Gas-Phase Reactivity of Organosilane Radical Cations. An FT-ICR Study

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The bimolecular reactivity of organosilane radical cations ($RSiMe_3^{\bullet+}$) toward selected bases/nucleophiles (N) has been studied in the gas phase by the FT-ICR technique. The two major reaction pathways are H^+ and Me_3Si^+ transfer, whose branching ratio depends on the features of R and N. The onset for Me_3Si^+ transfer is close to its thermochemical threshold. Deprotonation of ionized benzyltrimethylsilane is unprecedented in solution but is highly efficient in the gas phase when a strong nitrogen base is used, suggesting a potentially useful route to obtain silylated radicals. The kinetic study of a model degenerate reaction suggests that the activation barrier for Me_3Si^+ transfer between oxygen centers is negligible, as observed for the corresponding proton-transfer process.

Introduction

There is a growing interest in the chemistry of organosilane radical cations.[1] In particular, the cleavage of the C−Si bond of organosilane radical cations has been the subject of numerous investigations in recent years.[2] The mechanism of the cleavage reaction, extensively discussed, can conceivably involve a nucleophile-assisted process, with the solvent acting as the nucleophile.[3] Recent studies have indeed suggested that for benzyltrialkylsilane cation radical the cleavage reaction does, in fact, proceed via this mechanism. An extension of these studies to the gas phase is desirable for several reasons. Among them, the lack of a solvent allows one to elucidate the role of selected neutral molecules in the bimolecular reactivity of organosilane radical cations. Valuable information may thus be obtained on a class of reactions of increasing synthetic interest.[4] Furthermore, whereas several gas-phase studies have focused on the unimolecular dissociation of ionized organosilanes and on the ion−molecule reactions of silylenium ions,[5] little is known on the bimolecular reactivity of organosilane cation radicals.[6] In this perspective we became interested in investigating the reactivity of organosilane radical cations ($RSiMe_3^{\bullet+}$) toward selected bases/nucleophiles in the gas phase by the FT-ICR technique.

Experimental Section

Materials. Most of the organosilanes ($RSiMe_3$) used as the precursors of the radical cations and the chemicals used as the neutral reagents were obtained from commercial sources and used without further purification. $C_6H_5CD_2SiMe_3$ and $C_6H_5CH_2CH_2SiMe_3$ were prepared by the reaction of the Grignard reagent from $C_6H_5CD_2Br$ and $C_6H_5CH_2CH_2Br$, respectively, with Me_3SiCl. Methyl fluoride was purchased from Fluorochem Ltd. and ethylene from UCAR Specialty Gases.

Procedure. The FT-ICR experiments were performed on a Bruker Spectrospin Apex TM 47e mass spectrometer equipped with an external ion source and with a cylindrical "infinity" cell of 12 cm length and 6 cm radius located in the bore of a 4.7 T superconducting magnet. The organosilanes were introduced into the ion source in the EI configuration at 2×10^{-6} to 1×10^{-5} mbar (1 mbar = 100 Pa) and ionized by electron impact at 30 eV electron energy, using a 100 ms electron beam pulse and a 10 μA emission current. A few experiments involved the formation of $(CX_3)_2COE^+$ ions (X = H, D; Y = H, $SiMe_3$) in the external ion source. The source was operated in the CI mode at the pressure of ca. 4×10^{-5} mbar. $(CX_3)_2COH^+$ ions were obtained by i-C_4H_8/CI of $(CX_3)_2CO$, and $(CX_3)_2COSiMe_3^+$ ions were formed by the reaction of $(CX_3)_2CO$ with $SiMe_3^+$ in a 20:1 CH_4/Me_4Si mixture.The resultant ion population was transferred into the ICR cell containing a known pressure of the neutral reagent. The ion of interest was selected by broad band selection and quenched of excess internal and translational energy by collisions with Ar, admitted through a pulsed magnetic valve up to the peak pressure of 10^{-5} mbar. After a suitable pumping time, further isolation from all other fragment or product ions was achieved by a soft selective-ejection technique, using low-energy "single shots".

