increased in the order of BNK-1$^+$ < BNK-5$^+$ < BNK-10$^+$. Importantly, all k_f values obtained were of the order of 10^7 M^{-1} s^{-1}. The latter value is below that for the diffusion-controlled reaction and is rather insensitive to the system involved. On the other hand, k_b was sensitive to the detergent and CD structure and was found to vary between 270 and 50 000 s^{-1}.

From temperature dependencies of K, k_f, and k_b of BNK-10$^+$ and γ-CD system, the free energies (ΔG, $\Delta G^{\ddagger}{}_f$ and $\Delta G^{\ddagger}{}_b$), enthalpies (ΔH, $\Delta H^{\ddagger}{}_f$ and $\Delta H^{\ddagger}{}_b$), and entropies (ΔS, $\Delta S^{\ddagger}{}_f$, and $\Delta S^{\ddagger}{}_b$) of the complexation reaction and activation were derived (Table II). The values of ΔH and ΔS estimated here are similar to those reported previously for the various kinds of inclusion reactions of CD.[3a,14]

Discussion

The bromonaphthyl group is too large to be inserted into the cavity of α-CD (4.5 Å in diameter). Further, the overall size of the quaternary ammonium groups is slightly larger than that of the α-CD's cavity. Thus, no inclusion of α-CD with any of our probes is expected and is experimentally confirmed. ^{1}H NMR measurements support the inclusion of the detergent probes into the inner cavity of γ-CD. The type I inclusion (Scheme II) of the bromonaphthyl group into the cavity explains the quenching results. In general, the cationic group may be placed outside and cover the cavity. The postulate that the size of bromonaphthyl group is small enough to be included in the cavity of β- or γ-CD but not in the cavity of α-CD is supported also by the low values of $k_{q,obsd}/k_{q,0}$.

A type of complexation that is different from type I is required to explain the data for the system of BNK-10$^+$ and γ-CD. The association constant for this system is exceptionally high, 16 300 M^{-1} (at 25 °C). A molecular model shows that the BNK-10$^+$ molecule in a folded form fits in the cavity of γ-CD. In this case, the naphthyl and carbonyl parts are buried entirely in the cavity and the bromine atom, and the cationic group are located outside the cavity. The differential quenching of the two emissions observed for BNK-10$^+$ in γ-CD (Figure 5) may be associated with either a more effective quenching due to a differential reactivity of the Type I and Type II complexes or a different equilibrium concentration of the two complexes or some combination of both factors. At this point we speculate that it is the escape rate that determines the probe triplet lifetimes. Thus the type I structure dissociates faster than the type II structure for BNK-10$^+$.

As is seen in Table I, the strength of complexation increases in the order BNK-1$^+$ < BNK-5$^+$ < BNK-10$^+$ for γ-CD (Type I). This order is consistent with an important role of hydrophobic interactions in the course of inclusion. As is clear further from Table I, all k_f values were of the order of 10^7 M^{-1} s^{-1} and are quite insensitive to the inclusion system. On the other hand, k_b varied significantly between 270 and 50 000 s^{-1}. These facts suggest that the rate-determining step of the host–guest association is the breakdown of the water structure inside CD and/or around probe. The important role of the dehydration to the association process was discussed earlier by Cramer et al.[3a]. Finally, it should be noted that, strictly speaking, our data applies to *triplet* probes and not to ground-state probes. The results are expected to be representative of ground-state behavior because of the nonpolar nature of the triplet of the BNK moiety.

Acknowledgment. We acknowledge our gratitude to the National Institutes of Health and the National Science Foundation for its generous support of this work and Professor R. C. D. Breslow for a stimulating and informative discussion of the interpretation of the data.

Registry No. [*N*-(4-Bromo-1-naphthoyl)methyl]trimethylammonium bromide, 80214-62-6; [*N*-(4-bromo-1-naphthoyl)pentyl]trimethylammonium bromide, 79671-16-2; [*N*-(4-bromo-1-naphthoyl)decyl]trimethylammonium bromide, 79671-17-3; α-cyclodextrin, 10016-20-3; β-cyclodextrin, 7585-39-9; γ-cyclodextrin, 17465-86-0; α-CD-BNK-1$^+$ complex, 80800-13-1; α-CD-BNK-5$^+$ complex, 80800-14-2; α-CD-BNK-10$^+$ complex, 80822-20-4; β-CD-BNK-1$^+$ complex, 80800-15-3; β-CD-BNK-5$^+$ complex, 80800-16-4; β-CD-BNK-10$^+$ complex, 80822-21-5; γ-CD-BNK-1$^+$ complex, 80800-17-5; γ-CD-BNK-5$^+$ complex, 80800-18-6; γ-CD-BNK-10$^+$ complex, 80822-22-6.

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(14) (a) Van Etten, R. L.; Clowes, G. A.; Sebastian, J. F.; Bender, M. L. *J. Am. Chem. Soc.* **1967**, *89*, 3242. (b) Straub, T. S.; Bender, M. L. *Ibid.* **1972**, *94*, 8881. (c) Lewis, E. A.; Hansen, L. D. *J. Chem. Soc., Perkin Trans. 2* **1973**, 2081.

(15) It was found from conductance measurements that the hydrocarbon moieties of sodium dodecylsulfate and hexadecyltrimethylammonium bromide are included into the cavities of α-, β-, and γ-CD. See ref 16.

(16) Okubo, T.; Kitano, H.; Ise, N. *J. Phys. Chem.* **1976**, *80*, 2611.

Proton Affinity and Ion–Molecule Reactions of a Simple Silyl Enol Ether

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Abstract: The gas-phase positive ion–molecule chemistry of the simple silyl enol ether, 2-(trimethylsiloxy)propene (**1**), has been studied by using ion cyclotron resonance spectroscopy. A lower bound to the proton affinity (PA) of **1** is found to be 16 ± 1 kcal/mol above PA(NH$_3$). The experimental results are consistent with C-protonation forming an ion with a structure equivalent to that of the adduct of the trimethylsilyl cation with acetone. The reactivity of the protonated enol ether suggests that most of the positive charge is localized on the trimethylsilyl group. This is in agreement with molecular orbital calculations on a model complex. On the basis of thermochemical data, the protonated enol ether is calculated to be stable by 42 ± 10 kcal/mol with respect to the trimethylsilyl cation and acetone. Trimethylsilyl cation transfer reactions to various bases B have been observed from both the adduct and protonated **1**. A dual group transfer reaction involving transfer of a proton from BH$^+$ to **1** and abstraction of the trimethylsilyl cation by the base to form the products B–SiMe$_3$$^+$ and acetone has been observed to occur in a single reactive encounter. A brief comparison with solution results is made.

