

the native oxide of a silicon substrate.<sup>17</sup> These studies found that the first layer, which is tethered to the oxide via acid-base chemistry, is  $\sim 1000$  times more resistive to wear than the subsequent layers held together primarily by van der Waals forces. Together, the above results attest to the ability of organic films with structures similar to alkanethiolate monolayers to withstand forces similar to those used to acquire our images.

As stated previously, we attribute our images to interactions between the AFM tip and the alkyl chain structure of the monolayer. This conclusion, supported by the above literature findings,<sup>10a,11a,15-17</sup> is based on the differences in the capabilities of AFM and STM to image the atomic structure of short-chain ( $n \leq 3$ ) alkanethiolates at Au(111). With STM,<sup>4</sup> for example, we have routinely obtained atomically resolved images of ethanethiolate ( $n = 1$ ) monolayers. We have ascribed these images to electrons tunneling between the STM tip and the gold surface through the sulfur head group, placing the STM tip near the gold surface. If the AFM tip images the gold-bound sulfur, one would then reasonably expect to obtain images with the hexagonal pattern for all chain lengths,<sup>31</sup> not only for  $n \geq 4$ . This result argues that the atomically resolved images of the longer chain ( $n \geq 4$ ) monolayers arise from interactions between the AFM tip and the alkyl chain structure. The aforementioned chain length dependence of the range of forces that gave atomically resolved images is consistent with this interpretation. Interestingly, the inability to obtain images for  $n \leq 3$  further suggests that most likely position of the AFM tip to be near the outermost carbons of the alkyl chains. However, it is not clear if the tip probes the packing arrangement of the chain terminus or pushes through the first few carbons and images the underlying polymethylene chain structure. The latter possibility may have relevance to the inability to obtain atomically resolved images of the short-chain ( $n \leq 3$ ) monolayers (i.e., the tip induces disorder). The inherent disorder of the short alkyl chain structures<sup>1,13b,14a,18c,d</sup> may also be a contributing (and possibly the dominant) factor. We are currently designing experiments in an attempt to resolve these issues.

(31) This contention is further supported by recent electrochemical measurements of surface coverage.<sup>12,19</sup> These studies found that the surface coverage of alkanethiolate monolayers at Au(111) is constant from  $n = 2$  to 17. We also note that the measured coverage of  $(8.4 \pm 0.7) \times 10^{-10}$  mol/cm<sup>2</sup> compares reasonably well with the  $7.6 \times 10^{-10}$  mol/cm<sup>2</sup> coverage expected for a  $(\sqrt{3} \times \sqrt{3})R30^\circ$  adlayer on Au(111).

## Conclusions

This paper has demonstrated that it is possible to resolve atomic scale features of organic monolayer films at gold using AFM under ambient laboratory conditions and reaffirms the presence of a  $(\sqrt{3} \times \sqrt{3})R30^\circ$  adlayer structure for alkanethiolate on Au(111). This and other recent findings suggest that AFM may prove valuable in providing detailed microscopic information for developing insights into interfacial structure-reactivity relationships. Both cohesive interactions between neighboring chains and the covalent linkage between the sulfur head group and gold surface have been identified as factors that play an important role in the ability to obtain these images. Experiments are in progress to evaluate further the capability of this technique to reveal the structure of various other monolayer films. We are particularly interested in developing further insight into the AFM imaging mechanism to facilitate a detailed comparison of our findings with those from He diffraction,<sup>1</sup> noting the possible complementary nature of the information supplied by the two methods. Extension to characterizations under thin layers of contacting liquids is also under way.