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Table 1. Gas-Phase Reactions of Organosilane Radical Cations ($RSiMe_3^{\bullet+}$) with Selected Neutrals (N)

					product ions (%)		
$RSiMe_3$	N	TMSA[a]	k[b]	eff (%)	Me_{3SiN}^+	NH^+	other
$PhCH_2SiMe_3$	C_2H_4	23.6					
	H_2O	30.1					
	MeOH	39.2	1.0	7	100		
	EtOH	42.0	4.8	32	100		
	Me_2CHOH	43.9	5.7	41	100		
	Me_2CO	45.0	14	74	100		
	AcOEt	48.7	5.5	46	95	5	
	4MP	≈64[c]	18	≈100	33	66	
$PhCH_2CH_2SiMe_3$	EtOH		0.7	5	100		
	Me_2CO		0.6	3	60	40	
	AcOEt		2.3	18	58	42	
	4MP		3.9	22	15	85	
$CH_2CHCH_2SiMe_3$	C_2H_4						
	MeF	30[d]	0.8	5	100		
	H_2O		4.0	22	100		
	MeOH		4.1	26	100		
	EtOH		5.6	37	100		
	Me_2CO		17	85	90	10	
	AcOEt		15	≈100	80	20	
	4MP		20	≈100	25	75	
$PhSiMe_3$	Me_2CO						
	4MP		6.0	33		100	
$CHCCH_2SiMe_3$	Me_2CO		15	75	16	12	$[RSiMe_2N]^+$ 72
	AcOEt		16	≈100	12	25	$[RSiMe_2N]^+$ 63
$CH_2CHSiMe_3$	Me_2CO		3.0	15		100	
	AcOEt		10	67	25	60	$[Me_2SiN]^+$ 15
	4MP		20	≈100		60	$[Me_2SiN]^+$ 30 $[RSiMe_2N]^+$ 10

[a] In kcal/mol. See ref 5c. [b] $\times 10^{10}$ cm^3 s^{-1}. Since the product ions are formed from the ionized organosilane in parallel reactions, the rate constants for their formation processes can be obtained as $k \times$ (%/100). [c] See text. [d] See ref 9.

The selected ion was then allowed to react with the neutral reagent introduced at the pressure of $(1-4) \times 10^{-8}$ mbar by a needle valve from an inlet system at room temperature. The cell was also maintained at the room temperature of 25 °C, which is considered as the effective reaction temperature. Neutral pressures were read from an ion gauge located in front of the turbo pump and calibrated with the reference reaction $CH_4^{\bullet+} + CH_4 \rightarrow CH_5^+ + CH_3^\bullet$, using the value of $k = 1.1 \times 10^{-9}$ molecule^{-1} cm^3 s^{-1} as its rate constant.[7] Pressure readings for each neutral reagent were further corrected utilizing individual response factors.[8]

Kinetic processes were followed by recording relative ion intensities on increasing reaction times. Pseudo-first-order rate constants were obtained from the logarithmic decrease of the reactant ion intensity and were divided by the concentration of the neutral to obtain second-order rate constants. Reported values of second-order rate constants are usually the average of three experiments run at different neutral pressures. The error in the rate constants (ca. ±30%) arises largely from the uncertainty affecting the concentration of the neutral reagent. The product ratio from competitive reaction channels was evaluated from the ion intensities of the product ions extrapolated at initial time, to minimize the interference by possible subsequent reactions.

Results and Discussion

The results concerning the gas-phase reactions of organosilane radical cations with selected neutrals (N), including oxygen nucleophiles and a nitrogen base, 4-methylpyridine (4MP), are summarized in Table 1. A major reaction product involves the transfer of Me_3Si^+ to N to form Me_3SiN^+ as the product ion. Therefore, the neutrals are ordered according to their increasing affinity for the Me_3Si^+ cation (TMSA $= -\Delta H°(1)$), namely, according to the increasing exothermicity for the association reaction.[5c]