Silyl enol ethers are among the most commonly used organosilicon reagents.[1] For the most part, however, the mechanisms of their chemical reactions have not been systematically studied.[2] Among the mechanistic questions that remain poorly defined are (1) the factors that govern the site of electrophilic attack on silyl

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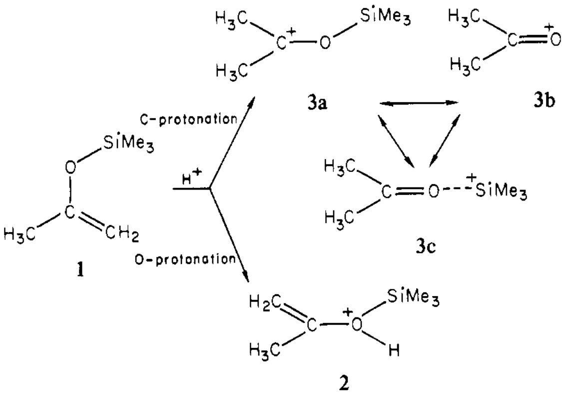
[†] Camille & Henry Dreyfus Teacher-Scholar (1978–1983); A. P. Sloan Foundation Fellow (1977–1981); DuPont Young Faculty Grantee (1978).

(1) Rasmussen, J. *Synthesis*, **1977**, 91.

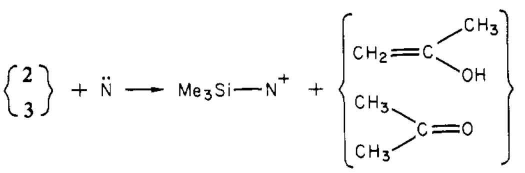
0002-7863/82/1504-1794$01.25/0

enol ethers and (2) the role of trimethylsilyl cations in solution-phase processes. We are interested in investigating the gas-phase ion–molecule chemistry of synthetically important compounds like silyl enol ethers. Such studies help to elucidate the role of solvent in the ion chemistry of these compounds. Our studies, at present, are specifically directed toward compounds with double bonds conjugated to heteroatoms, for example, enamines.[3-5] In this paper, we report work on the gas-phase ion chemistry of 2-(trimethylsiloxy)propene (**1**), the trimethylsilyl enol ether of acetone. An examination of its protonation and subsequent or concurrent trimethylsilyl cation transfer reactions leads to useful insights into the relationship between gas- and solution-phase mechanisms in organosilicon chemistry.

There are two reasonable sites for protontation of silyl enol ethers. Protonation at carbon leads to a conjugate acid represented by the hybrid of structures **3a**, **3b**, and **3c**. Protonation at oxygen leads to the conjugate acid **2**. Either **2** or **3** could be subject to nucleophilic attack at silicon to generate the enol or the ketone, respectively, and a trimethylsilyl–nucleophile complex (reaction 2). Indeed this combination of steps (reaction 1 plus reaction 2) is apparently involved in the solution-phase acid-catalyzed hydrolysis of trimethylsilyl enol ethers[2] although the site of protonation and the concerted or stepwise nature of the process is still uncertain. Our data suggest that, for isolated molecules in the gas phase, protonation occurs at carbon and that the protonated silyl enol ether is structurally identical with the long-lived complex formed in collisions of trimethylsilyl cations with acetone.



(1)



(2)

Experimental Section

This work was carried out by using a modified Varian V-5900 ICR spectrometer operated in the drift mode. All experiments employed a rectangular cell at the ambient temperature of the spectrometer. This instrumentation has been previously described in detail.[6] Electron energies were approximately 20–30 eV, and phase-sensitive detection of the ions was accomplished by pulsing the electron beam. Total pressures as measured by an ion gauge were in the range 10^{-5}–10^{-4} torr. Double-resonance studies were performed by sweeping the frequency of a second oscillator applied to the analyzer region.

Compound **1** was synthesized by following standard methods from $(CH_3)_3SiCl$ and acetone.[7] All other chemicals used in this study were obtained from commercial sources and were used without further purification. The compounds were degassed by several freeze–pump–thaw cycles. Mass spectra showed no significant impurities.

Table I. Proton-Transfer Reactions for Determining the Proton Affinity (PA) of 1 from the Reaction
Base·H$^+$ + 1 → Base + (1 + H$^+$)

base	PA(base) relative to NH_3[a]	observation of proton transfer
EtOH	+14.7	yes
Me_2O	+11.9	yes
$\overline{CH_2CH_2CH_2CH_2O}$	+5.4	yes
Et_2O	+4.6	yes
NH_3	0.0	yes
$(i\text{-Pr})_2O$	−1.0	yes
$MeNH_2$	−9.1	yes
$EtNH_2$	−12.1	yes
Me_2NH	−15.5	yes
$t\text{-BuNH}_2$	−16.3	no
Me_3N	−19.3	no
$(n\text{-Pr})_2NH$	−22.4	no
$(i\text{-Pr})_2NH$	−23.9	no
Et_3N	−26.2	no

[a] In kcal/mol from ref 10b. Positive values correspond to proton affinities less than PA(NH_3). Negative values correspond to proton affinities greater than PA(NH_3).

The proton affinity was obtained by the bracketing technique.[8] Compound **1** is protonated by conjugate acids of bases of known proton affinity. At a certain threshold value, compound **1** can no longer be protonated by a base (B) since the value of PA(**1**) is less than PA(B). In general one then observes proton transfer from the protonated unknown to the reference base. As discussed below, proton transfer from protonated **1** to bases with higher proton affinities is not observed. All observed reactions were confirmed by double resonance.

Electron bombardment of tetramethylsilane leads to almost completely specific formation of $Si(CH_3)_3^+$ (>95%) at low electron energies (~20 eV). Adduct formation (P + 73) occurs within a small number of collisions (possibly one) and was confirmed by double resonance from *m/e* 73 to the adduct. Subsequent reactions of the adduct were monitored by double resonance. These experiments were performed with total pressures of (5 – 10) × 10^{-5} torr.

