Study of ion/molecule reactions of ion derived from *tert*-butyl methyl ether and trimethylsilyl methyl ether

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Abstract

The ion/molecule reactions of the ions $(CH_3)_2C^+$–OCH_3 (**1a**) and $(CH_3)_2Si^+$–OCH_3 (**2a**), which are the main fragment ions in the electron ionization mass spectrum of *tert*-butyl methyl ether (MTBE, **1**) and trimethylsilyl methyl ether (MTSE, **2**), respectively, and of the protonated MTBE (**1H**$^+$) and protonated MTSE (**2H**$^+$), generated by chemical ionization, with MTBE or MTSE, with acetone and with ammonia have been studied by Fourier transform ion cyclotron resonance (FTICR) spectrometry. The carbenium ion **1a** is practically unreactive toward these substrates whereas the silicenium ion **2a** efficiently forms adduct ions with all three reactants. Clearly **1a** is a very stable tertiary carbenium ion due to the resonance stabilization of the methoxy group so that it lacks significant electrophilic character, whereas **2a** does not gain much stabilization by this substituent. This interpretation is supported by the results of ab initio calculations at the restricted Hartree-Fock/6-31G(*d*) level of the structures and stabilities of these ions, of the *tert*-butyl cation and of the trimethylsilicenium ion and of their adducts with H_2O, $(CH_3)_2O$, and NH_3. The reactions of the protonated silyl ether **2H**$^+$ are straightforward and correspond to transfer of the trimethylsilyl group to the reactants, as expected for a silylation reagent. Silyl group transfer competes effectively with proton transfer even in the case of NH_3 as reactant. The typical reaction of the protonated *tert*-butyl ether **1H**$^+$ with the three substrates is an efficient elimination of C_4H_8 to generate a proton bound heterodimer of the attacking reactant with methanol as the primary product ion. This reaction also takes place when NH_3 is the substrate, although in this case proton transfer is the main process. In view of the easy interconversion of the protonated ether **1H**$^+$ with its isomeric ion/neutral complexes consisting of proton bound isobutene and methanol (*β* complex), as proven by Audier et al. [J. Orig. Chem. 60 (1995) 7198], it is suggested that this fast elimination process is in fact a ligand switching process of the *β* complex which is either present as a stable species in the gas phase of the FTICR cell or is generated from **1H**$^+$ by electrostatic activation in the encounter complex of the reactants. (Int J Mass Spectrom 199 (2000) 141–154) © 2000 Elsevier Science B.V.

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1. Introduction

Tert-butyl derivatives have played an exceptional role in the elucidation of organic reaction mecha-
nisms, partly because of the steric effect of the bulky group but primarily because of the latent possibility to form a stable *tert*-cation in the course of polar reactions. Thus, *tert*-butyl derivatives with a nucleo-

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fugal group are prototype compounds for the S_N1 reaction [1]. Abundant formation of *tert*-butyl cations in the gas phase is also a wide spread phenomenon in mass spectrometry by using both electron impact ionization (EI) and chemical ionization (CI). In particular, the possibility to form an intermediary ion/neutral complex (INC) of the *tert*-butyl cation with the neutral fragment during decomposition of adequate radical cations and protonated organic molecules has attracted considerable interest. For example, the formation of INC of *tert*-butyl cations associated with arene molecules from protonated *tert*-butyl-arenes is well established [2,3], and protonated *tert*-butyl alcohol and di-*tert*-butyl ether produced in the gas phase by CI have been suggested to be in fact the INC of the *tert*-butyl cation with H_2O or *tert*-butanol [4,5].

We were interested in using *tert*-butyl methyl ether (**1**, MTBE) and its element/organic homologue trimethylsilyl methyl ether (**2**, MTSE) as reactants for substituted alkene radical cations in a corresponding Fourier transform ion cyclotron resonance (FTICR) study. Among the expected ion/molecule reactions are electron transfer and proton transfer from the alkene radical cation to the ether molecules to produce the molecular ions and "quasimolecular ions", respectively, of MTBE and MTSE. Subsequently these ions give rise to secondary product ions by reaction with **1** and **2** present in the FTICR cell. Therefore, we decided to investigate separately the ion/molecule reactions of relevant ions observed in the EI and CI mass spectra of MTBE and MTSE, respectively. MTBE is of extensive industrial use, and a study of ion/molecule reactions of ions derived from this compound are of interest in connection with environmental problems arising from its industrial application. The trimethylsilyl cation is also a stable ion in the gas phase [6]. Therefore, the molecular ion **2**$^{.+}$ and the protonated molecule **2H**$^+$ of MTSE may also exhibit a tendency to be transformed into an INC of the trimethysilyl cation. As will be shown by the results, the ions derived from MTBE and MTSE exhibit indeed some similarities, but there are clear differences that can be attributed to the very different

gas phase acidity and to the different electrophilicity of the *tert*-butyl cation and the trimethylsilyl cation.

