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Gas phase reactivity of aromatic silanes. The reaction of $Ph(CH_2)_xSiMe_3$ ($x = 0$ or 1) with cationic electrophiles

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Abstract

The reactivity of BTS ($x = 1$) and PTS ($x = 0$) towards charged electrophiles has been studied in the gas phase with the aim of assessing the activating and directive properties of the $Me_3Si(CH_2)_x$ group in a solvent-free environment. BTS is confirmed to be highly activated towards electrophilic attack, which is directed to the *ortho/para* positions, consistent with a PA value of 200 ± 1 kcal mol^{-1}. *Ipso* attack followed by desilylation is a dominant pathway in the reactions of PTS, tending to obscure its intrinsic reactivity. However, the reaction of a mild methylating agent, Me_2Cl^+, yields a meaningful reactivity scale: BTS > *p*-xylene > PTS > toluene.

Key words: Silane; Gas phase; Ion cyclotron resonance; Radiolysis

1. Introduction

The reactivity of aromatic compounds bearing a R_3Si group is of considerable interest, in view of the mildness of silicon as a metal and of its dichotomous electron donor/acceptor properties [1]. The reactivity of silylated compounds, however, may be rather sensitive to specific interactions between the R_3Si group and the solvent, both in the ground and the transition state of the reaction of interest. This is especially true of ionic reactions, typically run in solvents of high dielectric constant, characterized by the presence of one or more atoms of highly electronegative elements, such as F, O, and Cl. These have a high affinity towards silicon, as shown by the higher Si–X covalent bond strengths, compared to the corresponding C–X bond strengths [2]. This is responsible for specific solvation interactions, masking the inherent reactivity properties of silicon compounds. In order to overcome these problems, which affect to an appreciable if variable extent all reactivity studies carried out in the condensed phase, the reactivity of certain aromatic silicon compounds has been investigated in the gas phase.

Compounds of the general type $ArSiMe_3$ (Ar = phenyl or tolyl) undergo a facile desilylation process upon protonation or alkylation by gaseous cations such as CH_5^+, $C_2H_5^+$, i-$C_3H_7^+$, t-$C_4H_9^+$, and $(CH_3)_2F^+$ [3]. This remarkably easy acid-induced desilylation reaction is well documented in solution, where it occurs by nucleophilic assistance [4]. However, it is a nuisance if one is interested in ascertaining the activating and directive effects in the primary step of electrophilic attack on the aromatic ring of $ArSiMe_3$. We have undertaken a study of the gas-phase reactivity of ionic electrophiles towards $PhCH_2SiMe_3$ (benzyltrimethylsilane, BTS), which displays the intrinsic electronic effects played by the Me_3SiCH_2 group in an electrophilic aromatic substitution reaction. The reactivity of BTS has been compared to that of $PhSiMe_3$ (phenyltrimethylsilane, PTS) under conditions which minimize

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undesired desilylation of the latter. In all cases, the reactions were run at relatively high pressure (*ca.* 1 atm), as required to obtain meaningful kinetic information using the well established radiolytic technique [5]. The study has been combined with a FT-ICR investigation of the major ionic processes occurring in gaseous mixtures of BTS and various reactant gases at pressures in the range of 10^{-6}–10^{-7} Torr, which provided support for some of the proposed reaction sequences.

2. Experimental section

2.1. Materials

The gases were research grade samples from Matheson Co., whose stated purity exceeded 99.9 mol%, and were used without further purification. The chemicals were obtained from commercial sources or prepared according to standard procedures. When appropriate, their identity was established by NMR and mass spectrometry and their purity checked by GC.

2.2. Radiolytic experiments

The gaseous samples were prepared using standard vacuum procedures. Pyrex vessels (135 ml), equipped with a side arm ending with a breakable seal, were thoroughly outgassed and filled with the gaseous components in the required ratio. Components which are liquid at ordinary conditions, *e.g.* the substrates BTS and PTS, had been previously introduced into the vessel in sealed fragile glass ampoules. After sealing off the Pyrex vessel, the ampoules were broken and thus emptied of their contents by shaking them against the walls of the vessel. The contents vaporized. The resultant gaseous mixtures were irradiated in a 220 Gammacell (Nuclear Canada Ltd.) at 40°C, to a total dose of 10^4 Gy, at a dose rate of 5×10^3 Gy h^{-1}. The radiolytic products mixture was extracted by freezing the vessel at 77 K and washing its inner walls with ethyl acetate, injected through a rubber septum tightly connected to the side arm, whose fragile seal was thus opened under airtight conditions. After repeated freeze-thaw cycles, the final solution was analyzed by GC-MS using the following columns mounted in a Hewlett Packard 5890 A gas chromatograph equipped with a Model 5970 B mass selective detector: (i) a 50 m 0.2-mm i.d. fused silica column coated with a 0.5-μm cross-linked methylsilicone film (PONA column from Hewlett Packard) operated isothermally (2 min) at 60°C and then heated at the rate of 5° min^{-1} to 120°C and subsequently at 15° min^{-1} to 200°C; (ii) a 60 m 0.25-mm i.d. fused silica column coated with a 0.25-μm film of 20% diphenyl-, 80% dimethylpolysiloxane (SPB-20 column from Supelco Co.) operated at 100°C (5 min) and then heated at the rate of 10° min^{-1} to 120°C and at 15° min^{-1} to 220°C; (iii) a 30 m, 0.2-mm i.d. fused silica column coated with a 0.2-μm film of cross-linked polyethylene glycol (Supelcowax 10 column from Supelco Co.) operated at 65°C (2 min) and then heated at the rate of 4° min^{-1} to 120°C and at 15° min^{-1} to 200°C. The identity of the isomeric products from alkylation of BTS and PTS has been checked by comparison of their retention times and EI mass spectra with those of authentic samples under the same operating conditions. The amounts of the products formed were determined from the areas of the corresponding elution peaks using the internal standard calibration method.

The ^1H and ^2H NMR spectra were recorded on a Bruker AMX 600 spectrometer.