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**Registry No.** Au, 7440-57-5; CH<sub>3</sub>(CH<sub>2</sub>)<sub>n</sub>SH ( $n = 1$ ), 75-08-1; CH<sub>3</sub>(CH<sub>2</sub>)<sub>n</sub>SH ( $n = 2$ ), 107-03-9; CH<sub>3</sub>(CH<sub>2</sub>)<sub>n</sub>SH ( $n = 3$ ), 109-79-5; CH<sub>3</sub>(CH<sub>2</sub>)<sub>n</sub>SH ( $n = 4$ ), 110-66-7; CH<sub>3</sub>(CH<sub>2</sub>)<sub>n</sub>SH ( $n = 5$ ), 111-31-9; CH<sub>3</sub>(CH<sub>2</sub>)<sub>n</sub>SH ( $n = 6$ ), 1639-09-4; CH<sub>3</sub>(CH<sub>2</sub>)<sub>n</sub>SH ( $n = 7$ ), 111-88-6; CH<sub>3</sub>(CH<sub>2</sub>)<sub>n</sub>SH ( $n = 8$ ), 1455-21-6; CH<sub>3</sub>(CH<sub>2</sub>)<sub>n</sub>SH ( $n = 9$ ), 143-10-2; CH<sub>3</sub>(CH<sub>2</sub>)<sub>n</sub>SH ( $n = 10$ ), 5332-52-5; CH<sub>3</sub>(CH<sub>2</sub>)<sub>n</sub>SH ( $n = 11$ ), 112-55-0; CH<sub>3</sub>(CH<sub>2</sub>)<sub>n</sub>SH ( $n = 12$ ), 19484-26-5; CH<sub>3</sub>(CH<sub>2</sub>)<sub>n</sub>SH ( $n = 13$ ), 2079-95-0; CH<sub>3</sub>(CH<sub>2</sub>)<sub>n</sub>SH ( $n = 14$ ), 25276-70-4; CH<sub>3</sub>(CH<sub>2</sub>)<sub>n</sub>SH ( $n = 15$ ), 2917-26-2; CH<sub>3</sub>(CH<sub>2</sub>)<sub>n</sub>SH ( $n = 16$ ), 53193-22-9; CH<sub>3</sub>(CH<sub>2</sub>)<sub>n</sub>SH ( $n = 17$ ), 2885-00-9.

## Intrinsic (Gas-Phase) Basicity of Some Anionic Bases Commonly Used in Condensed-Phase Synthesis

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**Abstract:** The gas-phase acidities of a number of alkylamines and alkylsilanols, used widely in organic synthesis, have been determined. They fall in the expected order based on polarizability, but the value for hexamethyldisilazane is anomalous. It is a considerably stronger acid in the gas phase, relative to other common functional groups, than in solution. The disilazide anion cannot deprotonate ketones in the gas phase, while it does so readily in solution. This is attributed to the effect of the lithium counterion in solution.

There are a variety of strong anionic Brønsted bases, such as butyllithium, lithium diisopropylamine, potassium hydride, etc., commonly utilized for deprotonation of substrates. Chemists tend to use the strongest base available to ensure deprotonation on the

first attempt, with modification to reduce nucleophilicity only when necessary.<sup>1</sup> In the usual solvent systems employed for such work, however, the nature and concentration of the counterion,<sup>2</sup> solvent,

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**Table I.** Gas-Phase Acidities of OH and NH Acids Determined in This Work

acid	method <sup>a</sup>	$\Delta G_{\text{acid}}^b$	$\Delta H_{\text{acid}}^c$	source of data	$\Delta G_{\text{acid}}^{b,d}$
(iPr) <sub>2</sub> NH	Eq.	382.8 ± 0.4	390.2 ± 1.0	0.1 weaker than pyridine	(382.7)
TMP <sup>e</sup>	Eq.	382.3 ± 0.4	389.7 ± 1.0	0.5 stronger than iPr <sub>2</sub> NH	(382.8)
Me <sub>3</sub> SiNH <sub>2</sub>	Br.	371.0 ± 5.0	378.4 ± 5.6	between MeOH, tBuOH	(374.0, 368.0)
Me <sub>3</sub> SiOH	Br.	356.0 ± 4.0	362.5 ± 4.6	stronger than Me <sub>2</sub> C=NOH, ~tBuCH=NOH	(359.1) (355.8)
Et <sub>3</sub> SiOH	Eq.	351.5 ± 2.0	358.0 ± 2.3	0.6 weaker than pyrrole	(350.9)
(Me <sub>3</sub> Si) <sub>2</sub> NH	Eq.	349.0 ± 2.0	356.0 ± 2.3	0.1 weaker than EtSH	(348.9)

<sup>a</sup> Eq. = equilibrium measurement. Br. = bracketing between two acids of known reactivity. <sup>b</sup> Uncertainties are absolute values; relative uncertainties are ±0.2 kcal/mol for the equilibrium method and 2.0 kcal/mol smaller than the absolute value for the bracketing method. <sup>c</sup> Calculated from an entropy of acidity estimated from statistical mechanics: ref 14. The OH and NH groups next to Si are taken as free rotors (see text). <sup>d</sup> Acidities of the compounds in the "Source of Data" column, from ref 21. Uncertainties: ±2.0 kcal/mol absolute, ±0.2 kcal/mol relative. <sup>e</sup> 2,2,6,6-Tetramethylpiperidine.