$$Me_3Si^+ + N \rightarrow Me_3SiN^+ \tag{1}$$

The TMSA values for a series of oxygen- and nitrogen-containing bases have been reported to obey linear correlations with proton affinity (PA) values, so that the increasing TMSA values listed in Table 1 are paralleled by an increasing PA of N.[5c] The amine correlation has indeed been used to evaluate the TMSA of 4-methylpyridine (4MP). The observed bimolecular rate constants for the decay of the organosilane radical cation normalized by the collisional rate constant yield the reported reaction efficiencies. They measure the fraction of collisions leading to product ions. Most of the organosilane radical cations yield as major ionic products the ones formed by either Me_3Si^+ or proton transfer, as described for the $C_6H_5CH_2SiMe_3^{\bullet+}$ reaction by eqs 2a and 2b, respectively. Only in few cases do other product ions ($RSiMe_2N^+$, Me_2SiN^+) appear from other competitive fragmentation pathways.

$$C_6H_5CH_2SiMe_3^{\bullet+} + N \rightarrow C_6H_5CH_2^\bullet + NSiMe_3^+ \tag{2a}$$

$$\rightarrow C_6H_5CHSiMe_3^\bullet + NH^+ \tag{2b}$$

The overall reactivity trend conforms to an increase of reaction efficiency versus the PA/TMSA of the neutral for most of the ionized organosilanes. Among them, the one that has been most extensively studied in solution is benzyltrimethylsilane (BTS) radical cation. Once formed in solution after chemical, electrochemical, or photoinduced one-electron oxidation, $BTS^{\bullet+}$ is known to undergo exclusively $C-SiMe_3$ bond cleavage.[3] A substantial body of evidence has grown pointing that the

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(8) Bartmess, J. E., Georgiadis, R. M. *Vacuum* **1983**, *33*, 149.

Table 2. Thermochemical Data Related to Gaseous $RSiMe_3^{\bullet +}$ Ions

$R^\bullet$	$TMSA(R^\bullet)^a$ (kcal/mol)	$PA(R^\bullet)^a$ (kcal/mol)
$C_6H_5^\bullet$	58	
$C_6H_5CH_2^\bullet$	31	
$C_6H_5CH_2CH_2^\bullet$	36	
$CH_2CH^\bullet$	35	
$CH_2CHCH_2^\bullet$	16	
$CHCCH_2^\bullet$	15	
$Me_3SiC_6H_4^\bullet$		239
$C_6H_5CHSiMe_3^\bullet$		211
$C_6H_5CHCH_2SiMe_3^\bullet$		≈202
$Me_3SiC_2H_2^\bullet$		216
$Me_3SiCHCHCH_2^\bullet$		197
$Me_3SiCHCCH^\bullet$		196
$Me_3SiCH_2^\bullet$		191

[a] See ref 11.

cleavage reaction occurs by a nucleophilic mechanism with the involvement of a counterion, the solvent itself, or adventitious nucleophiles such as water. A unimolecular cleavage mechanism was considered highly unlikely, involving a barrier of 31 kcal/mol, namely, the value derived from extrapolation of gas-phase data[3c] for the bond dissociation energy (BDE) of the benzylic C−Si bond in $BTS^{\bullet +}$. However, it has been pointed out that an S_N1 mechanism from $BTS^{\bullet +}$ could be feasible since the solution-phase BDE might be considerably less than the gas-phase value.[10] This ambiguity is solved in gas-phase studies where thermochemical data for isolated species may be appropriately used. Accordingly, in the following discussion reference will be made to the data reported in Table 2, where the evaluated BDEs of the R−Si bond in $RSiMe_3^{\bullet +}$ are reported. These values are listed as TMSA of the $R^\bullet$ radical, because they correspond to $\Delta H°(3)$.