2.3. ICR experiments

ICR specra were performed on a Nicolet FT-MS 1000 spectrometer with a 2.0 T superconducting magnet and with a 2.54 cm cubic cell. Sample pressures (uncorrected) were measured with a Granville-Phillips 280 Bayard-Alpert ion gauge.

3. Results

3.1. FT-ICR mass spectrometry

The 70 eV electron impact mass spectrum of BTS, 3.7×10^{-7} Torr, is characterized by the following ions: *m/z* 164 ($[M]^{+\cdot}$, 30% relative intensity); *m/z* 149 ($[M - Me]^+$, 10%); *m/z* 121 (10%); *m/z* 73 ($[Me_3Si]^+$, 100%). Some of these ions react with BTS, as shown in the FT-ICR spectrum taken after a 100 ms reaction time (Fig. 1), where the relative abundance of ions at *m/z* 73 decreases; the abundance of ions at *m/z* 149 increases. At longer reaction times, a decrease of the abundance of ions at *m/z* 149 corresponds to the

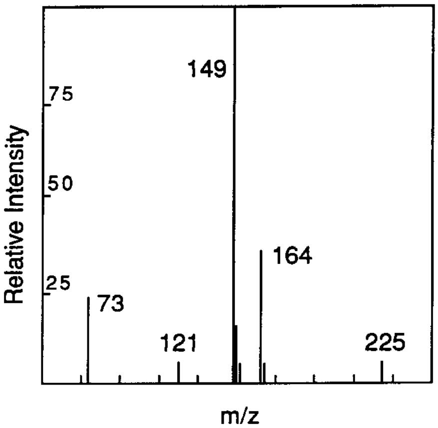


Fig. 1. ICR mass spectrum of BTS, 3.7×10^{-7} Torr, taken after 70 eV EI ionization and a 100 ms reaction time.

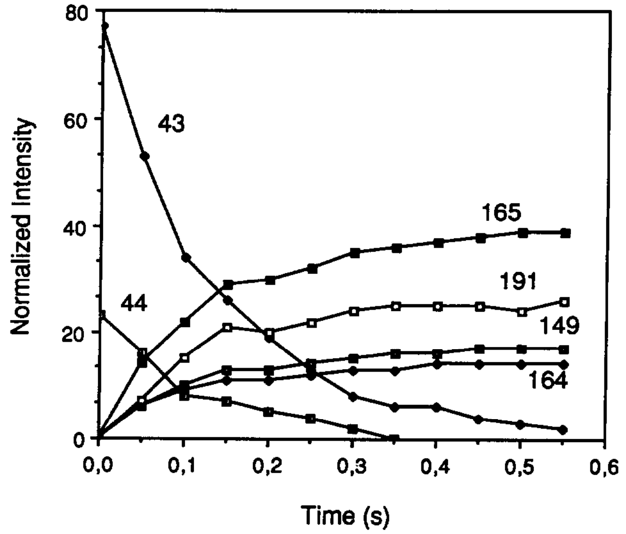


Fig. 2. Time-dependence of normalized intensities of major ions observed after an ionizing pulse in a C_3H_8/BTS (8:1) mixture at 4.5×10^{-7} Torr.

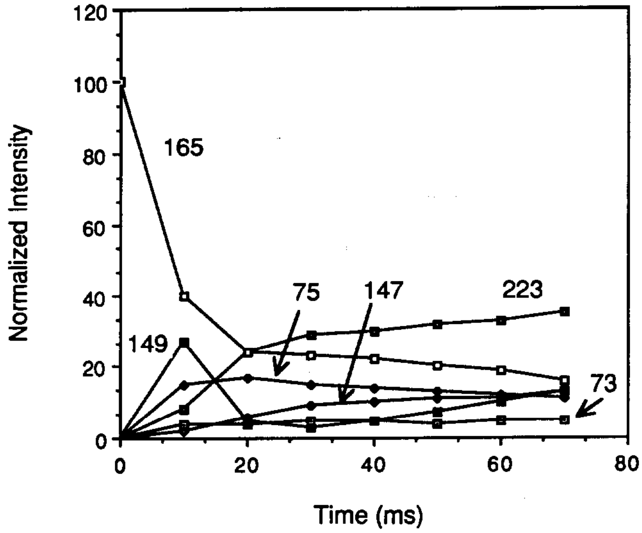


Fig. 3. Time dependence of normalized intensities of major ions observed after an ionizing pulse in a Et_2O/BTS (1.5:1) mixture at 5×10^{-7} Torr, after triple resonance selection of ions at *m/z* 165 ($BTSH^+$).

appearance of ions at *m/z* 225. The dependence of the ion intensities on the reaction time suggests that reactions (1) and (2) are taking place, driven by the higher stability of more heavily substituted silylenium ions.

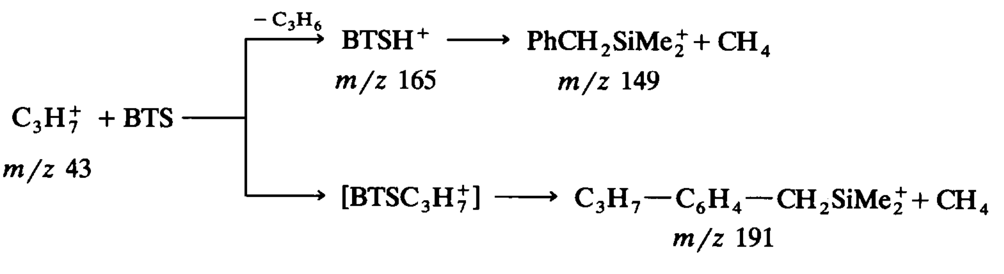
$$\underset{m/z\ 73}{Me_3Si^+} + BTS \longrightarrow \underset{m/z\ 149}{PhCH_2SiMe_2^+} + Me_4Si \qquad (1)$$

$$PhCH_2SiMe_2^+ + BTS \longrightarrow \underset{m/z\ 225}{(PhCH_2)_2SiMe^+} + Me_4Si \qquad (2)$$

The molecular ion at *m/z* 164 is apparently unreactive towards BTS.