Results and Discussion

Proton-transfer reactions between 2-(trimethylsiloxy)propene and the various bases (B) shown in Table I were examined. There is a distinct break in the observation of proton transfer from BH^+ to **1** between $(CH_3)_2NH_2^+$ and $(CH_3)_3CNH_3^+$. As shown in separate double-resonance experiments, a peculiarity of the proton-transfer chemistry of **1** is the nonobservation of proton transfer from protonated **1** to the apparently more basic compounds (entries **7–11**). The conventional assumption of gas-phase proton-transfer chemistry that all exothermic proton transfers will be observed[9] is apparently violated in this system. Thus the usual bracketing methods for determining proton affinities cannot be directly applied to the determination of the proton affinity of **1** because of the possibility of the presence of a kinetic effect which is suggested by the nonoccurrence of exothermic proton transfer from protonated **1**. Nevertheless, the threshold observed in Table I provides a lower bound to the proton affinity of **1**, giving PA(**1**) > 16 kcal/mol relative to PA(NH_3).[10]

The observed lower bound for the proton affinity can be compared with what would be expected for O-protonation of **1**. This can be reasonably estimated from substituent effects observed in other systems. The proton affinity of *tert*-butyl isopropyl ether is 3.8 kcal/mol greater than that of NH_3.[10b] Both substitution

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(2) Novice, M. H.; Seikaly, H. R.; Seiz, A. D.; Tidwell, T. T. *J. Am. Chem. Soc.* **1980**, *102*, 5835.

(3) Ellenberger, M. R.; Eades, R. A.; Thomsen, M. W.; Farneth, W. E.; Dixon, D. A. *J. Am. Chem. Soc.* **1979**, *101*, 7151.

(4) Ellenberger, M. R.; Farneth, W. E.; Dixon, D. A. *J. Am. Chem. Soc.* **1981**, *103*, 5377.

(5) Eades, R. A.; Weil, D. A.; Ellenberger, M. R.; Farneth, W. E.; Dixon, D. A.; Douglass, C. H., Jr. *J. Am. Chem. Soc.* **1981**, *103*, 5372.

(6) Beauchamp, J. L. *Annu. Rev. Phys. Chem.* **1971**, *22*, 527.

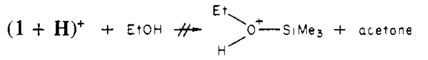
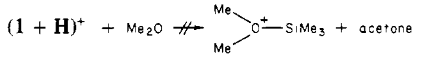
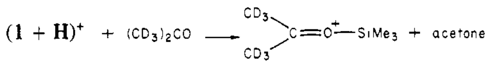
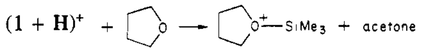
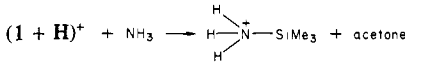
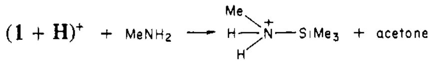
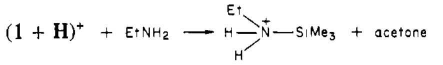
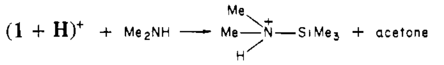
(7) Krüger, C. R.; Rochow, E. G. *J. Organomet. Chem.* **1964**, *1*, 476.

(8) (a) Brauman, J. I.; Blair, L. K. *J. Am. Chem. Soc.* **1970**, *92*, 5986. (b) DeFrees, D. J.; McIver, R. T., Jr.; Hehre, W. J. *Ibid.* **1977**, *99*, 3854. (c) Smith, D. E.; Munson, B. *Ibid.* **1978**, *100*, 497.

(9) Bohme, D. K. In "Interactions Between Ions and Molecules"; Ausloos, P., Ed.; Plenum: New York, 1974.

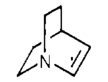
(10) Eades, R. A.; Scanlon, K.; Ellenberger, M. R.; Dixon, D. A.; Marynick, D. S. *J. Phys. Chem.* **1980**, *84*, 2840. (b) Aue, D. H.; Bowers, M. T. In "Gas Phase Ion Chemistry"; Bowers, M. T. Ed.; Academic Press: New York 1979; Vol. 2, p 2.

Table II. Trimethylsilyl Cation Transfer Reactions from Protonated 1

PA(base)[a]	reaction
+14.7	 $(\mathbf{1}+\mathrm{H})^+ + \mathrm{EtOH} \nrightarrow \mathrm{Et(H)\overset{+}{O}{-}SiMe_3} + \text{acetone}$
+11.9	 $(\mathbf{1}+\mathrm{H})^+ + \mathrm{Me_2O} \nrightarrow \mathrm{Me_2\overset{+}{O}{-}SiMe_3} + \text{acetone}$
+7.8	 $(\mathbf{1}+\mathrm{H})^+ + \mathrm{(CD_3)_2CO} \rightarrow \mathrm{(CD_3)_2C{=}\overset{+}{O}{-}SiMe_3} + \text{acetone}$
+5.4	
0.0	 $(\mathbf{1}+\mathrm{H})^+ + \mathrm{NH_3} \rightarrow \mathrm{H_3\overset{+}{N}{-}SiMe_3} + \text{acetone}$
−9.1	 $(\mathbf{1}+\mathrm{H})^+ + \mathrm{MeNH_2} \rightarrow \mathrm{MeH_2\overset{+}{N}{-}SiMe_3} + \text{acetone}$
−12.1	 $(\mathbf{1}+\mathrm{H})^+ + \mathrm{EtNH_2} \rightarrow \mathrm{EtH_2\overset{+}{N}{-}SiMe_3} + \text{acetone}$
−15.5	 $(\mathbf{1}+\mathrm{H})^+ + \mathrm{Me_2NH} \rightarrow \mathrm{Me_2H\overset{+}{N}{-}SiMe_3} + \text{acetone}$

[a] See footnote *a*, Table I.

of a trimethylsilyl group for the *tert*-butyl group and of an isopropenyl group for an isopropyl group would be expected to lower the proton affinity at oxygen, on the basis of analogous substituent effects in amine chemistry. Substitution of the trimethylsilyl group for the *tert*-butyl group in *tert*-butyldimethylamine leads to a decrease of 5 kcal/mol in the proton affinity.[11] Incorporation of unsaturation into the carbon chain adjacent to an amine has been shown[12] to cause a decrease of ~3 kcal/mol in the proton affinity for the quinuclidene skeleton (**4**). Here, geometric