$$RSiMe_3^{\bullet +} \rightarrow R^\bullet + Me_3Si^+ \qquad (3)$$

The dissociation of the benzylic C−Si bond in $BTS^{\bullet +}$ is indeed endothermic by 31 kcal/mol. Accordingly, also in the gas phase, where the reported data are correctly applied, $BTS^{\bullet +}$ ions, thermalyzed by unreactive collisions with argon, do not display any tendency to undergo a unimolecular dissociation process according to reaction 3 or other pathways. Instead, they may be expected to undergo Me_3Si^+ transfer to neutrals endowed with a TMSA in excess of 31 kcal/mol, the TMSA value pertaining to the benzyl radical. In agreement with these predictions an onset for the occurrence of a Me_3Si^+ transfer reaction is observed with MeOH, whose TMSA value is significantly above 31 kcal/mol. H_2O, whose TMSA is only 30.1 kcal/mol, is unreactive. A narrower threshold for Me_3Si^+ transfer reactivity is prevented by the lack of neutrals with reported TMSA between H_2O and MeOH. The reaction of $BTS^{\bullet +}$ with 4MP, the strongest base/nucleophile used, shows that proton transfer is favored by a factor of 2 over Me_3Si^+ transfer, the overall reactivity characterized by 100% efficiency. This behavior conforms to the known reactivity of strong nitrogen-bases, especially if sterically hindered, which preferably attack the proton rather than Me_3Si^+ from gaseous silylated arenium ions.[5d] The proton-transfer pathway is, however, unprecedented in the reactivity of $BTS^{\bullet +}$ ions in solution. The benzylic hydrogens were confirmed to be involved in the deprotonation of $BTS^{\bullet +}$, because the labeled species $C_6H_5CD_2SiMe_3^{\bullet +}$ was found to transfer D^+ to 4MP. From a thermochemical standpoint, the acid−base properties of $BTS^{\bullet +}$ have been estimated from $\Delta H_f°$ of the ionized organosilane and $\Delta H_f°$ of the radical that is obtained by deprotonation. The latter values were obtained by group additivity rules, considering a stabilizing contribution of 40 kcal/mol when a Me_3Si group replaces a hydrogen atom. Therefore no specific steric or electronic effect of the Me_3Si group in the radical was taken into account. Thus, for example, a unique value for $\Delta H_f°(Me_3SiC_6H_4^\bullet)$ is reported, irrespective of whether the Me_3Si group is in the ortho, meta, or para position with respect to the radical site. The general assertion that the effect of an α-Me_3Si substituent provides little stabilization to carbon-centered radicals provides a legitimate basis for this approximation.[12] The PA of the $C_6H_5CHSiMe_3^\bullet$ radical, which is observed to be the conjugate base of $BTS^{\bullet +}$ by removal of a benzylic proton, is estimated to be equal to 211 kcal/mol. This relatively high value justifies the occurrence of an efficient proton transfer only when the base is as strong as 4MP. The regioselective removal of the benzylic hydrogens from $C_6H_5CD_2SiMe_3^{\bullet +}$ by 4MP provides an insight into one further important point, namely, the possibility that the ionized silane might isomerize to an alternative structure. $BTS^{\bullet +}$ is the most likely species to rearrange according to the well-known toluene−cycloheptatriene radical cation type of rearrangement.[13] However a toluene−cycloheptatriene rearrangement is known to scramble the H (D) atoms on the aromatic ring and those on the benzylic methylene group. This scrambling is not found in the labeled $BTS^{\bullet +}$ ion. From this negative evidence regarding a rearranged $BTS^{\bullet +}$ we assume that also the other ionized organosilanes that were examined do not undergo structural rearrangements.

The presence of an additional CH_2 in the side chain with respect to $BTS^{\bullet +}$ introduces a quite remarkable change in the reactivity of the organosilane radical cation. Thus, $C_6H_5CH_2CH_2SiMe_3^{\bullet +}$ is characterized by a lower reactivity relative to $BTS^{\bullet +}$ and by a greater ease to undergo proton transfer rather than the Me_3Si^+ transfer reaction, in agreement with the estimated thermochemical parameters shown in Table 2. However,

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(9) Maerker, C.; Kapp, J.; von R. Schleyer, P. In *Organosilicon Chemistry II. From Molecules to Materials*; Auner, N., Weis, J., Eds.; VCH: Weinheim, 1996.

(10) Mella, M.; d'Alessandro, N.; Freccero, M.; Albini, A. *J. Chem. Soc., Perkin Trans. 2* **1993**, 515.