The reactivity of protonated BTS has been investigated by admitting a second gas, C_3H_8, into the ICR cell. In this gaseous mixture, $C_3H_7^+$ ions from propane promoted both protonation and alkylation of neutral BTS (Fig. 2). The ions at *m/z* 165, corresponding to $BTSH^+$, may fragment in part to *m/z* 149 by loss of CH_4 allowed by the exothermicity of the protonation process. The alkylation pathway again involves loss of a CH_4 molecule, the exothermicity of the $C_3H_7^+$ attack preventing the observation of an addition product. This reaction should proceed by alkylation of the phenyl ring to yield ions at *m/z* 191, of the probable structure shown in eqn. (3b). The odd-electron ions at *m/z* 42 and 44 from the EI ionization of propane react with BTS by charge exchange, forming $BTS^{+\cdot}$ ions which fragment in part by losing a methyl radical.

The protonation of BTS may also be effected by milder acids, *e.g.* the fragment ions from the EI ionization of Et_2O and ^iPrOH. In gaseous mixtures of BTS and Et_2O or ^iPrOH, the reactivity of $BTSH^+$ may thus be observed. The reaction of $BTSH^+$ ions, selected by triple resonance pulse sequences, with Et_2O (Fig. 3) occurs by two major pathways, the first (4a) involving proton transfer and the second (4b) involving Me_3Si^+ transfer. Whereas the intensity of silylated product ions at *m/z* 147 shows a steady increase with time, the abundance of protonated ions Et_2OH^+ at *m/z* 75 parallels the gradual depletion of $BTSH^+$ after an initial rise. In addition, in the mirror experiment of triple resonance selection of Et_2OH^+ ions, their reaction with BTS leads to stationary concentrations of the two protonated species for fairly long times. This sets the proton affinity (PA) value of BTS equal to 200 ± 1



$$\underset{m/z\ 43}{C_3H_7^+} + BTS \xrightarrow{-C_3H_6} \underset{m/z\ 165}{BTSH^+} \longrightarrow \underset{m/z\ 149}{PhCH_2SiMe_2^+} + CH_4 \qquad (3a)$$

$$\underset{m/z\ 43}{C_3H_7^+} + BTS \longrightarrow [BTSC_3H_7^+] \longrightarrow \underset{m/z\ 191}{C_3H_7{-}C_6H_4{-}CH_2SiMe_2^+} + CH_4 \qquad (3b)$$

$$\mathrm{BTSH^+} \xrightarrow{+\mathrm{Et_2O}} \underset{m/z\ 75}{\mathrm{Et_2OH^+}} + \mathrm{BTS} \qquad (4a)$$

$$\mathrm{BTSH^+} \xrightarrow{+\mathrm{Et_2O}} \underset{m/z\ 147}{\mathrm{Et_2OSiMe_3^+}} + [\mathrm{C_7H_8}] \qquad (4b)$$

$$\mathrm{BTSH^+} \xrightarrow{-\mathrm{CH_4}} \underset{m/z\ 149}{\mathrm{PhCH_2SiMe_2^+}} \xrightarrow{+\mathrm{Et_2O}} \underset{m/z\ 223}{[\mathrm{PhCH_2SiMe_2^+ \cdot Et_2O}]} \qquad (4c)$$

TABLE 1. Gas phase reactions of $Ph(CH_2)_xSiMe_3$ (x = 0 or 1) with charged electrophiles

System composition (Torr) [a]			Ionic reactant(s)	Product yields (G_{+M}) [b]		
$Ph(CH_2)_xSiMe_3$	Bulk gas	Additives		$RC_6H_4(CH_2)_xSiMe_3$ ($o:m:p$)	Toluene	Others
x = 1, 0.23	D_2, 590		D_3^+, R = D	n.d. [c]	0.060	
x = 1, 0.27	D_2, 650 CD_4, 50		CD_5^+, R = D	0.24 (66:12:22)	0.080	
x = 1, 1.2	CH_4, 690		CH_5^+, $Et^+ = R^+$	0.039 (41:24:35)	0.075	$PhCH_2Et$, 0.0026 $PhCH_2Si(OH)Me_2$, 0.018
x = 1, 0.51	CH_4, 180		CH_5^+, $Et^+ = R^+$	0.14 (41:26:33)	0.19	$PhCH_2Et$, 0.0052 $PhCH_2Si(OH)Me_2$, 0.018
x = 1, 2.1	CH_4, 680	^iPrOH, 1.4	CH_5^+, $Et^+ = R^+$	0.027 (40:25:35)	0.0047	$PhCH_2Si(O^iPr)Me_2$, 0.0049 $^iPrC_6H_4CH_2SiMe_3$, 0.016
x = 1, 1.3	CH_4, 670	PhMe, 1.6 TEA, 0.54	CH_5^+, $Et^+ = R^+$	0.011 (40:27:33)		$Et\text{-}C_6H_4Me$, 0.019 (42:33:25) [d]
x = 1, 1.3	C_3H_8, 690		$^iPr^+ = R^+$	0.12 (47:24:29)	0.028	$^iPr\text{-}C_6H_4Me$, 0.0052 (47:25:28)
x = 1, 1.8	C_3H_8, 650	TEA, 0.88	$^iPr^+ = R^+$	0.085 (44:25:31)	0.0021	
x = 1, 1.6	C_3H_8, 690	^iPrOH, 1.1	$^iPr^+ = R^+$	0.076 (46:24:30)	0.0026	
x = 1, 1.6	C_3H_8, 640	TEA, 1.1 ^iPrOH, 0.95	$^iPr^+ = R^+$	0.068 (47:25:28)	2.3×10^{-4}	
x = 1, 2.4	C_3H_8, 650	TEA, 1.3 ^{c}Hexanone, 1.4	$^iPr^+ = R^+$	0.064 (43:26:31)	1.6×10^{-4}	
x = 1, 1.5	C_3H_8, 700	PhMe, 1.6 TEA, 0.54	$^iPr^+ = R^+$	0.074 (46:26:28)		$i\text{-}C_3H_7\text{-}C_6H_4Me$, 0.090 (46:24:30) [d]
x = 1, 1.4	$i\text{-}C_4H_{10}$, 650		$Me_3C^+ = R^+$	0.15 (0:6:94)	0.014	
x = 1, 1.0	$i\text{-}C_4H_{10}$, 650	PhMe, 1.1	$Me_3C^+ = R^+$	0.13 (0:3:97)		$^tBu\text{-}C_6H_4Me$, 0.090 (0:12:88) [d]
x = 1, 1.0	$i\text{-}C_4H_{10}$, 700	PhMe, 1.0 Pyridine, 2.3	$Me_3C^+ = R^+$	0.060 (0:4:96)		$^tBu\text{-}C_6H_4Me$, 0.040 (0:5:95) [d]
x = 1, 1.4	MeF, 700		Me_2F^+, R = Me	0.20 (50:17:33)		
x = 1, 1.6	MeF, 680	PhMe, 1.6 TEA, 0.54	Me_2F^+, R = Me	0.057 (47:18:35)		$Me\text{-}C_6H_4Me$, 0.044 (51:26:23) [d]
x = 1, 1.6	MeCl, 690	p-Xylene, 1.3	Me_2Cl^+, R = Me	0.017 (67:9:24)		1,2,4-$Me_3C_6H_3$, 0.0038 [e]
x = 0, 0.79	$i\text{-}C_4H_{10}$, 700	PhMe, 0.91 Pyridine, 3.9	$Me_3C^+ = R^+$	0.030 (0:63:37)		$Me_3C\text{-}C_6H_5$, 0.0013 $Me_3C\text{-}C_6H_4Me$, 0.024 (0:6:94) [d]
x = 0, 1.9	MeF, 720	PhMe-d_8, 1.1	Me_2F^+, R = Me	0.042 (14:72:14)	0.012 (C_7H_8)	$Me\text{-}C_6D_4CD_3$, 0.034 (44:23:33) [d]
x = 0, 1.6	MeCl, 700	p-Xylene, 0.72	Me_2Cl^+, R = Me	0.0012 (14:64:22)	0.0067	1,2,4-$Me_3C_6H_3$, 0.012 [e]