**Table II.** A Gas-Phase Acidity Scale of Groups of Synthetic Interest<sup>a</sup>

acid	$\Delta G_{\text{acid}}^b$	acid	$\Delta G_{\text{acid}}^b$
MeH	408.6 ± 1.2	tBuOH	368.0
nBuH	407.1 ± 2.6	1,3-dithiane <sup>d</sup>	366.8
tBuH	405.7 ± 2.6	CH <sub>3</sub> C≡N	365.2
NH <sub>3</sub>	396.1 ± 0.7	CH <sub>3</sub> CO <sub>2</sub> Me	365.1
H <sub>2</sub>	394.2 ± 0.1	CH <sub>3</sub> COCH <sub>3</sub>	361.9
Me <sub>2</sub> NH	389.2 ± 0.6	Et <sub>3</sub> COH	364.3
H <sub>2</sub> O	384.1 ± 0.2	Me <sub>3</sub> SiOH	356.0 ± 4 <sup>c</sup>
(iPr) <sub>2</sub> NH	382.8 ± 0.4 <sup>c</sup>	Et <sub>3</sub> SiOH	351.5 <sup>c</sup>
TMP <sup>e</sup>	382.3 ± 0.4 <sup>c</sup>	(Me <sub>3</sub> Si) <sub>2</sub> NH	349.0 <sup>c</sup>
Me <sub>3</sub> SiCH <sub>3</sub>	381.6 ± 2.9	phenol	342.3
MeOH	374.0	MeCO <sub>2</sub> H	341.5
Me <sub>3</sub> SiNH <sub>2</sub>	371.0 ± 5.0 <sup>c</sup>		

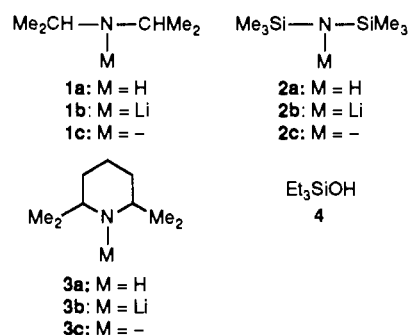
<sup>a</sup> All data from ref 21 unless otherwise noted. <sup>b</sup> ±2.0 kcal/mol absolute, ±0.2 kcal/mol relative, unless otherwise stated. <sup>c</sup> This work. <sup>d</sup> 5,5-Dimethyl-1,3-dithiane; the parent dithiane is probably 0.1–0.2 kcal/mol weaker as an acid than this. <sup>e</sup> 2,2,6,6-Tetramethylpiperidine.

chelating agents,<sup>3</sup> and degree of aggregation<sup>4</sup> can appreciably alter the reactivity of the bases. It would therefore be useful to know the intrinsic basicity of such species, relative to various acidic functional groups, in order to analyze the effect of these perturbations on the reactivity.

Fraser and co-workers<sup>5,6</sup> have measured equilibrium ion-pair acidities of a number of such species in tetrahydrofuran, with lithium as a counterion. Although a complete scale of such acidities, including a wide variety of functional groups such as ketones, esters, nitriles, etc., has not been published, quantitative data for a number of lithioamide bases are available. Diisopropylamine (**1a**) is 2.4 pK<sub>a</sub> units stronger as an acid than 2,2,6,6-tetramethylpiperidine (**3a**), and hexamethyldisilazane (**2a**) is 11.5 pK<sub>a</sub> units stronger than **3a**.<sup>5</sup> Other literature data on the occurrence of proton transfer to such species from common functional groups can be used to determine an ordering of acidities: lithium 2,2,6,6-tetramethylpiperidide is a slightly stronger base than lithium diisopropylamide.<sup>7</sup>

Arnett and his co-workers have determined, using calorimetry, the enthalpies of proton transfer to many such lithioamides from common functional groups.<sup>4,8</sup> They find that lithium diisopropylamide (**1b**) is about 25 kcal/mol stronger as a base than a typical enolate ion, but that lithium hexamethyldisilazide (**2b**) is only 8 kcal/mol stronger. Bordwell and co-workers,<sup>9</sup> as part

of the extensive scale of pK<sub>a</sub>s in DMSO solvent, have obtained a pK<sub>a</sub> for hexamethyldisilazane (**2a**) of 26, comparable to that of ketones (acetone 26.5).<sup>9</sup> The dialkylamines such as **1a** are more weakly acidic than the solvent DMSO (pK<sub>a</sub> = 35),<sup>9</sup> so that their pK<sub>a</sub>s cannot be obtained in that solvent. We therefore have undertaken a study of the gas-phase acidities of the conjugate acids of some of the anionic bases commonly used in synthetic chemistry, specifically diisopropylamine (**1a**), hexamethyldisilazane (**2a**), 2,2,6,6-tetramethylpiperidine (**3a**), and triethylsilanol (**4**). These intrinsic acidities, relative to the acidities of many of the functional groups utilized in solution,<sup>9</sup> will provide the framework which one can use to estimate the counterion and solvent effects which may control the thermochemistry in solution.