(11) Thermodynamic calculations are based on the ionization energy and $\Delta H_f°$ of organosilanes and $\Delta H_f°$ of the corresponding radicals ($R^\bullet$). Data were taken from: (a) Hunter, E. P.; Lias, S. G. In *NIST Chemistry Webbook, NIST Standard Reference Database Number 69*; Mallard, W. G., Linstrom, P. J., Eds.; National Institute of Standards and Technology: Gaithersburg MD (http://webbook.nist.gov), 1998. (b) Lias, S. G.; Bartmess, J. E.; Liebman, J. F.; Holmes, J. L.; Levin, R. D.; Mallard, W. G. *J. Phys. Chem. Ref. Data* **1988**, *17*, Suppl. 1. For certain organosilanes $\Delta H_f°$ was not available. Calorimetric methods are in fact particularly difficult for organosilicon compounds. In such cases an estimate was obtained by group additivity rules, which is sometimes preferable with respect to experimental data that are not convincing. Cf.: (c) Becerra, R.; Walsh, R. In *The Chemistry of Organic Silicon Compounds*; Rappoport, Z., Apeloig, Y., Eds.; Wiley: New York, 1998; Vol. 2. A $\Delta H_f°(Me_3Si^+)$ value equal to 145 kcal/mol was used, as reported by: Shin, S. K.; Corderman, R. R.; Beauchamp, J. L. *Int. J. Mass Spectrom. Ion Processes* **1990**, *101*, 257.

(12) Bausch, M. J.; Gong, Y. *J. Am. Chem. Soc.* **1994**, *116*, 5963.

(13) (a) Lifshitz, C. *Acc. Chem. Res.* **1994**, *27*, 138. (b) Kuck, D. *Mass Spectrom. Rev.* **1990**, *9*, 187. (c) Harting, N.; Thielking, G.; Grützmacher, H.-F. *Int. J. Mass Spectrom. Ion Processes* **1997**, *167/168*, 335.

the major reactivity difference regards the occurrence of a homolytic reaction pathway. A number of reactivity pathways of radical cations have been described in recent years.[2a] Most of them are not displayed by gaseous $RSiMe_3^{\bullet+}$ ions. For example, in no instance was a nucleophilic addition of the selected neutrals ever observed, although the Me_3Si^+ transfer reaction might in principle occur by way of a transient $[RSiMe_3N^{\bullet+}]$ adduct. A homolytic bond cleavage process has been recently demonstrated to occur in alkylaromatic radical cations.[14] Therefore, both $BTS^{\bullet+}$ and $C_6H_5CH_2CH_2SiMe_3^{\bullet+}$ have been tested in the search of any $H^\bullet$ or $Me_3Si^\bullet$ transfer reaction. The odd-electron species NO_2 and NO have been used as neutral reagents in the FT-ICR cell. $BTS^{\bullet+}$ proved to be unreactive, but $C_6H_5CH_2CH_2SiMe_3^{\bullet+}$ was found to undergo a $H^\bullet$ abstraction process, conceivably leading to $C_6H_5CHCH_2SiMe_3^+$ ions (eq 4).

$$C_6H_5CH_2CH_2SiMe_3^{\bullet+} + NO_{(2)}^{\bullet} \xrightarrow[5-7\%]{\text{eff}} C_6H_5CHCH_2SiMe_3^{+} + [HNO_{(2)}] \quad (4)$$

The driving force of this reaction should be ascribed to the high stability of the product ion which may benefit from the conjugative interaction of the vacant orbital on the positively charged carbon with both the phenyl ring and the Si−C bond in β-position, the so-called β-effect exerted by the silyl group.[15]

Ionized allyltrimethylsilane is unreactive toward C_2H_4 despite a TMSA of the allyl radical that is estimated to be 16 kcal/mol, so that Me_3Si^+ transfer is predicted to be exothermic. The onset for Me_3Si^+ transfer is observed with MeF (TMSA = 30 kcal/mol).[9] The reason for this result may be bound either to an activation barrier for Me_3Si^+ transfer which is thus not simply governed by the reaction thermochemistry or to gross uncertainties in the TMSA values of the $R^\bullet$ radicals, derived from ΔH_f° of ionized organosilanes, known to be affected by possibly large errors.[11] Proton transfer becomes a competitive pathway with Me_3Si^+ transfer also with neutrals less basic than 4MP, such as Me_2CO and AcOEt. These neutrals are endowed with PA values close to or in excess of 197 kcal/mol,[11] the estimated PA of $CH_2CHCHSiMe_3^\bullet$.