[a] All systems contain O_2 (10 Torr) as radical scavenger. [b] Units: μmol J^{-1}. [c] Not determined. [d] From the reaction of PhMe. [e] From the reaction of p-xylene.

kcal mol^{-1}, confirmed with the reference bases, dimethylcarbonate and cyclohexanone.

This PA value suggests that BTS is a stronger base than ^{i}PrOH (PA = 191.2 kcal mol^{-1}) [6] consistent with the observation that no proton transfer is observed from $BTSH^+$ to *i*-PrOH in a 2:1 mixture of ^{i}PrOH and BTS at 9×10^{-7} Torr, although the trimethylsilylation pathway leading to $^{i}PrO(H)SiMe_3^+$ ions is still efficient and leads to complete consumption of $BTSH^+$. In contrast, the reaction of $BTSH^+$, obtained from protonation of BTS by $C_3H_7^+$ ions in a gaseous mixture of BTS/propane/triethylamine (TEA) in 6:3:1 molar ratio at 1×10^{-6} Torr, occurs mainly by proton transfer to TEA, only very tiny amounts of $TEASiMe_3^+$ being formed. Such behaviour stems from the high basicity of TEA (PA = 232.3 kcal mol^{-1}) [6] in conjunction with its poor nucleophilicity due to steric hindrance, that has been taken advantage of to effect deprotonation rather than desilylation of intermediate arenium ions [7].

3.2. Radiolytic reactions

The reactions have been carried out at 40°C, at pressures ranging from 180 to 700 Torr. The composition of the irradiated systems, the absolute yields and the isomeric composition of products are listed in Table 1. The absolute yields of products are given by their G_{+M} values, affected by somewhat large errors, related to the precise knowledge of the irradiation dose and to the possible presence of spurious bases/nucleophiles which may compete with the substrate for the ionic reactant, either present as minor impurities in the bulk gas or formed from its radiolysis. Nevertheless, the overall G_{+M} values of radiolytic products formed in the absence of added bases typically vary from 0.13 to 0.35 μmol J^{-1}.

This shows that the observed products derive from major reaction pathways of the reactant ion(s) of interest, because its G_{+M} is *ca.* 0.3 μmol J^{-1}, under the experimental conditions adopted. The composition of the gaseous systems is dictated by the need to produce the desired reactant ions by known ion-molecule reaction sequences triggered by the ionizing radiation, with the least interference by the substrate and occasional additives which are therefore introduced in less than 1 mol% with respect to the bulk gas. The ionic reactants, also listed in Table 1, may dispose of any excess of energy content by unreactive collisions with the bulk gas prior to reactive encounter with the substrate molecule. The expected role of additives is as follows: (i) oxygen is introduced in all experiments as a hydrogen and alkyl radical scavenger to inhibit possible radical contributions to the observed products; (ii) oxygen bases, ^{i}PrOH and cyclo-hexanone, are expected to behave as desilylating agents on the basis of the above ICR evidence and of previous mass spectrometric and radiolytic studies on silylated arenium ions [7,8]; (iii) TEA and pyridine are strong nitrogen bases which should enable fast deprotonation of ionic intermediates; (iv) toluene has been used as a reference substrate to establish relative reactivities, replaced by *p*-xylene in the reaction with Me_2Cl^+ because of its poor reactivity with this reagent.

The reaction of BTS with cationic electrophiles yields mainly two types of product, the first deriving from a "normal" electrophilic aromatic substitution reaction, with a ring proton finally replaced by the electrophile R^+, and the second involving a side-chain desilylation process following the electrophilic attack. The ring-substitution products, $RC_6H_4CH_2SiMe_3$, are characterized by a predominant *ortho/para* orientation. This is highest in the case of $R^+ = {}^tBu^+$ showing a *para*/$\frac{1}{2}$*meta* ratio of *ca.* 50, while *ortho* substitution to the encumbered electrophile appears hindered. The lowest selectivity is observed in the case of $R^+ = Et^+$ and $^{i}Pr^+$, giving *para*/$\frac{1}{2}$*meta* ratios of *ca.* 2.3 in the presence of added bases.