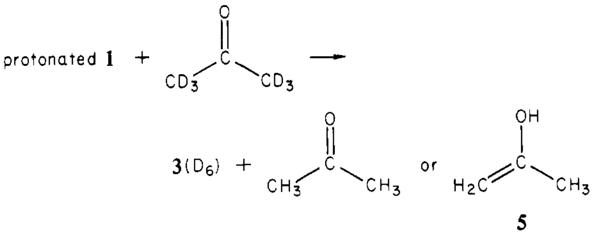
4

constraints prevent lone pair–π conjugation in the neutral enamine (**4**) so that this value is a lower limit to the decrease in proton affinity in a system where conjugation is possible. For N-protonation of the unstrained enamine, $H_2C{=}CH{-}NH_2$, where conjugation is found, the effect of unsaturation is much larger, a decrease of 16 kcal/mol relative to $CH_3CH_2NH_2$.[13] The conjugative interaction in this enamine has been calculated to be 6 kcal/mol.[5] Thus the effects of introducing silicon for carbon and of unsaturation combined with the proton affinity of *tert*-butyl isopropyl ether suggest that the proton affinity for O-protonation of **1** should be lower than that of NH_3. In contrast, the observed value of ≥16 kcal/mol above NH_3 suggests that protonation at O is not the process observed.

The absence of proton transfer from protonated **1** to other bases is also consistent with C-protonation. The simple expectation from the Lewis structures of **2** and **3** is that the positive charge is localized further from the proton-transfer site in **3** than in **2**. This expectation is largely confirmed by molecular orbital calculations (discussed below) which show that for **3** the charge is localized in the region of the silicon–oxygen bond. Thus deprotonation at carbon in **3** requires substantial electron reorganization. It has been shown in negative ion chemistry that these are circumstances in which exothermic proton transfer can become much slower than usual.[14] Benzyl anions, allyl anions, and enolate anions, all delocalized species, show thermoneutral proton-transfer rates at least an order of magnitude slower than anions like alkoxides, in which proton transfer occurs between charge-localized sites. Furthermore the initial attack of the nucleophile is likely to be directed at the area of electron deficiency, which for **3** is remote from the hydrogen to be transferred. This too should decrease the likelihood of rapid proton transfer, while facilitating transfer of the trimethylsilyl cation as discussed below.

Although proton transfer has not been observed, the conjugate acid of the silyl enol ether is not chemically inert. Transfer of the trimethylsilyl cation to various Lewis bases occurs as shown in Table II. If these bases are ranked in the order of their proton affinity, a threshold for cation transfer is again observed, this time at acetone. Bases with proton affinities lower than that of acetone do not accept the trimethylsilyl cation from protonated **1**.

These trimethylsilyl cation (Me_3Si^+) transfer reactions provide additional evidence for the structure of protonated **1**. Protonated **1** is observed to transfer Me_3Si^+ with high efficiency to acetone-d_6. Since the only plausible silylation site on acetone is the oxygen atom, the ionic product from the reaction of protonated **1** with acetone must be **3**. The neutral product may be either acetone itself or its less stable enol tautomer (**5**).[15] For the overall process



(3)

to be thermoneutral or exothermic (and thus observable), protonated **1** must be comparable to or less stable than **3**. That is if protonated **1** is **2**, it cannot be more stable than **3**. One must then conclude that either protonation of **1** occurs at oxygen to produce **2** because of a kinetic rather than a thermodynamic preference and there is a barrier preventing isomerization to the C-protonated form (**3**) or the structure of protonated **1** is, in fact, **3** and the Me_3Si^+ transfer to acetone-d_6 is a thermoneutral process. The second hypothesis is more consistent with observations described earlier as well as those detailed below.

Ions of structure **3** can be obtained directly from the reaction of Me_3Si^+ (from electron impact on tetramethylsilane) and acetone. It has been shown[16-20] that Me_3Si^+ is a fairly indiscriminate Lewis acid that will form complexes with most bases. It has also been shown that Me_3Si^+ transfers can be carried out from the initially formed complex to other electron-pair donors.[16-20] Indeed, the scale of trimethylsilyl cation affinities generally follows the proton-affinity scale.[16-20] In Table III we present our results on Me_3Si^+-transfer reactions carried out on the Me_3Si^+–acetone adduct. Comparison of Tables II and III shows that precisely the same Me_3Si^+-transfer reactivity pattern is observed for the protonated silyl enol ether and for the acetone–Me_3Si^+ adduct. The nonobservable reactions of protonated **1** in Table II for compounds with proton affinities lower than that of acetone were shown to occur in the opposite direction in acetone, base, and Me_3Si^+ mixtures. Since the only plausible silylation site in acetone is on oxygen to produce a structure like **3**, we again conclude that protonation of the silyl enol ether occurs on carbon. Thus all of

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(11) Hendewerk, M. L.; Dixon, D. A., unpublished results.

(12) Reference 10b, p 24.

(13) The value for N-protonation has been calculated to be 18.3 kcal/mol less than that for C-protonation in ref 5. Using the experimental value for the proton affinity of the enamine[4] together with this calculated quantity we obtain the value given here.

(14) Farneth, W. E.; Brauman, J. I. *J. Am. Chem. Soc.* **1976**, *98*, 7891.

(15) The enol of acetone has been shown to be 14 kcal/mol less stable than acetone in the gas phase. Pollack, S. K.; Hehre, W. J. *J. Am. Chem. Soc.* **1977**, *99*, 4845.

(16) Hendewerk, M. L.; Weil, D. A.; Charlier, P. A.; Stone, T. L.; Ellenberger, M. R.; Farneth, W. E.; Dixon, D. A., unpublished work.