## Experimental Section

Acidities were determined using a previously described ion cyclotron resonance (ICR) spectrometer,<sup>10</sup> with a capacitance bridge detector operated in rapid scan mode.<sup>11</sup> Neutral gas pressures were measured using a Bayard-Alpert style ionization gauge, calibrated against a capacitance manometer to obtain true pressures. Care was taken that the rapid scan method did not perturb the measured equilibria by translational excitation of an endothermic reaction.<sup>12</sup>

Hexamethyldisiloxane, diisopropylamine (**1a**), hexamethyldisilazane (**2a**), 2,2,6,6-tetramethylpiperidine (**3a**), and triethylsilanol (**4**) were used as obtained commercially; purities were checked by gas chromatography and by the ICR mass spectra. Fluoride ion was generated by dissociative attachment (4.2 eV) of electrons to nitrogen trifluoride at ca. 5 × 10<sup>-7</sup> Torr partial pressure. Methoxide was formed by dissociative attachment (thermal electrons) of in situ generated methyl nitrite<sup>13</sup> at 1 × 10<sup>-7</sup> Torr partial pressure.

## Results

Using the usual gas-phase equilibrium techniques,<sup>14</sup> the acidity of hexamethyldisilazane (**2a**) was determined to be 0.1 kcal/mol weaker (numerically larger in  $\Delta G_{\text{acid}}$ )<sup>15</sup> than that of ethanethiol.

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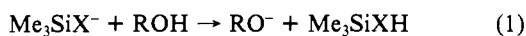
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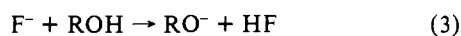
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Similarly, triethylsilanol (**4**) is 0.6 kcal/mol weaker in acidity than pyrrole. Diisopropylamine (**1a**) is 0.1 kcal/mol weaker than pyridine, and 2,2,6,6-tetramethylpiperidine (**3a**) is 0.5 kcal/mol stronger an acid than diisopropylamine (**1a**). The acidities derived from these data are presented in Table I.

Trimethylsilanol and (trimethylsilyl)amine are not readily available, so their conjugate anions were generated by fluoro-desilylation<sup>16</sup> of the corresponding disilyl ether and disilylamine compounds. The acidities were then determined by the bracketing method, by reacting these anions with acids of successively stronger acidity, until the anion of interest reacts completely to generate the conjugate anion of the standard acid. A serious problem in the present work was found to be the generation of the  $\text{Me}_3\text{SiX}^-$  anions ( $\text{X} = \text{O}, \text{NH}$ ) not only by fluoride but also by the anions of the standard acids



This cycle results in the continued presence of the  $\text{Me}_3\text{SiX}^-$  anion in the mass spectrum, even after the thermochemical threshold for reaction 1 becoming exothermic is exceeded. Double resonance ejection of  $\text{RO}^-$  halts reaction 2, and the near-collision rate disappearance of  $\text{Me}_3\text{SiX}^-$  is taken as an indication that reaction 1 has become exothermic. The cycle is further complicated by the reaction



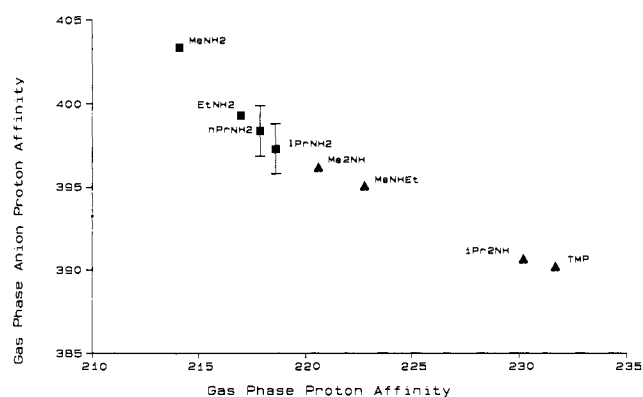
being exothermic for R larger than neopentyl. Care was taken that production of  $\text{RO}^-$  by this method was not mistaken for reaction 1. The acidities obtained are given in Table I.

For **1a** and **3a**,  $\Delta S_{\text{acid}}$  is calculated to be  $21.3 \pm 2.0$  cal/(mol·K), based on statistical mechanics calculations, principally involving the loss of the umbrella vibrational mode on proton loss, plus change in symmetry number.<sup>14,17</sup> For **2c**, the symmetry correction for the apparent linear Si–N–Si structure (see below) of the conjugate anion is balanced by the symmetry of the planar structure about nitrogen in the acid **2a**,<sup>18</sup> for a  $\Delta S_{\text{acid}}$  of  $26.0 \pm 2.0$  cal/(mol·K). For the silanols, the OH is taken as a free rotor, for a loss of 4.6 cal/(mol·K)<sup>19</sup> on proton transfer, for  $\Delta S_{\text{acid}} = 21.4 \pm 2.0$  cal/(mol·K).