BTS deuterated by CD_5^+ has been analyzed by ^2H NMR spectrometry to obtain information on the pattern of deuterium distribution. The ^2H NMR spectrum of BTS from the radiolytic experiment run in the D_2/CD_4 mixtures in cyclo-hexane solution displays signals at 0.05 δ (belonging to the three methyl groups), 2.10 δ (belonging to the methylene group) and a set of three at 6.96, 7.04 and 7.18 δ (belonging to the aromatic ^2H in *ortho, meta*, and *para* positions, respectively). The signal at 0.05 δ may be ascribed to natural abundance ^2H in the methyl groups and its integral is in the statistical 9:2 ratio with the signal at 2.10 δ. This is evidence that there is no isotopic enrichment in either the methylene or methyl groups. However, if one considers the integrated aromatic signals, they yield a *R*(S) value of 16 if compared to the methyl ^2H, instead of the value of 5 expected for uniform ^2H distribution over all positions [9]. Such a difference greatly exceeds the minor ^2H enrichment found for the ring compared to side-chain positions in ethylbenzene [9] and can be attributed to deuteron transfer from CD_5^+ to the aromatic ring of BTS. The positional ^2H distribution determined by NMR spectroscopy and reported in Table 1 is affected by a larger error (±10%) than all others, determined by GLC (±3%).

The desilylation products include toluene, a protodesilylation product, formed by reaction of BTS both with pure Brønsted acids such as D_3^+ and CD_5^+, and with Brønsted/Lewis acids, *i.e.* the alkyl cations, which are capable of protonating BTS (PA = 200 ± 1 kcal mol^{-1}) in view of the lower PA values of their conjugate bases (C_2H_4 162.6; C_3H_6 179.5; i-C_4H_8 195.9 kcal mol^{-1}) [6]. The toluene from the reaction of D_3^+ and CD_5^+ incorporates a substantial amount of deuterium. Attempts to determine its positional distribution within the molecule by ^2H NMR analysis have failed, because of the low sensitivity of this nucleus combined with the relatively small amounts of material that may be recovered from radiolytic experiments designed to obtain kinetic information, which are run to no more than *ca.* 10% substrate conversion. In the methane experiments, a minute amount of an alkyldesilylation product, $PhCH_2Et$, accompanies the formation of toluene. The formation of both products is suppressed or strongly reduced by adding O- or N-bases. It is remarkable that hardly any alkyldesilylation product of the type $RC_6H_4CH_3$ or $PhCH_2R$ is ever observed, the only exception being a very minor yield of $^iPrC_6H_4CH_3$ in propane with no added bases.

The tendency to form silylenium ions, detected by ICR mass spectrometry, does not appear to be relevant under the conditions of the radiolysis experiments. The only evidence of an intermediate $PhCH_2SiMe_2^+$ ion in the methane systems comes from the formation of the corresponding silanol, due to the presence of unavoidable traces of water, or the i-propyl ether, $PhCH_2Si(O^iPr)Me_2$, when ^iPrOH is present.

A few representative reactions of PTS are also reported in Table 1 for comparison purposes. The well known tendency for extensive desilylation emerges also in the t-butylation reaction run in the presence of 3.9 Torr pyridine, where the 63% *meta*- and 37% *para*-substituted products are accompanied by a 4% alkyldesilylation product, ^tBuPh. The last product becomes by far the major one in the absence of strong N-bases. With respect to BTS, the intramolecular distribution is greatly changed, showing a *para*/$\frac{1}{2}$*meta* ratio of 1.2. The *para*/$\frac{1}{2}$*meta* ratio is 0.4 and 0.7 in the reaction of Me_2X^+ (X = F or Cl, respectively), although Me_2Cl^+ ions yield toluene as the major product. Kinetic information on the preferred site of electrophilic attack cannot be obtained from the reaction of Me_2X^+ (X = F or Cl), because the extensive desilylation following the electrophilic methylation may affect the various isomers to different extent.

TABLE 2. Relative reactivities of $Ph(CH_2)_xSiMe_3$ ($x = 0$ or 1) towards selected gaseous electrophiles [a]

Electrophile	k_{BTS}/k_R [b,c]	k_{PTS}/k_R [b,c]
Et^+	0.68	–
$^iPr^+$	0.88	1.4 [d]
Me_3C^+	1.5	1.5
Me_2F^+	1.3	0.93
Me_2Cl^+	3.6	0.16

[a] Values derived from data reported in Table 1, unless stated otherwise. [b] Ratios calculated by the standard equation for competing reactions: $k_1/k_2 = ([P_1]/[P_2]) \times ([S_2]/[S_1])$ where P_1 and P_2 are the products of substrates S_1 and S_2, respectively. [c] The reference substrate R is toluene except in the reaction of Me_2Cl^+ for which *p*-xylene has been used. [d] Ref. 3b.

TABLE 3. Thermochemical data concerning reactions of the selected gaseous electrophiles

Process [a]	$-\Delta H°$ (kcal mol^{-1})
$Et^+ + C_6H_6 \rightarrow EtC_6H_6^+$	44
$^iPr^+ + C_6H_6 \rightarrow {}^iPrC_6H_6^+$	25
$Me_3C^+ + C_6H_6 \rightarrow Me_3CC_6H_6^+$	6
$Me_2F^+ + C_6H_6 \rightarrow MeC_6H_6^+ + MeF$	29
$Me_2Cl^+ + C_6H_6 \rightarrow MeC_6H_6^+ + MeCl$	22
$H_3^+ + BTS \rightarrow BTSH^+ + H_2$	99
$CH_5^+ + BTS \rightarrow BTSH^+ + CH_4$	69
$Et^+ + BTS \rightarrow BTSH^+ + C_2H_4$	37
$^iPr^+ + BTS \rightarrow BTSH^+ + C_3H_6$	20
$Me_3C^+ + BTS \rightarrow BTSH^+ + i\text{-}C_4H_8$	4

[a] The structure of the product ions is taken to be that of the primary *ipso* σ-complex.