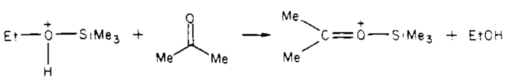
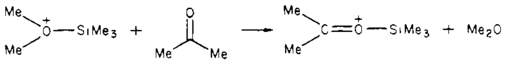
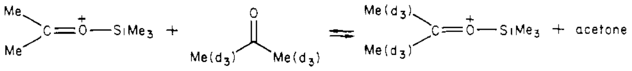
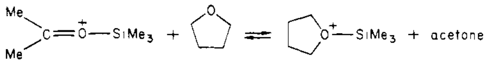
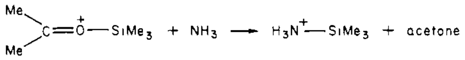
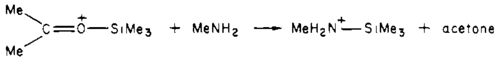
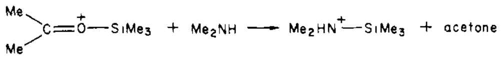
(17) Shea, K. J.; Gobeille, R.; Bramblett, J.; Thompson, E. *J. Am. Chem. Soc.* **1978**, *100*, 1611.

(18) (a) Blair, J. H.; Phillipou, G.; Bowie, J. H. *Aust. J. Chem.* **1979**, *32*, 59. (b) Blair, I. A.; Bowie, J. H. *Ibid.* **1979**, *32*, 1389. (c) Trenerry, V. C., Bowie, J. H.; Blair, I. A. *J. Chem. Soc. Perkin Trans. 2* **1979**, 1640.

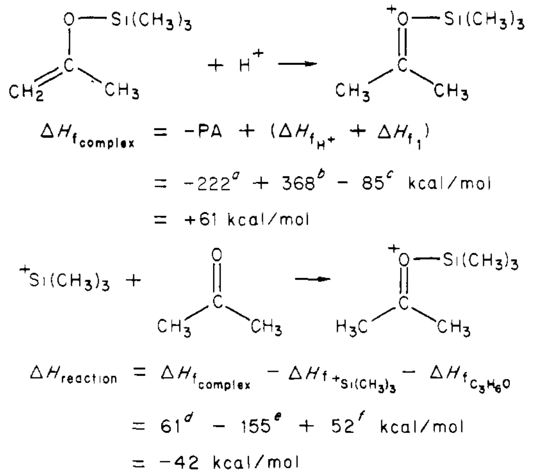
(19) Trenerry, V. C.; Blair, I. A.; Bowie, J. H. *Aust. J. Chem.* **1980**, *33*, 1143.

(20) (a) Bowie, J. H.; *Acc. Chem. Res.* **1980**, *13*, 76. (b) Blair, I. A.; Bowie, J. H.; Trenerry, V. C. *J. Chem. Soc., Chem. Commun.* **1979**, 230.

Table III. Trimethylsilyl Cation Group Transfer Reactions from the Trimethylsilyl Cation-Acetone Adduct

PA(base)[a]	reaction
+14.7	
+11.9	
+7.8	
+5.4	
0.0	
−9.1	
−15.5	

[a] See footnote *a*, Table I.



$$\Delta H_{f_{\text{complex}}} = -PA + (\Delta H_{f_{H^+}} + \Delta H_{f_1})$$

$$= -222^{a} + 368^{b} - 85^{c} \text{ kcal/mol}$$

$$= +61 \text{ kcal/mol}$$

$$\Delta H_{\text{reaction}} = \Delta H_{f_{\text{complex}}} - \Delta H_{f\,^{+}Si(CH_3)_3} - \Delta H_{f_{C_3H_6O}}$$

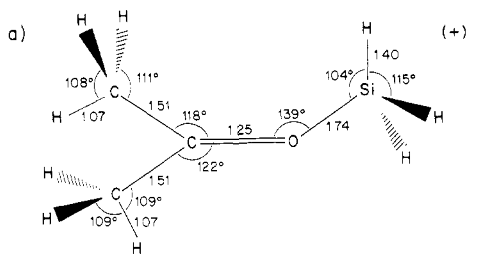
$$= 61^{d} - 155^{e} + 52^{f} \text{ kcal/mol}$$

$$= -42 \text{ kcal/mol}$$

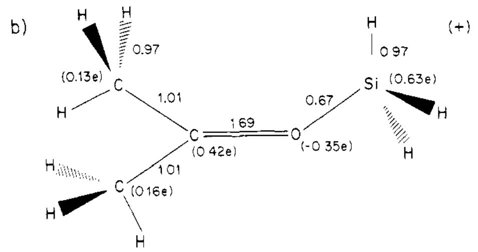
Figure 1. Thermochemical estimate of the energy released in the formation of the adduct of the trimethylsilyl cation and acetone from its two constituents. (*a*) The value is a lower limit (vide infra), based on proton affinity of NH_3 = 206 kcal/mol.[10] (*b*) Bartmess, J. E.; McIver, R. G. In "Gas Phase Ion Chemistry"; Bowers, M. T., Ed.; Academic Press: New York 1979; Vol. 2, p 87. (*c*) From $\Delta H_f(\cdot Si(CH_3)_3)$ (Davidson, I. M. T. *J. Organomet. Chem.* **1979**, *170*, 365), $\Delta H_f(CH_2{=}C(O\cdot)CH_3)$ (Zabel, F.; Benson, S. W.; Golden, D. M. *Int. J. Chem. Kinet.* **1978**, *10*, 295), and average Si–O (B.D.E. Tacke, R.; Wannagat, U. *Top. Curr. Chem.* **1979**, *84*, 1). As calculated above. (*e*) Murphy, M. K.; Beauchamp, J. L. *J. Am. Chem. Soc.* **1977**, *99*, 2085. (*f*) Benson, S. W. "Thermochemical Kinetics"; Wiley; Wiley: New York, 1978.

our data are internally consistent and lead to the conclusion that protonation of **1** occurs at carbon, rather than at oxygen, and that the resulting structure does not have strong carbonium ion character.