Using a literature lower limit for the homolytic N–H bond strength for **2a** of  $>106.3 \pm 3.0$  kcal/mol,<sup>20</sup> we derive an electron affinity of  $>63.1 \pm 5.3$  kcal/mol ( $>2.74$  eV) for  $(\text{Me}_3\text{Si})_2\text{N}^*$ , larger than that of  $\text{Me}_2\text{N}^*$  at  $9.0 \pm 3.5$  kcal/mol.<sup>21</sup>

## Discussion

The acidities of the dialkylamines are in the expected polarizability order of  $\text{Me}_2 < \text{iPr}_2 \ll (\text{Me}_3\text{Si})_2$ .<sup>22</sup> An early report of the acidity of  $\text{Et}_2\text{NH}$  being comparable to that of water<sup>23</sup> is consistent with the present ordering. As indicated by the data in Table II, replacing a hydrogen with a trimethylsilyl group strengthens the acidity of methane by  $27.0 \pm 4$  kcal/mol,<sup>24</sup> of



**Figure 1.** Gas-phase acidity vs gas-phase basicity of alkylamines, in kcal/mol: (■) primary amines, (▲) secondary amines.

water by  $28.1 \pm 5$  kcal/mol, and of ammonia successively by  $25.1 \pm 6$  and  $22.0 \pm 7$  kcal/mol. The uncertainties of these values are too large to draw conclusions concerning saturation effects<sup>25</sup> in the amine, but it can be seen that the  $\text{Me}_3\text{Si}$  group has a fairly constant anion stabilizing effect, regardless of the atom type.  $\text{Et}_3\text{SiOH}$  is a stronger acid in the gas phase than  $\text{Me}_3\text{SiOH}$  by  $4.5 \pm 2.5$  kcal/mol, again consistent with polarizability effects,<sup>22</sup> and paralleling its larger gas-phase basicity as well.<sup>26</sup> For comparison,  $\text{Et}_3\text{COH}$  is likewise a stronger acid than  $\text{Me}_3\text{COH}$  by  $3.7 \pm 0.3$  kcal/mol.<sup>21</sup> The silicon strengthens the acidity relative to carbon: **4** is 12.8 kcal/mol stronger as an acid than  $\text{Et}_3\text{COH}$ .<sup>21</sup>

There is a recent report of the bracketed acidity of  $\text{Me}_3\text{SiOH}$  in the flowing afterglow,<sup>27</sup> which places it  $3 \pm 2$  kcal/mol stronger as an acid than found in this work. It was reported<sup>27</sup> that  $\text{Me}_3\text{SiO}^-$  was not protonated by  $\text{CF}_3\text{CH}_2\text{OH}$ , which is 1.7 kcal/mol more acidic<sup>21</sup> than our lower bracketing limit of  $\text{tBuCH}=\text{NOH}$ . We have found that in the ICR spectrometer, trifluoroethanol is sometimes troublesome as a bracketing acid, in that anions can react with it in an elimination reaction to yield fluoride ion, a much stronger base than  $\text{CF}_3\text{CH}_2\text{O}^-$ . We also note that the  $\text{Me}_3\text{SiO}^-$  ions were prepared differently in the two studies: ours was from  $\text{F}^-$  plus  $(\text{Me}_3\text{Si})_2\text{O}$ , and that of Damrauer and co-workers<sup>27</sup> was from  $\text{HO}^-$  plus  $\text{Me}_3\text{SiH}$ . We have repeated our work with the same results and have no other obvious reason for this discrepancy, though it is a slight one. Our equilibrium acidity of  $\text{Et}_3\text{SiOH}$  agrees with the bracketed acidity for it in the flowing afterglow.<sup>27</sup> The  $4.5 \pm 2.5$  kcal/mol greater acidity of  $\text{Et}_3\text{SiOH}$  than  $\text{Me}_3\text{SiOH}$  found here is reasonable, in terms of known substituent effects, as discussed above. The report of "equal" acidities for  $\text{Me}_3\text{SiOH}$  and  $\text{Et}_3\text{SiOH}$  in ref 27 is carefully qualified there: they are stated to be equal within the uncertainty of the bracketing method,  $\pm 4$  kcal/mol.