Finally, the relative reactivities of BTS and PTS towards the selected electrophiles are summarized in Table 2, using toluene as the reference compound and a powerful base to prevent possible transalkylation processes by the primary arenium ions. Only the methylation reaction by Me_2Cl^+ ions was run without any added base because this would lower the already poor methylation yields arising from the low reactivity of this ion towards aromatics. However, this should not be a source of errors in the relative reactivity ratios since methylated arenium ions have never been reported to undergo transmethylation processes in the gas phase. The reference substrate is *p*-xylene, again because the poorly electrophilic Me_2Cl^+ ions are unable to methylate toluene in the radiolytic experiments at 40°C. The relative reactivity figures in Table 2 are all close to unity for both BTS and PTS, with the notable exception of the methylation by Me_2Cl^+ ions, which discriminates between the higher (BTS) and lower (PTS) reactivity of the compounds under study.

4. Discussion

4.1. The ionic reactants

The formation of the selected reagent ions from the radiolysis of the parent neutral gas ($CH_5^+/C_2H_5^+$ in 1.9:0.9 ratio from CH_4; i-$C_3H_7^+$ from C_3H_8; Me_3C^+ from i-C_4H_{10}; D_3^+ from D_2; Me_2X^+ from MeX, X = F or Cl) is well known from previous mass spectrometric and radiolytic work [10]. CD_5^+ ions have been obtained by fast protonation of CD_4 by D_3^+ ions in a D_2/CD_4 mixture in 13:1 molar ratio [11]. The reactant ions undergo several unreactive collisions with the inert gas in the radiolytic systems, reaching thermal equilibrium with the environment, and possibly forming cluster ions, before a reactive encounter with the substrate takes place.

Ionic electrophiles fall into three categories as judged by their reactivities: (a) pure Brønsted acids, *e.g.*, D_3^+ and CH_5^+ (CD_5^+); (b) alkylating agents reacting by addition, *e.g.*, Et^+, $^iPr^+$, Me_3C^+; (c) methyl transfer agents, *e.g.*, Me_2F^+ and Me_2Cl^+. Ions of type (b) may also act as proton donors to BTS, because of its PA value of 200 kcal mol^{-1}. The enthalpy changes of protonation processes are given in Table 3. The thermodynamic features of σ-complex formation from attack to BTS by ions (b) and (c) cannot be easily estimated and the calculated $\Delta H°$ values for their reactions with benzene are given as a measure of their relative electrophilicity (Table 3) [12*]. These data provide only a lower limit to the $\Delta H°$ values for electrophilic attack to BTS and may be in error by as much as 20 kcal mol^{-1}, which is the PA difference between benzene and BTS.

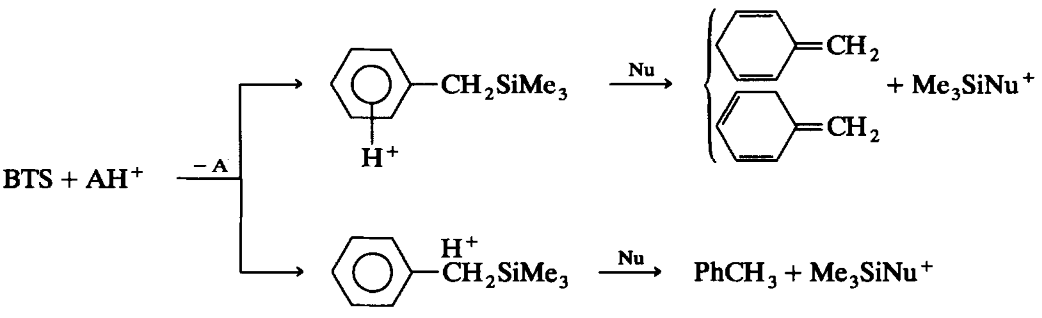
4.2. The protonation reaction

The PA value of 200 ± 1 kcal mol^{-1} places BTS among the most basic of substituted benzenes (the PA value of anisole is 200.3 kcal mol^{-1}) [6]. Such a relatively high gaseous basicity and the known ease of heterolytic cleavage of C–Si bonds shown by trimethylsilylated gaseous cations account for the dual behaviour of $BTSH^+$ as proton and Me_3Si^+ ion donor, as revealed by FT-ICR. Me_3Si^+ ions are most efficiently transferred to O-bases, such as Et_2O, cyclo-hexanone and ^iPrOH, rather than to hindered N-bases, such as TEA, releasing a neutral of gross formula $[C_7H_8]$. The structure of this neutral species poses an interesting question. If BTS is, in fact, protonated on the aromatic ring, simple Me_3Si^+ cleavage leaves an isotoluene type structure (reaction (5)). However, the formation of high energy *ortho* or *para* isotoluene intermediates (ΔH_f° = 41 and 35 kcal mol^{-1}, respectively) [6] is thermodynamically allowed only in the case of Et_2O and cyclohexanone as Me_3Si^+ acceptors [8]. To be thermodynamically permitted, the reaction with ^iPrOH must involve the formation of the more stable toluene (ΔH_f° = 12 kcal mol^{-1}). Thus the Me_3Si^+ ion transfer to ^iPrOH should either proceed from ring protonated BTS undergoing H migration concerted with Me_3Si^+ transfer or might involve a side-chain-protonated BTS, leading directly to toluene. The reported ion-molecule reactions displayed by $BTSH^+$ under ICR conditions do not provide by themselves an unambiguous indication of the protonation site(s) of BTS and therefore it is not known whether its thermodynamic PA value refers to a ring (π) or side-chain (σ) protonated species.

In principle, evidence on the kinetic site(s) of electrophilic attack can be obtained with the radiolytic technique. In the high pressure radiolytic experiments, the reaction of strong Brønsted acids (*e.g.*, D_3^+ in D_2 and $CH_5^+/C_2H_5^+$ in CH_4) induces a rather extensive desilylation process leading to significant amounts of toluene, the only $[C_7H_8]$ neutral species detected.