An estimate of the heat of formation of **3** can be made from the proton affinity of the silyl enol ether. Since **3** is equivalent to the adduct formed in collisions of acetone with Me_3Si^+, it is also possible to estimate the exothermicity of complex formation. The value of 42 ± 10 kcal/mol calculated in Figure 1 constitutes only a lower limit because of constraints on the proton affinity discussed earlier and uncertainties in the Si–O bond strength. The observation of direct complex formation in ion–molecule collisions at low pressures is relatively rare although it is not unprecedented in silicon chemistry.[21,22] In order for such a direct complex to be observed in an ICR experiment, it must have a lifetime for dissociation to reactants of ≥0.1 ms.[23] Complexes between SiH_3^+ and ethylene have been observed to have long lifetimes (~8 μs)[22] although a rearrangment is postulated. Meot-Ner[24] has shown, for example, that the complex of ethylamine with the *tert*-butyl cation which forms with an exothermicity of 38 kcal/mol has a lifetime ≥10 μs. If one considers the large number of vibrational (and internal rotational) modes available to the acetone–Me_3Si^+



Bond Distances and Angles



Bond Orders and Group Charges

Figure 2. Structure of protonated **1** (and the adduct of trimethylsilyl cation with acetone) as determined by the approximate molecular orbital method, PRDDO. (a) Geometry-optimized structure. Bond distances are in Å. (b) Bond orders and group charges. Bond orders are given as defined in ref 33. Group charges are obtained by adding the charge of a hydrogen to the charge on the adjacent heavy atom to which it is bonded.

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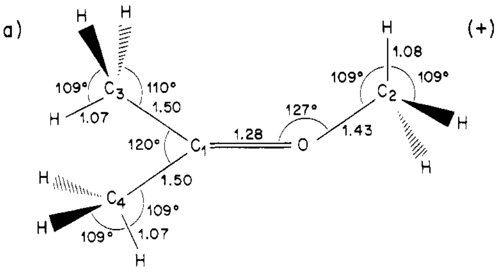
(21) (a) Abernathy, R. N.; Lampe, F. W. *J. Am. Chem. Soc.* **1981**, *103*, 2573. (b) Allen, W. N.; Lampe, F. W. *Ibid.* **1977**, *99*, 6816. (c) Allen, W. N.; Lampe, F. W. *J. Chem. Phys.* **1976**, *65*, 3378.

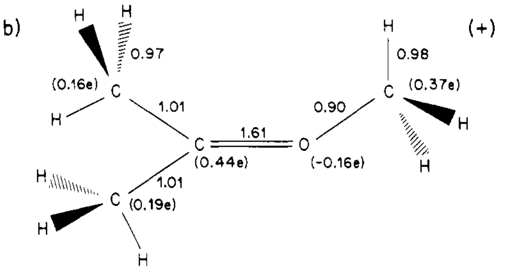
(22) We have observed the complex of the trimethylsilyl cation with acetone at total pressures down to 4×10^{-6} torr in the drift cell for which the time between collisions estimated by using a Langevin cross section is $(2-4 \times 10^{-3}$ s.

(23) This is based on the estimate that a minimum of 10 cycles of the marginal oscillator frequency are needed to observe a peak in the spectrum. A more detailed discussion is given by: Henis, J. M. S. In "Ion Molecule Reactions"; Franklin, J. L., Ed.; Plenum: New York, 1972; Vol. 2, p 395.

(24) Meot-Ner, M. *J. Am. Chem. Soc.* **1979**, *101*, 2389.



Bond Distances and Angles



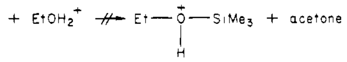
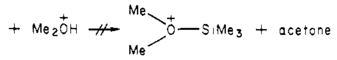
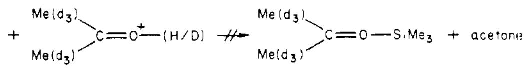
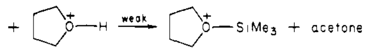
Bond Orders and Group Charges

Figure 3. Structure of the protonated vinyl ether (**6**) as determined by the approximate molecular orbital method, PRDDO. See Figure 2 caption for details. (a) Geometry-optimized structure showing atomic numbering; (b) bond orders and group charges.

complex and postulates rapid energy randomization,[25] a long lifetime to dissociation is not unreasonable.[26]

In order to provide more information about the structure of the Me_3Si^+–acetone complex, we carried out a set of molecular orbital calculations on the adduct of SiH_3^+ with acetone. The calculations were done by using the PRDDO program package.[27,28] The structure was geometry optimized.[29] The geometry, bond orders, and charge distribution are shown in Figure 2. The structure strongly resembles an adduct of SiH_3^+ with acetone and shows significant oxonium character. The C–O distance is slightly longer than that of a double bond (1.22 Å)[30] while the Si–O distance is longer than normal Si–O single bonds (1.60 Å).[31] The C–O–Si angle is significantly larger than 120°. The H–Si–H bond angles are larger than tetrahedral and are quite close to the value of SiH_3^+ (120°). The charge distributions show that most of the positive charge is localized on the SiH_3^+ group (0.63*e*). The oxygen, surprisingly, remains negative while the carbon attached to it carries a canceling positive charge. This is typical of the charge distribution in carbonyl compounds showing the retention of the character of the acetone fragment in the complex.[32] The remaining positive charge is found on the CH_3 groups (~0.15*e* each). The C=O bond has a bond order[33] of 1.67 as compared to a value of 2.0 for a double bond while the bond order of the Si–O bond is only 0.68, much less than that for a single bond. The molecular orbital calculations on this model adduct are in excellent agreement with the experimental results. The theoretical results show that the structure is similar to a polarized acetone (increased polarization of the C=O bond) bonded to SiH_3^+ and that the positive charge is essentially localized on the SiH_3^+ group.

Table IV. Dual Group Transfer Reactions

PA-(base)[a]	reaction
+14.7	**1**  $+ EtOH_2^+ \nrightarrow Et—\overset{+}{O}(H)—SiMe_3$ + acetone
+11.9	**1**  $+ Me_2\overset{+}{O}H \nrightarrow (Me)_2\overset{+}{O}—SiMe_3$ + acetone
+7.8	**1**  $+ (Me(d_3))_2C=\overset{+}{O}—(H/D) \nrightarrow (Me(d_3))_2C=O—SiMe_3$ + acetone
+5.4	**1** 
0.0	**1** $+ NH_4^+ \rightarrow H_3N^+\text{-}SiMe_3$ + acetone
−9.1	**1** $+ MeNH_3^+ \rightarrow MeH_2N^+\text{-}SiMe_3$ + acetone
−12.1	**1** $+ EtNH_3^+ \rightarrow EtH_2N^+\text{-}SiMe_3$ + acetone
−15.4	**1** $+ Me_2NH_2^+ \rightarrow Me_2HN^+\text{-}SiMe_3$ + acetone

[a] See footnote *a*, Table I.