This effect of silyl versus alkyl groups on gas-phase acidities is in contrast to the effect of a silyl group on cations: theoretical calculations<sup>28</sup> indicate that  $\text{H}_3\text{SiNH}_2$  should be a weaker base than  $\text{H}_3\text{CNH}_2$  by 7 kcal/mol, but  $\text{H}_3\text{SiOH}$  should have the same basicity as  $\text{CH}_3\text{OH}$ . Experimentally,  $\text{Me}_3\text{SiOSiMe}_3$  is similar in basicity to  $\text{Me}_3\text{C}-\text{O}-\text{CMe}_3$ ,<sup>26,29</sup> and  $\text{Me}_3\text{SiOH}$  is comparable to  $\text{Me}_3\text{COH}$ ,<sup>30</sup> indicating that the trimethylsilyl group on oxygen behaves similarly to an alkyl group.

One of the first unexpected results reached in modern gas-phase ion chemistry<sup>22</sup> was that, because alkyl groups stabilize both anions and cations (i.e., make the corresponding neutral species both

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stronger acids and stronger bases), polarizability must be the major interaction between the substituent and the ionic center. If the gas-phase acidities of a number of these alkyl- and dialkylamines are plotted against their gas-phase basicities,<sup>21</sup> a linear correlation is seen (Figure 1,  $r = 0.980$ ,  $\Delta G_{\text{acid}} = -0.74\Delta G_{\text{base}} + 547.8$ ). A similar correlation has been noted for the gas-phase acidity and basicity of alcohols;<sup>31</sup> the slope in that case is comparable at  $-0.75$ . This implies that the alkyl groups are stabilizing both positive and negative charges, consistent with polarizability being a major mode of this stabilization.

As noted above, the trimethylsilyl group, relative to an alkyl group, strengthens the gas-phase acidity of XOH species, but has little effect on the gas-phase basicity of XOH or XOX. The trimethylsilyl group has a comparable polarizability to the *tert*-butyl group,<sup>32,33</sup> which should strengthen the acidity and basicity of species with these substituents equally.<sup>31</sup> This implies that the SiR<sub>3</sub> group must be acting as an electron-accepting group, to partially offset the polarizability effect. Taft and co-workers<sup>34</sup> have derived a master equation for expressing gas-phase acidities in terms of field/polar effects  $\sigma_1$ , polarizability effects  $\sigma_\alpha$ , and resonance effects  $\sigma_R$ . Applying that equation to the present data, using parameters for the SiMe<sub>3</sub> group,<sup>32</sup> a gas-phase acidity of 364.6 kcal/mol is calculated for Me<sub>3</sub>SiOH, over 10 kcal/mol weaker than observed experimentally. Trimethylsilyl has usually been considered a polar electron-donating group<sup>34,35</sup> based on its electronegativity and  $\sigma_1$  value. It does have a slightly positive  $\sigma_R^-$  value,<sup>34,35</sup> however, indicating that it is capable of resonance stabilization of negative charge under the proper circumstances. It would appear that the  $\sigma$  constants for Me<sub>3</sub>Si, obtained from cationic data, are not appropriate for the present anionic systems.

We have examined this larger than expected effect of the trimethylsilyl group on stabilization of nitranions and oxyanions, using semiempirical molecular orbital calculations. The relative gas-phase enthalpies of acidity ( $\Delta H_{\text{acid}}$ ) for Me<sub>2</sub>NH and for **2a** have been calculated using the MNDO and AM1 methods.<sup>36</sup> These methods in general result in localized anions being too high in energy,<sup>36</sup> and for the present case they calculate **2a** to be only 7 kcal/mol more acidic than dimethylamine, disagreeing with the experiment by 32 kcal/mol. However, an intriguing result for **2c** is found: while the geometries for Me<sub>2</sub>NH, Me<sub>2</sub>N<sup>-</sup>, and **2a** are much as expected, with approximately tetrahedral geometry at nitrogen for the dialkylamines, and trigonal planar for **2a**, **2c** has a linear Si-N-Si structure! The HOMO of **2c** is 1.7 eV more bound than that for Me<sub>2</sub>N<sup>-</sup> consistent with the difference of 2.06 eV in the electron affinities derived above from the experimental data. The lithiated species, including **2b**, are all of the expected tetrahedral or trigonal geometries, however. We are further pursuing these results at the more appropriate ab initio level.<sup>37</sup>

Turning to the comparison with solution-phase reactivity of these anions, in all solvents where data are available,<sup>4-6,8,9</sup> **2a** is at least 10 pK<sub>a</sub> units (14 kcal/mol) more acidic than the di-