This finding does not exclude the possibility that isotoluene is formed primarily and then tautomerizes to toluene upon workup and analysis of the radiolytic product mixture (*e.g.*, in the hot injector of the GLC/MS instrument). We have sought evidence for this possibility using a deuterated Brønsted acid, CD_5^+, which marks the protonation site(s) in the toluene product. If toluene resulted from protonation at the methylene carbon followed by desilylation, a deuterium atom should enter the methyl group only. On the other hand, if the reaction leading to toluene involved ring protonation of BTS followed by desilylation with concerted or subsequent tautomerization, then the D atoms should be in the ring and in the methyl group.

A map of D distribution may be obtained by NMR analysis, a technique which has been exploited to yield structural information on the neutral products of ion-molecule reactions performed by the radiolytic technique [13]. Unfortunately, the required ^2H NMR analysis of the toluene-*d* product is of very low sensitivity and very little material was available. The same information could be obtained for BTS itself, which was found to be D-enriched on the phenyl ring. This is



(5)

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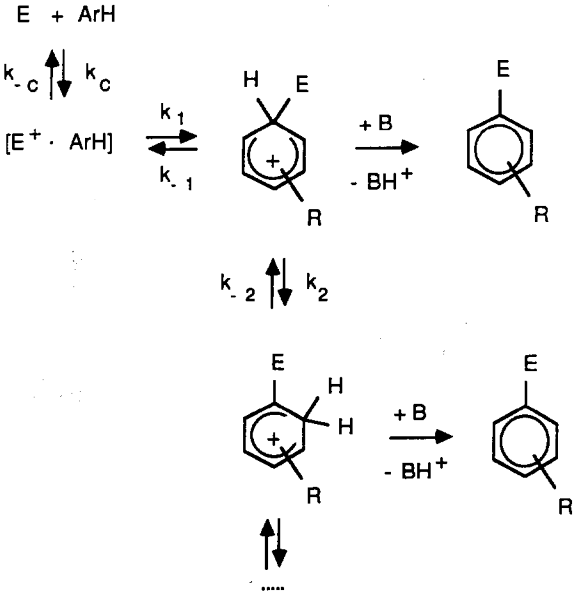
* Reference number with asterisk indicates a note in the list of references.



Scheme 1.

indicative of D^+ transfer from CD_5^+ followed by deprotonation, a process not involving the methylene group. However, this finding cannot be extended to toluene since, conceivably, D^+ transfer to the methylene group does occur but is always followed by desilylation rather than deprotonation.

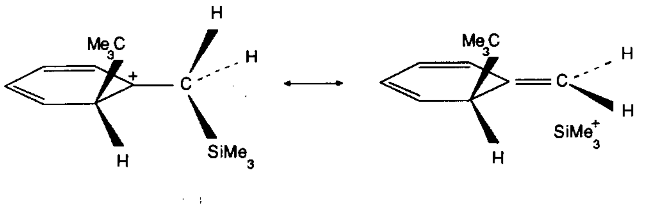
4.3. Alkylation of BTS and PTS: intramolecular selectivity

The electrophilic aromatic substitution by alkylating cations, depicted in the general Scheme 1, in principle allows the evaluation of the reactivity of the aromatic substrate.

The radiolytic technique allows one to determine directly the intra- and inter-molecular product distribution from the reaction of a fairly wide range of alkylating species of varying electrophilic power. The alkylating cations allowed to react with BTS and PTS belong to two types, carbenium ions and dimethylhalonium ions. The reaction of ethyl and isopropyl carbenium ions is characterized by a high exothermicity, which is reflected kinetically in the low intramolecular selectivity yielding *para*/$\frac{1}{2}$*meta* ratios of *ca.* 2, similar to those obtained from attack on toluene. These ions induce a minor but detectable reaction pathway leading to ring or even side-chain alkylation-desilylation products (*e.g.*, n-propylbenzene from Et^+ or i-propyltoluenes from $^{i}Pr^+$) probably involving nucleophilic assistance to Me_3Si^+ departure. Both Et^+ and $^{i}Pr^+$ ions may protonate BTS in a highly exothermic process. However, the protonation/alkylation branching ratio, which is > 1 for $^{i}Pr^+$ under ICR conditions (Fig. 2), is conceivably lower in the high pressure radiolytic conditions [14].

The reaction of Me_3C^+ ions is more informative of the selectivity properties of BTS towards electrophilic attack. Me_3C^+ cations react with toluene only at the *meta* and *para* positions, and display a high intramolecular selectivity in the *para*/$\frac{1}{2}$*meta* ratio of *ca.* 40. A very similar selectivity is shown in the t-butylation of BTS. In particular, no products of *ortho* substitution are formed. In order to achieve electrophilic attack *ortho* to a methyl group, the steric disadvantage has to be offset by the electronic activation of two methyl groups *ortho* and *para* to the carbon of interest, as in *m*-xylene, which yields large amounts of 4-t-butylated product under kinetic control at 37°C [15]. Thus it appears either that the activating power of the Me_3SiCH_2 group is less effective than that of two *ortho*/*para* methyl groups or that the Me_3SiCH_2 group presents greater steric hindrance than a methyl group.

The first hypothesis is at odds with the proton affinity of BTS (200 kcal mol^{-1}) which exceeds that of *m*-xylene (195.6 kcal mol^{-1}), relative PAs being directly related to relative activation to electrophilic attack. An objection to the second hypothesis is that the bulky Me_3Si substituent on the methyl group in BTS may minimize steric congestion in the transition state for σ-complex formation, as it lies on the opposite side of the molecular plane with respect to the incoming electrophile and is still perpendicular to the phenyl ring which is held responsible for the hyperconjugative activation with the Me_3SiCH_2 phenyl ring substituent (**Ib**). However, steric hindrance may not be exerted in the formation of the *ortho* σ-complex, but rather in its deprotonation, forcing the Me_3C and Me_3SiCH_2 groups into coplanarity [16].