The phenyl radical is predicted to have the highest TMSA values among the $R^\bullet$ radicals from ionized $RSiMe_3$, paralleled by a high PA value of the $Me_3SiC_6H_4^\bullet$ radical, according to thermochemical estimates. As a result, ionized phenyltrimethylsilane is the least reactive among $RSiMe_3^{\bullet+}$, reacting only by proton transfer to 4MP with less than 100% efficiency. In view of the high basicity of a silyl-substituted phenyl radical, markedly higher than that of $Me_3SiCH_2^\bullet$, it is likely that the proton is abstracted from a methyl group of the Me_3Si substitutent.

Ionized propargyltrimethylsilane and vinyltrimethylsilane react to a certain extent by proton transfer with few selected neutrals with appropriate PA, the proton possibly arising from the Me_3Si group. When the attack occurs at silicon, the $C-SiMe_3$ cleavage competes with other reaction pathways.

In the foregoing discussion the accent was stressed on the thermochemistry of competing pathways, implying that this factor was paramount in determining reactivity. This assertion is justified by the notion that ion−molecule reactions that are favored on thermodynamic grounds are generally fast in the gas phase, their rates limited by the collision frequency. However, when substantial activation barriers are involved, combined with a relatively small ion−neutral association energy, and/or in the presence of unfavorable entropic factors, an ion−molecule reaction may be characterized by a low efficiency even if thermochemically favorable. Such a condition appears to hold in the Me_3Si^+ transfer reaction displayed by ionized organosilanes. In fact, although a relatively large uncertainty may be attached to the estimated TMSA values of the $R^\bullet$ radicals, it appears that the efficiency of Me_3Si^+ transfer reactions may be well below 100% even when the reaction is substantially exothermic. This finding prompted us to ascertain whether the slow kinetics were a common feature of Me_3Si^+ transfer reactions in the gas phase or whether they regarded the specific systems under investigation where Me_3Si^+ departs from an organic radical. Moreover, on considering the exclusive Me_3Si^+ transfer undergone by $BTS^{\bullet+}$ in solution and the competing pathways 2a,b observed in the gas phase, the question arises as to whether proton or Me_3Si^+ transfer might be intrinsically faster under otherwise identical conditions. To this end, FT-ICR experiments have been performed to probe the efficiency of thermoneutral reactions of proton and Me_3Si^+ transfer. The reactions of $(CH_3)_2COE^+$ (E = H, Me_3Si) with $(CD_3)_2CO$ are degenerate (eqs 5, 6), if allowance is made for the d_3-labeled methyl groups of $(CD_3)_2CO$. The efficiency of E^+ transfer is ca. 35%. The same value within experimental error is obtained for both H^+ and Me_3Si^+ transfer, to be compared with the uppermost 50% value allowed for these nearly degenerate reactions.[16]

$$(CH_3)_2COH^+ + (CH_3)_2CO \xrightarrow[35\%]{\text{eff}} (CH_3)_2CO + (CD_3)_2COH^+ \quad (5)$$

$$(CH_3)_2COSiMe_3^+ + (CD_3)_2CO \xrightarrow[35\%]{\text{eff}} (CH_3)_2CO + (CD_3)_2COSiMe_3^+ \quad (6)$$

The same efficiency was obtained in mirror experiments where $(CD_3)_2COE^+$ (E = H, Me_3Si) was reacted with $(CH_3)_2CO$. The similarly high efficiencies for both H^+ and Me_3Si^+ transfer suggest that both processes involve negligible activation barriers and that kinetic factors are not likely to affect the competition between H^+ and Me_3Si^+ transfer between small molecules adding E^+ to a lone pair, when other factors are held constant. This observation confirms the recognized ease of Me_3Si^+ transfer, accordingly described as "super proton".[17]

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(14) Baciocchi, E.; Del Giacco, T.; Elisei, F.; Lanzalunga, O. *J. Am. Chem. Soc.* **1998**, *120*, 11800.

