Si\overset{-}{N}H)]} \rightarrow MeS^- + Me_3SiNH_2 \qquad (4)$$

$$MeO^- + Me_3SiCH_2SH \rightarrow [Me_3\overset{-}{Si}(OMe)(CH_2SH)] \rightarrow [^-CH_2SH(Me_3SiOMe)] \rightarrow (MeSH[^-CH_2(Me)_2SiOMe]) \rightarrow MeS^- + Me_3SiOMe \qquad (5)$$

4. Nucleophilic addition forms a which decomposes through b.

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[18] Stringer, M. B.; Bowie, J. H.; Eichinger, P. C. H.; Currie, G. J. *J. Chem. Soc., Perkin Trans. 2* **1987**, 387 and references cited therein. Graul, S. T.; Squires, R. R. *J. Am. Chem. Soc.* **1988**, *110*, 607.

[19] DePuy, C. H.; Bierbaum, V. M.; Flippin, L. A.; Grabowskii, J. J.; King, G. K.; Schmitt, R. J.; Sullivan, S. A. *J. Am. Chem. Soc.* **1979**, *101*, 6443. Klass, G.; Trenerry, V. C.; Sheldon, J. C.; Bowie, J. H. *Aust. J. Chem.* **1981**, *34*, 519.

[20] The CA and CR mass spectra of *m/z* 47 from the CA mass spectrum of $HSCH_2CO_2^-$ (CA/MS/MS/MS and CR/MS/MS/MS spectra, respectively) were measured with the triple sector Kratos MS 50-TA instrument at the University of Nebraska—Lincoln. Operating procedures have been described previously.[21] Specifically, deprotonation was effected by MeO^- (from MeONO[22]) in a Kratos Mark IV CI source: ion source temperature, 100 °C; electron energy, 280 eV; emission current, 500 μA; accelerating voltage, −8 kV; measured source pressures, thioglycollic acid (2×10^{-5} Torr), methyl nitrite (1×10^{-6} Torr) (estimated total source pressure 10^{-1} Torr); He pressure in each collision cell, 2×10^{-6} Torr, producing a decrease in the main beam signal of 30%.

[21] For general experimental details, see: Burinsky, D. J.; Cooks, R. G.; Chess, E. K.; Gross, M. L. *Anal. Chem.* **1982**, *54*, 295. Gross, M. L.; Chess, E. K.; Lyon, P. A.; Crow, F. W.; Evans, S.; Tudge, H. *Int. J. Mass Spectrom. Ion Phys.* **1982**, *42*, 243.

[22] Ridge, D. P.; Beauchamp, J. L. *J. Am. Chem. Soc.* **1974**, *96*, 3595 and references cited therein.

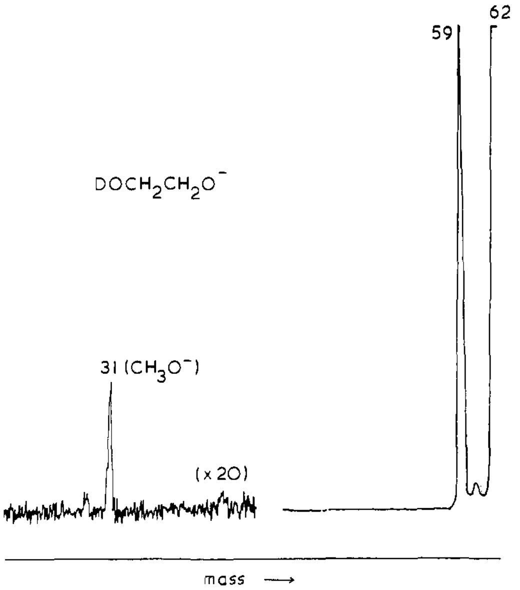

Figure 2. Collisional activation mass spectrum of $DOCH_2CH_2O^-$ (VG ZAB 2HF instrument).

Within complex b, $^-CH_2SH$ deprotonates Me_3SiNH_2 [$\Delta H°_{acid}$ for CH_3SH (see above) and Me_3SiNH_2[23] are 399 and 379 kcal mol^{-1}, respectively] to yield c in which Me_3SiNH^- deprotonates MeSH to yield MeS^- and Me_3SiNH_2.[24]

(b) Hydroxymethylene Anion ($^-CH_2OH$). We have been unable to detect $^-CH_2OH$ directly. For example, no species at *m/z* 31 is present in the CA mass spectrum of $HOCH_2CO_2^-$ (Table V). However, the transient formation of the ion may be inferred by indirect evidence. The CA mass spectrum of deprotonated ethylene glycol (Table V) shows a peak at *m/z* 31 whereas decomposition of $DO(CH_2)_2O^-$ does not give *m/z* 32 ($^-CH_2OD$) but yields *m/z* 31 (MeO^-) (Figure 2). Thus $^-CH_2OD$ may be formed as part of an ion complex d (eq 6) in which $^-CH_2OD$ deprotonates formaldehyde yielding e which subsequently decomposes to MeO^-.

$$DOCH_2CH_2O^- \rightarrow \underset{d}{[DOCH_2^-(CH_2O)]} \rightarrow \underset{e}{[(MeOD)HCO^-]} \rightarrow MeO^- + HDCO \quad (6)$$

$$NH_2^- + Me_3SiCH_2OH \rightarrow [Me_3\bar{Si}(NH_2)(CH_2OH)] \rightarrow [^-CH_2OH(Me_3SiNH_2)] \rightarrow [MeOH(Me_3Si\bar{N}H)] \rightarrow MeO^- + Me_3SiNH_2 \quad (7)$$