(Ia) **(Ib)**

Whereas Me_3C^+ is certainly a mild electrophile, the reversibility of its electrophilic attack on aromatics may render other steps of the overall electrophilic substitution reaction rate-determining. A hint of such reversibility emerges from the change towards a higher proportion of *meta* substitution from toluene in the absence of a strong base which causes fast deprotonation of the primary arenium intermediates. In contrast, the presence of a base does not affect the isomer distribution of the t-butylation products of BTS (Table

1), which may indicate higher stability of the *p*-t-butylated σ-complex by virtue of the more effectively stabilizing Me_3SiCH_2 substituent, which brings about a decrease of k_{-1}.

The dimethylhalonium ions react by methyl cation transfer to the selected aromatics in a S_N2 type process which may involve significant activation barriers. This, together with the irreversible character of the k_1 step and the sluggish tendency of the formed arenium ion to undergo any intramolecular Me group shift, make these electrophiles more suitable for establishing the intrinsic reactivity of BTS and PTS. In the reaction of Me_2F^+ ions with BTS and toluene, a distinct difference emerges from the $p/\frac{1}{2}m$ ratios of 4 and 2, respectively, which may be compared with the value of 0.4 obtained for PTS under conditions minimizing parasitic desilylation processes. The direction and relative strength of orienting power towards electrophilic attack by gaseous cations displayed by the three substituents may thus be stated as follows. Me_3SiCH_2 is a more effectively *para* orienting substituent than the methyl group whereas Me_3Si directs electrophilic attack, preferably to the *meta* position. This conclusion does not emerge clearly from σ constant values available from reactivity studies in solution [1].

4.4. Alkylation of BTS and PTS: relative reactivities

The relative reactivities of the alkylating ions toward BTS and PTS reflects the kinetically significant steps of each reaction. The highly exothermic reaction of Et^+ and $^iPr^+$ ions take place within each encounter complex, thus proceeding with collisional efficiency and displaying almost no substrate discrimination. The modest deviations from unity of the values reported in Table 2 are possibly due to differential branching between the alkylation and protonation pathway.

The Me_3C^+ cation shows relative reactivity ratios which should not be significantly affected by a competing protonation. However, they do not reveal a straightforward relationship to the relative rate of σ-complex formation (k_1 step) in view of the known reversibility of the t-butylation reaction [17]. Such a relationship may be obtained from the relative reactivities displayed by the dimethylhalonium ions. In particular, Me_2Cl^+ ion, the least reactive, which is unable to methylate toluene at 40°C, allows us to establish a relative reactivity scale as follows: BTS > *p*-xylene > PTS > toluene.

Whereas the higher reactivity of BTS with respect to toluene reflects the relative σ_p^+ values determined in solution for Me ($\sigma_p^+ = -0.3$) and Me_3SiCH_2 ($\sigma_p^+ = -0.6$), the activation of PTS is remarkably high, judged by the same criterion (σ_p^+ (Me_3Si) ≈ 0) [1]. Such behaviour stems in part from the fact that Me_3Si activates the *meta* position more than the *para*. Moreover, whereas electrophilic attack is directed to unsubstituted ring positions of BTS, the Me_3Si-substituted position is predominantly concerned in the case of PTS. This is shown by the high fraction of toluene formed from the reaction of Me_2Cl^+, even higher than that formed from Me_2F^+. This finding suggests that primary *ipso* attack, more selective in the case of Me_2Cl^+ than of Me_2F^+, predominates over processes involving methylation at an unsubstituted carbon followed by H migration to the silicon-substituted position and final nucleophilic desilylation. Instead, this multistep pathway should be relatively favoured in the more exothermic reaction of Me_2F^+ ions.

5. Conclusions

The intrinsic activating and directive effects of Me_3Si in the electrophilic aromatic substitution of compounds of the type $Ph(CH_2)_xSiMe_3$ ($x = 0$ or 1) have been investigated in the gas phase reaction of cationic electrophiles. BTS is highly activated towards electrophilic attack: a measure of its activation is given by the high PA value of 200 ± 1 kcal mol^{-1}. Protonation of BTS may be followed by a nucleophile-assisted desilylation process, possibly involving a methylene-protonated form. Mild electrophiles, such as Me_2X^+ ions, reveal a pattern of intra- and inter-molecular reactivities, reflecting a higher activating power and greater *para*-directive effect of Me_3SiCH_2 compared to Me. Thus, the gas-phase reactivity of BTS clearly reflects a pronounced electron-donating effect exerted by the Me_3SiCH_2 group on the adjacent phenyl ring. Such electron-releasing effect is well documented in solution, accounting both for the reactivity of BTS towards electrophilic attack, *e.g.*, in detritiation of Me_3SiCH_2-$C_6H_4{}^3H$ in trifluoroacetic acid [18] and for ground-state properties of benzylsilanes [19]. It is recognized that the major contribution of this effect is due to hyperconjugative release, as first suggested by Eaborn in 1956 [20]. Since this appears to hold in the gas-phase, it follows that the importance of resonance components such as **Ib** reflects the intrinsic electronic features of the Me_3SiCH_2 and is not specifically related to favourable solvent interactions with the positively polarized trimethylsilyl group. The inherent effect of the Me_3Si group directly bound to the aromatic ring is more difficult to understand owing to the comparatively easier parasitic desilylation processes. For this reason, a measure of the PA value of PTS has not yet been achieved by equilibrium methods. In view of this, one may use the PA value of 193 kcal mol^{-1}, which has been calculated by *ab initio* MO methods [3a] or the PA value of 204 kcal mol^{-1} which can be derived from the binding energy of Me_3Si^+ to benzene [8]. Both values, though suffering from large error limits, point to a relatively higher overall activation towards electrophilic attack, compared to toluene (PA = 189.8 kcal mol^{-1}). This is consistent with the relative reactivity trend towards Me_2Cl^+, showing that the higher activation of PTS with respect to toluene is a property not related to σ_p^+ or σ_m^+ values, but rather to a pronounced tendency to undergo *ipso* attack, which is favoured both on kinetic and thermodynamic grounds.

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