It is appropriate to compare the adduct of acetone and the methyl cation, $(CH_3)_2{}^+COCH_3$ (**6**) with **3**. The heat of formation of **6** has been determined by Lossing[34] to be 114 kcal/mol. This can be combined with a value of −34.9 kcal/mol estimated for ΔH_f of the corresponding vinyl ether from Benson additivity rules[35] to yield a proton affinity of 217 kcal/mol. This value is similar to our lower bound for PA(**1**) of 222 kcal/mol. We have carried out comparable molecular orbital calculations on **6** in order to compare its charge distribution with that of **3**. The optimized geometry for **6** is shown in Figure 3, together with bond orders and the charge distribution. The structure for **6** has a short C–O bond (C_1–O) and a long C–O bond (C_2–O). The latter bond length is that expected for a C—O single bond (1.43 Å) while the shorter C—O bond is intermediate between a C=O (1.22 Å) and a $(C)_2C$—O single bond length of 1.36 Å.[30] The bond order for the C_2–O bond (0.90) is similar to the value of 1.0 expected for a C–O single bond. As expected from this result, the geometry of the methyl group bonded to oxygen is found to be essentially tetrahedral. The bond order for the C_1—O bond (1.61) is significantly smaller than the predicted value of 2.0 for a C=O. The largest positive charge is found on C_1 while the methyl group bonded to oxygen has the next highest charge. The positive charge on C_1 is somewhat higher than that expected from acetone (0.44*e* as compared to 0.25*e*) as is the charge on the oxygen atom which is more positive than the corresponding atom in acetone. Thus although the largest positive charge is found on C_1, the charge is quite delocalized over the entire ion, and the structure of **6** can be viewed as a hybrid of oxonium and carbonium ion structures.

Comparison of the molecular orbital results for **3** and **6** shows some important quantitative differences. For example, (1) the total bond order about oxygen is different in **3** (2.36) as compared to **6** (2.51), (2) the charge difference between the oxygen and the R group (SiH_3 for **3** and CH_3 for **6**) is very different being 0.98*e* in **3** and 0.53e in **6**, (3) the total positive charge on the acetone moiety is higher in **6** (0.63e) than in **3** (0.36e), and (4) the location of the largest amount of positive charge in **3** is on the SiH_3^+ group while in **6** this charge is found on C_1. We conclude that the ion **3** corresponds closely to an adduct of SiH_3^+ with acetone while **6** is best described by a CH_3 group bonded in a normal fashion to oxygen.

As shown in Table IV, a second reaction type is observed to give silylated bases. This involves a simultaneous transfer of a

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(25) Robinson, P. J.; Holbrook, K. A. "Unimolecular Reactions"; Wiley-Interscience: New York, 1972.

(26) We have used the stabilization energy of 42 kcal/mol in an RRK expression for the lifetime $\tau = \omega^{-1}(E/E - E^*)^{S-1}$ where ω is an average frequency (10^{-13} s), E^* is the stabilization energy, E is the total energy, and S is the number of modes available for accommodating the excess energy. We assume that $E = E^* + 5$ kcal/mol and that $S = 0.5(3n - 6)$ where n is the number of degrees of freedom in **3**. The calculated value for τ is 10^{21} s. Although no quantitative significance should be attached to this result, it does suggest that the Me_3Si^+–acetone adduct should be very long lived.

(27) (a) Halgren, T. A.; Lipscomb, W. N. *J. Chem. Phys.* **1973**, *58* 1569. (b) Marynick, D. S., private communication.

(28) The exponents are the molecular STO values recommended by: Hehre, W. J.; Ditchfield, R.; Stewart, R. F.; Pople, J. A. *J. Chem. Phys.* **1970**, *52*, 2769.

(29) The conformation was taken from the optimized structure of the adduct of CH_3^+ and acetone. See below.

(30) Pople, J. A.; Gordon, M. *J. Am. Chem. Soc.* **1967**, *89*, 4253.

(31) Bürger, H. *Fortschr. Chem. Forsch.* **1967**, *9*, 1.

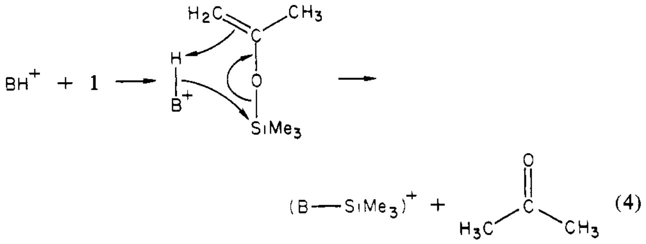
(32) In acetone, the charge on the oxygen is −0.25*e* and the charge on the adjacent, bonded carbon is 0.24*e*.

(33) Armstrong, D. R.; Perkins, P. G.; Stewart, J. P. *J. Chem. Soc., Dalton Trans.* **1973**, 838.

(34) Lossing, F. P. *J. Am. Chem. Soc.* **1977**, *99*, 7526.

(35) Benson, S. W. "Thermochemical Kinetics"; Wiley: New York, 1968.

proton from BH^+ to **1** and the reverse transfer of the trimethylsilyl cation to the base in a single reactive encounter. This single reactive encounter then competes with the two single-step mechanisms discussed previously in the conversion of BH^+ to $B–SiMe_3^+$.