The S_N2 (Si) reaction between NH_2 and Me_3SiCH_2OH yields *m/z* 31 whose CA and CR mass spectra are identical with those of MeO^- (Table VI). The analogous reaction between Me_3SiCH_2OD and NH_2^- gives *m/z* 31 (MeO^-) consistent with the mechanism shown in sequence 7.[25]

(c) Aminomethylene Anion ($^-CH_2NH_2$). We have been unable to detect this ion either directly or indirectly using the three standard methods. Neither deprotonated 1,2-diaminoethane nor glycine yields *m/z* 30 (Table V); similarly the S_N2 (Si) reaction between NH_2^- and $Me_3SiCH_2NH_2$ gives no peak at *m/z* 30.[26] However, the reaction between HO^- and $Me_3SiCH_2NH_2$ does form Me_3SiO^- (eq 8). This is a standard reaction[7] and does

$$HO^- + Me_3SiCH_2NH_2 \rightarrow [Me_3\bar{Si}(OH)(CH_2NH_2)] \rightarrow Me_3SiO^- + MeNH_2 \quad (8)$$

indicate that $^-CH_2NH_2$ has at least transient existence in an ion-dipole or ion-induced dipole complex.

Conclusions

A combination of experiment and theory has shown that (i) $^-CH_2SH$ is a stable species and can be observed experimentally; (ii) $^-CH_2NH_2$ and $^-CH_2OH$ are unstable with respect to their radicals, but may be detected indirectly as ion complexes in reaction pathways; and (iii) the relative basicities of the studied species are $^-CH_2NH_2 > {}^-CH_2OH > {}^-CH_2SH$.[27]

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[23] Thomas, D.; Bartmess, J. E., unpublished work. Cited in: Bartmess, J. E.; *The 1987 Gas Phase Acidity Scale*; University of Tennessee: Knoxville, TN.

[24] (a) The alternative three-body reaction

$$NH_2^- + Me_3SiCH_2SH \xrightarrow{NH_3} [^-CH_2SH(NH_3)] \rightarrow [(MeSH)NH_2^-] \rightarrow [MeS^-(NH_3)] \rightarrow MeS^- + NH_3$$

is unlikely because of the low probability of (i) the three-body collision and (ii) the initial deprotonation step. (b) A reviewer has suggested that the alternative reaction

$$Me_3SiCH_2SH + MeO^- \rightarrow Me_3SiCH_2S^- \rightarrow Me_3Si^-(CH_2S) \rightarrow MeS^- + Me_2Si{=}CH_2$$

must also be considered because of the exothermicity of the first step. This seems an unlikely reaction sequence, since (i) Me_3Si^- is not known as a hydride ion donor [Sheldon, J. C.; Bowie, J. H.; DePuy, C. H.; Damrauer, R. *J. Am. Chem. Soc.*, **1986**, *108*, 6794] and (ii) the reaction $Me_3Si^- \rightarrow H^- + Me_2Si{=}CH_2$ is strongly endothermic (calculated at 6-31$^+$G level, +116 kcal mol^{-1} –[Sheldon, J. C.; Bowie, J. H. *J. Chem. Soc., Perkin Trans. 2* **1988**, 1263].

[25] The abundance of MeO^- in this reaction is less by a factor of ~100 than that of the corresponding product ion MeS^- from Me_3SiCH_2SH (eq 4). This is consistent with the difficulty of the final deprotonation step shown in eq 7; i.e., $[MeOH(Me_3Si\bar{N}H)] \rightarrow MeO^- + Me_3SiNH_2$, since the reported $\Delta H°_{acid}$ values of MeOH and Me_3SiNH_2 are 381 ± 2[2] and 379 ± 3.5[23] kcal mol^-, respectively.

[26] The reaction sequence here would be $NH_2^- + Me_3SiCH_2NH_2 \rightarrow [Me_3\bar{Si}(NH_2)(CH_2NH_2)] \rightarrow [^-CH_2NH_2(Me_3SiNH_2)] \rightarrow [(MeNH_2)Me_3SiNH^-] \rightarrow MeNH^- + Me_3SiNH_2$. The final deprotonation step is unfavorable since $\Delta H°_{acid}$ of $MeNH_2$ and Me_3SiNH_2 are 403[3] and 379[23] kcal mol^{-1}, respectively.

[27] A reviewer has suggested that the corresponding $MeXCH_2^-$ ions are comparable in stability (to the $HXCH_2^-$ ions) based on expected substituent effects, but with a reduced chance of isomerization. The reviewer indicates that previous data bear directly upon, and support the $HXCH_2^-$ data presented in this paper; i.e., $MeSCH_2^•$, $MeOCH_2^•$, and $Me_2NCH_2^•$ have electron affinities of 20,[28] -0.4 ± 3,[29] and less than -8.7[30] kcal mol^{-1}, respectively.

[28] Moran, S.; Ellison, G. B. *J. Phys. Chem.* **1988**, *92*, 1794.

[29] DePuy, C. H.; Bierbaum, V. M.; Damrauer, R. *J. Am. Chem. Soc.* **1984**, *106*, 4051.

[30] Calculated from data given in Lias, S. G.; Bartmess, J. E.; Liebman, J. F.; Holmes, J. L.; Levin, R. D.; Mallard, W. G. (Gas Phase Ion and Neutral Thermochemistry) *J. Phys. Chem. Ref. Data* **1988**, *17*, Suppl 1, p 690.