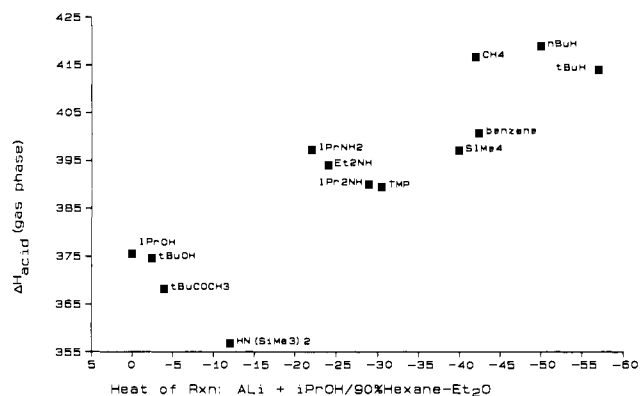


Figure 2. Gas-phase anion proton affinity ( $\Delta H_{\text{acid}}$ ) vs enthalpy of solution-phase proton transfer from 2-propanol to lithiated anions in 90% diethyl ether/hexane solvent, in kcal/mol.

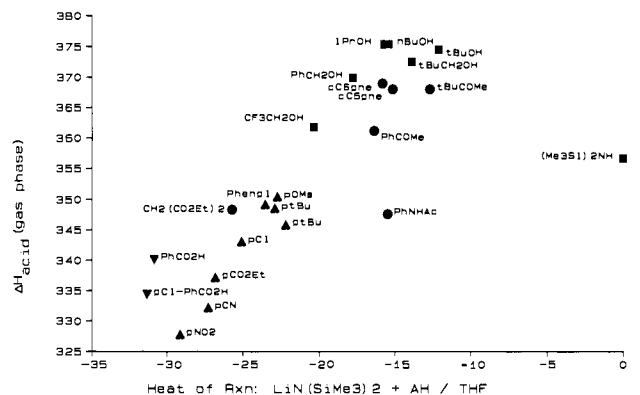


Figure 3. Gas-phase anion proton affinity ( $\Delta H_{\text{acid}}$ ) vs enthalpy of solution-phase proton transfer from various acids to lithiated hexamethyldisilazide (**2b**) in THF solvent, in kcal/mol: (▲) phenols, (▼) benzoic acids, (●) ketones and esters, (■) "localized" OH, NH acids.

alkylamines. This parallels the relative acidities in the gas phase, where **2a** is 32 kcal/mol stronger as an acid than **1a** and **3a**. The reduction in the size of the substituent effect on going to solution is attributable to partial stabilization in solution by the counterion and solvent, as well as an attenuation in the polarizability effect, due to charge delocalization by the above interactions.

What is more pertinent in comparing the gas-phase and solution-phase data is the relative acidities of functional groups of synthetic interest, such as ketones, alkynes, nitriles, etc., with the basicity of the anionic species examined here. In the gas phase, we have previously noted that methoxide will deprotonate all carbonyl compounds, nitriles, acetylenes, and most benzylic sites.<sup>38</sup> The anions **1c** and **3c** are intrinsically only 8 kcal/mol stronger as bases than methoxide. The only simple acids that fall between the amines and methanol are toluenes substituted with electron-donating groups, such as *p*-(dimethylamino)toluene. Thus methoxide and the anions of these amines should behave intrinsically almost identically. The preference for the use of the amine anions in solution is obviously due to their decreased nucleophilicity, for steric reasons.

In the gas phase, **2c** will not deprotonate simple ketones (other than CF<sub>3</sub>COCH<sub>3</sub>), nitriles, esters, or alkyl-substituted terminal alkynes.<sup>14</sup> It is more acidic than CF<sub>3</sub>CH<sub>2</sub>OH (pK<sub>a</sub> 9.2 in aqueous solution<sup>39</sup>) and is comparable in acidity to ethanethiol (pK<sub>a</sub> 10.61 in aqueous solution<sup>39</sup>). In organic solvents, however, **2b** readily deprotonates ketones<sup>4</sup> and esters.<sup>7,40</sup> The lithium counterion (THF solvent) must therefore stabilize the enolate anion more than the

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amide anion, to shift the equilibrium by at least 17 kcal/mol!

Arnett and Moe have measured the enthalpies of reaction for **2b** reacting with a number of acids in THF solvent,<sup>4</sup> as well as for a number of lithiated species reacting with 2-propanol in 90% hexane/10% diethyl ether.<sup>8</sup> If these enthalpies are plotted versus the gas-phase enthalpies of acidity,<sup>21</sup> as shown in Figures 2 and 3, it is evident that there is a general parallel trend in the two phases. For a given functional group, such as the alkyl- and dialkylamines in Figure 2, the largest substituents result in the amine being the least acidic in solution, but the most acidic in the gas phase, consistent with polarizability and solvation effects.<sup>22,14</sup> The position of **2a** is anomalous in these plots: it is considerably more weakly acidic in solution than expected from the gas-phase data and well removed from the other amine acids. This is further evidence for very different structures of **2b** and **2c**.