(15) (a) Lambert, J. B.; Zhao, Y.; Emblidge, R. W.; Salvador, L. A.; Liu, X.; So, J.-H.; Chelius, E. C. *Acc. Chem. Res.* **1999**, *32*, 183. (b) Chiavarino, B.; Crestoni, M. E.; Fornarini, S. *J. Am. Chem. Soc.* **1998**, *120*, 1523, and references therein.

(16) The 35% efficiency for thermoneutral proton transfer between protonated acetone and neutral acetone is reminiscent of the 25%−35% efficiency for the proton transfer between CH_3O^- and CH_3OH. A discussion of the reasons that may account for the discrepancy with the expected 50% value and a model of the reaction are presented in: Jasinski, J. M.; Brauman, J. I. *J. Am. Chem. Soc.* **1980**, *102*, 2906.

(17) Fleming, I. *Chem. Soc. Rev.* **1981**, *10*, 83.

Similar conclusions have been drawn from a flowing-afterglow study of the trimethylchlorosilane reaction with negatively charged nucleophiles.[18] Exothermic reactions were found to occur at the collision rate, only the rate of the thermoneutral reaction of $^{37}Cl^-$ being less than the collision rate. The detection of moderate amounts of a stable adduct suggested a pentacoordinate silicon anion to be a reaction intermediate, according to an addition−elimination pathway. The same mechanism may operate also in the positive ion reaction of Me_3Si^+ transfer between neutral molecules, although a concerted mechanism is also conceivable. The negligible activation energy barriers involved in Me_3Si^+ transfer, at least between oxygen-based nucleophiles, and the pronounced thermodynamic drive for the nucleophilic attack at Si by O- or halogen-based nucleophiles are largely responsible for the overwhelming Me_3Si^+ transfer reactivity displayed by organosilane radical cations such as $RSiMe_3^{\bullet+}$ ($R = C_6H_5CH_2$, CH_2CHCH_2) in solution. The same factors account for the minor role that stereoelectronic effects appear to play in the benzylic C−Si bond cleavage.[19] In view of these factors it is not surprising that the silyl group has been found to rank in the first position in experimental electrofugacity scales of leaving cations.[4,20] It should be noted, however, that the similar kinetic behavior of H^+ transfer and Me_3Si^+ transfer, as shown by the negligible activation barrier for the thermoneutral reaction with acetone, may also imply that energy or entropy barriers may appear when the Me_3Si^+ transfer involves electronic reorganization or steric hindrance, as it is well documented in gas-phase H^+ transfer reactions.[16,21] Such factors may well affect the observed reactivity of gaseous $RSiMe_3^{\bullet+}$.

Conclusions

The gas-phase reactivity of organosilane radical cations with selected neutrals has revealed distinctive features with respect to their chemistry in solution. Oxygen nucleophiles react with $RSiMe_3^{\bullet+}$ by a prevailing Me_3Si^+ transfer pathway, characterized by efficiencies that may be fairly high, up to the collision limit. The onset for the appearance of Me_3Si^+ transfer is close to the thermochemical threshold, although the available data regarding silylated ions and neutrals are rather scattered and affected in many cases by large uncertainties. The nearly degenerate Me_3Si^+ transfer between $(CH_3)_2COSiMe_3^+$ and $(CD_3)_2CO$ in the FT-ICR cell does not display any sizable activation energy barrier, a condition that may not hold when an oxygen nucleophile attacks at silicon from $RSiMe_3^{\bullet+}$ in a thermoneutral or mildly exothermic reaction. A proton transfer reaction starts to occur with increasingly strong bases/nucleophiles, as the PA of N rises more steeply than its TMSA does. A strong nitrogen base such as 4MP reacts efficiently by H^+ transfer with $RSiMe_3^{\bullet+}$, yielding an α-silylated radical as the neutral product. This reactivity behavior suggests a potential reagent to be tested to obtain silylated radicals in solution. For example, the formation of α-trimethylsilylbenzyl radicals has been reported in 3-methylpentane glass by UV photolysis of BTS.[22]

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