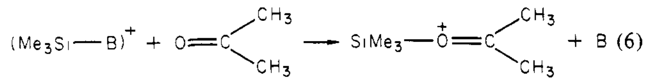


This reaction can be demonstrated by careful double-resonance experiments. The integral area of the double-resonance signal from BH^+ to $B–SiMe_3^+$ is significantly larger than that from **3** to $B–SiMe_3^+$ (and also than that from BH^+ to **3**), indicating that within the timescale window of our ICR experiments a reaction is proceeding from BH^+ to $B–SiMe_3^+$ without passing through the observed **3**. Because of the problems in performing quantitative double-resonance experiments, a double-resonance plus ion ejection experiment was performed. The ion **3** (m/e 131) was ejected in the source region while double resonance from BH^+ to $B–SiMe_3^+$ was performed in the analyzer region. Double resonance from BH^+ to $B–SiMe_3^+$ was still observed even when **3** was not present, confirming the existence of the reaction channel shown in (4). The double-resonance results clearly suggest that $B–SiMe_3^+$ is formed in a single reactive encounter of **1** with BH^+. In most cases the single encounter may be the dominant channel for formation of $B–SiMe_3^+$. There are a number of interesting features to these dual group transfer reactions. Compounds with trimethylsilyl cation affinities below that of acetone, i.e., those for which Me_3Si^+ transfer from **3** is endothermic, do not show this behavior even though the proton transfer from BH^+ to **1** to form **3** is highly exothermic. Even when the Me_3Si^+ transfer from **3** is thermoneutral as it is for acetone, the dual transfer process is not observed. Also, in a reaction for which Me_3Si^+ transfer is slightly favored (B = tetrahydrofuran), only a very weak dual group transfer signal is observed on the basis of double-resonance results. These observations suggest that even though the reactions are overall exothermic, $\Delta SA < \Delta PA$ (SA = Me_3Si^+ affinity), the exoergicity from the proton transfer cannot efficiently drive the Me_3Si^+ transfer. Dual group transfer reactions are observed to proceed only when $PA(\mathbf{B}) < PA(\mathbf{1})$ and $SA(\mathbf{B}) > SA(\text{acetone})$ ($\Delta PA < 0$, $\Delta SA < 0$). Thus, if both half-steps are exothermic the dual group transfer reaction can be observed. We have not observed any dual group transfer processes for the condition $PA(\mathbf{B}) > PA(\mathbf{1})$ and $SA(\text{acetone}) < SA(\mathbf{B})$ ($\Delta PA > 0$, $\Delta SA < 0$). Such an observation is consistent with the reaction being not concerted but proceeding by an ordered two-step process. The intermediate is a complex of **3** and B.

It has been shown that Me_3Si^+ transfer rates are subject to serious steric limitations.[16] A similar type of reaction, the transamination reaction (reaction 5) has not been observed in a drift

$$Me_3Si–^+NMe_2H + Me_3N \rightarrow Me_3Si–^+NMe_3 + NMe_2H \quad (5)$$

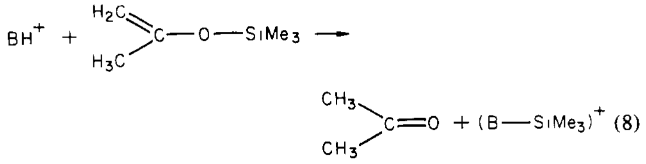
cell by us although it has been observed in a trapped ICR experiment where longer reaction times are available.[17] Similar difficulties in observing Me_3Si^+ transfer to amines have been reported by Bowie.[18-20] It is possible that a similar kinetic effect is operating in the case for $PA(\mathbf{B}) < PA(\mathbf{1})$ and $SA(\mathbf{B}) < SA(\text{acetone})$. This seems unlikely, however, since the reverse reaction is observed.



Tidwell et al.[2] have observed different mechanisms for the acid-catalyzed hydrolysis of *tert*-butyldimethylsilyl vinyl ethers and trimethylsilyl vinyl ethers in solution. For the former compounds, the rate-determining step is suggested to be proton transfer from the base to carbon to form the silylated ketone in accordance with our gas-phase observations. In contrast, the rate-determining step for the latter compounds is either proton transfer to oxygen or simultaneous water attack on silicon combined with proton transfer, i.e.,

$$H_2O + H^+(HA) + ROSiMe_3 \rightarrow ROH + HOSiMe_3 \quad (7)$$

This latter mechanism would not be inconsistent with a mechanism involving single-step dual group transfer followed by attack of H_2O



on $B–SiMe_3^+$. Presumably this mechanism does not occur for the *tert*-butyl substitution due to steric effects involved in the transfer of the now bulky silyl group.

Conclusions

Our studies show that the proton affinity of 2-(trimethylsiloxy)propene (**1**) is at least 16 kcal/mol greater than that for NH_3 in the gas phase. Our results for both proton transfer and trimethylsilyl cation transfer lead us to conclude that protonation occurs at carbon rather than at oxygen leading to an ion that is structurally equivalent to the adduct of Me_3Si^+–acetone. The equivalence of these two structures allows proton affinity data to be used to calculate a stabilization energy of ~42 kcal/mol for the Me_3Si^+–acetone adduct. The structure of **3** (and the adduct) is essentially that of a Me_3Si^+ group attached to acetone. This was confirmed by molecular orbital calculations. Furthermore, our nonobservation of proton transfer from **3** to any base shows a marked kinetic effect on a proton-transfer reaction involving positive ions. It was found that a dual group transfer of a proton from BH^+ to **1** with an accompanying abstraction of Me_3Si^+ by the departing base to form the Me_3Si^+–B adduct and acetone occurs in a single reactive encounter. The latter reaction and the simple proton-transfer reaction are consistent with the observation of two mechanisms for the acid-catalyzed hydrolysis of silyl enol ethers observed in solution.

Acknowledgment. This work was supported in part by a grant from the Graduate School of the University of Minnesota. We thank Patricia Charlier, Regina Frey, and Robert Eades for help in doing the calculations. We thank a referee for suggesting comparing **3** to **6**.

Registry No. **1**, 1833-53-0; **36**, 80754-53-6; **6**, 41798-19-0; $EtOH·H^+$, 18639-79-7; $Me_2O·H^+$, 17009-82-4; $Et_2O·H^+$, 17009-83-5; NH_4^+, 14798-03-9; $(i\text{-}Pr)_2O·H^+$, 17009-86-8; $MeNH_2·H^+$, 17000-00-9; $EtNH_2·H^+$, 16999-99-8; $Me_2NH·H^+$, 17000-01-0; $t\text{-}BuNH_2·H^+$, 22534-19-6; $Me_3N·H^+$, 16962-53-1; $(n\text{-}Pr)_2NH·H^+$, 29384-47-2; $(i\text{-}Pr)_2NH·H^+$, 21445-72-7; $Et_3N·H^+$, 17440-81-2; NH_3, 7664-41-7; $MeNH_2$, 74-89-5; $EtNH_2$, 75-04-7; Me_2NH, 124-40-3; $EtOSiMe_3·H^+$, 80754-54-7; tetrahydrofuran conjugate acid, 27659-93-4; tetrahydrofuran, 109-99-9; dimethyl trimethylsilyl oxonium, 80754-55-8; acetone, 67-64-1; 2-propanone-*1,1,1,3,3,3-d*$_6$, 666-52-4.