Such a change in reactivity based on the counterion implies that proper choice of solvent and/or counterion may allow considerable selectivity in this case. An example is the relative basicities of the sodium salt of **2c** vs the lithium salt **2b**; the latter resulted in only  $\gamma$ -deprotonation of an  $\alpha,\beta$  unsaturated ketone, but the sodium salt deprotonated an adjacent simple ketone in the same molecule.<sup>2</sup> Although kinetic control may be invoked as the difference here, the counterion may be controlling the equilibria at the stage of the initial proton transfer, since the  $\gamma$  site of the conjugated enone is comparable in intrinsic acidity to that of the amide anion.<sup>41</sup>

The anions of the trialkylsilanols have been used in solution primarily as nucleophiles which are the synthetic equivalent of  $O^{2-}$ .<sup>42</sup> The observed basicity, in that  $R_3SiO^-$  does not deprotonate the  $\alpha$ -H of esters in solution, is consistent with the anion's weak basicity in the gas phase.

### Conclusions

Knowledge of the intrinsic reactivity of species of this type, plus observing how this can be subsequently modified by solvation and counterions, allows the chemist better control and selection of the available reaction pathways. It has been shown that the observed reactivity of dialkylamide anions in solution is consistent with their intrinsic reactivity, but that hexamethyldisilazide anion appears to have its solution phase reactivity modified considerably by the counterion. Further exploration of counterion effects on the reactivity of **2c**, or possibly of species of the type  $Me_3Si-NHR$ , where R = some bulky alkyl group, would be of interest. The latter species should be intrinsically just a little weaker in acidity than any ester or ketone, so that counterion control might tune its reactivity through the range of synthetic interest.

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**Registry No.** **1a**, 108-18-9; **1b**, 414-54-0; **1c**, 94612-69-8; **2a**, 999-97-3; **2b**, 4039-32-1; **2c**, 92231-05-5; **3a**, 768-66-1; **3b**, 38227-87-1; **3c**, 138054-31-6; **4**, 597-52-4;  $Me_2NH$ , 124-40-3;  $Me_3SiNH_2$ , 7379-79-5;  $Me_3SiOH$ , 1066-40-6; lithium ion(+), 17341-24-1.

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## The Temperature and Coverage Dependences of Adsorbed Formic Acid and Its Conversion to Formate on Pt(111)

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**Abstract:** We have studied the adsorption of HCOOH on Pt(111) at 80–100 K and its conversion to formate with increasing surface temperature. The techniques employed are thermal desorption spectroscopy and high-resolution electron energy loss spectroscopy. At very low exposures (<0.2 langmuir), we posit that HCOOH exists molecularly as monomers or discrete dimer pairs. As exposure increases, there is evidence for hydrogen-bonded chains with the molecular plane of HCOOH nearly parallel to the surface. At an exposure of 0.2 L, these chains resemble the solid-phase  $\beta$ -polymorph as indicated by the vibrational frequencies of the OH out-of-plane bending vibration. Heating this surface causes the chains to break apart into discrete dimer pairs, followed by deprotonation to a bridging formate adspecies. The formate decomposes between 210 K and 280 K, causing  $CO_2$  desorption and leaving hydrogen adatoms. Increasing the exposure above 0.6 L causes the chains to adopt a structure similar to the denser  $\alpha$ -polymorph. Heating this surface causes molecular desorption in two states. One is centered at 160 K and is dominated by gaseous HCOOH dimers. Desorption in this state leaves bridging formate and  $\beta$ -polymorphic HCOOH coexistent on the surface. The other is centered at 200 K and is primarily gaseous monomers. Desorption in this state leaves only the formate adspecies. Its decomposition then proceeds as on the surface exposed to 0.2 L HCOOH.

### 1. Introduction

The adsorption of formic acid (HCOOH) on transition metal surfaces and its subsequent reactions are of ongoing interest within the surface scientific community. The majority of studies focus on the decomposition intermediates of the acid and their ultimate products.<sup>1–18</sup> Decomposition can occur via dehydrogenation, as on Pt<sup>1–4</sup> and Cu,<sup>5–7</sup> or by a combination of dehydrogenation and dehydration, as on Ni<sup>8–15</sup> and Ru.<sup>16–18</sup> The most commonly ob-

served intermediate is formate in a bridging configuration (bonding through the oxygen atoms to two surface atomic sites), although

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