2. Experimental

2.1. Compounds

All compounds used in this study are commercially available and were used without further purification: Ammonia (99.8%; Merck), isobutane (99.5%; Linde), MTBE ($\geq$99.8%; Merck), MTBE-O-d_3 ($\geq$99% atom D; Fluka), TMSE (>95%), acetone ($\geq$99.5% GC; J.T. Baker) and pyridine ($\geq$99.5% GC; Merck).

2.2. Mass spectrometry

The EI- or CI-mass spectra were acquired with a double focusing mass spectrometer Micromass VG Autospec. The ionization energy under EI or CI conditions was 70 eV, and the acceleration voltage was 8 kV for EI measurements and 6 kV for CI measurements. MTBE and MTSE, were introduced into the ion source via the high temperature inlet at a temperature of 160 °C. The temperature of the ion source was 135 °C. For CI isobutane was used at a pressure of 10^{-4} mbar in the ion source.

All EI and CI mass-analyzed ion kinetic energy (MIKE) spectra and collisional activation (CA) mass spectra were obtained with the same mass spectrometer at conditions equivalent to those described previously. The precursor ion was selected by the magnet and focused into the third field free room (3rd FFR) following the magnetic analyzer. By variation of the deflection voltage of the second electrostatic analyzer (2nd ESA), the signals of the precursor ion and the fragment ions formed in the 3rd FFR were detected. 20–50 single spectra were accumulated for optimization of the signal to signal/noise ratio. The distribution of the released energy [kinetic energy releases distributions (KERD)] during the fragmentation of metastable ions was determined by using the META program of Szilàgy and Vékey [7]. The low-energy half of the fragment-ion signal in the MIKE spectrum was smoothed by an averaging function without

changing the original peak form of the signal. Then these data and a parameter set for the type Micromass VG Autospec, was used for the calculation of the KERD.

For collision induced dissociation (CID) in the 3rd FFR argon was introduced into the collision cell until the intensity of the main ion beam was reduced to 50% (about 10^{-6} mbar).

2.3. FTICR spectrometry

All FTICR experiments were performed with a Spectrospin Bruker CMS 47X FTICR instrument [8], equipped with an Infinity™ cell of 6 cm in length [9], a 4.7 T superconducting magnet, a 24 bit/128k word Aspect 3000 computer and an external ion source [10]. The ions were generated in the external ion source either by EI with an electron energy of 25 eV or by CI with an electron energy of 40 eV by using isobutane as the CI gas, and the mixture of product ions was transferred into the FTICR cell by means of a transfer optic. The voltages at the front and back trapping plates were set to 1 ± 0.1 V, and that of the excitation plates to 00.0 ± 0.1 V. The ions under study were selected by broadband ejection (frequency sweep) of 88 $V_{p\text{-}p}$ and by rf pulses of 14 $V_{p\text{-}p}$ fixed frequency ejections (single shots). The ejection process was finished after 15–20 ms.

Following the isolation, the ions selected were thermalized by collisions with argon added by a pulsed valve (opened for 8–15 ms) prior to reaction. The argon was removed after a delay time of 0.8–1.5 s. Fragment ions and product ions formed during this period were ejected again by single shots of 14 $V_{p\text{-}p}$. This method is described in detail elsewhere [11]. The neutral reactant was introduced continuously by a leak valve giving a constant pressure of 2×10^{-8} to 5×10^{-7} mbar in the ICR cell. The readings of the ionization gauge were corrected for the sensitivity of the neutral gas used [12,13] and were calibrated by rate measurements of the reaction $NH_3^{+\bullet} + NH_3 \rightarrow NH_4^+ + NH_2$ ($k_{bi} = 21 \times 10^{-10}$ cm^3 molecule^{-1} s^{-1} [14]. The sensitivity of NH_3 was taken from [12].

To investigate the kinetics of the ion/molecule reactions, the reaction time was varied from 3 to 60 s.

After this delay, all ions within the FTICR cell were excited by a frequency sweep of 88 $V_{p\text{-}p}$ with a step width of 7.8 kHz and an excitation pulse of 8 μs. The FTICR spectra were averaged by 8 data acquisition cycles and recorded by 32 k data points for 10–30 different reaction times. Peak intensities were obtained by Gaussian multiplication and Fourier transformation of the time domain signal. For the evaluation of the rate constants, peak intensities of the magnitude spectra were normalized to the sum of all ions detected at each reaction time. By fitting these data to an exponential function by using the Microcal Origin 4.5 program [15], the pseudo-first order reaction rate constant k_{exp} was obtained. The bimolecular rate constant k_{bi} was calculated from k_{exp} by using the number density of the neutral reactant derived from the corrected pressure. The efficiency of the reaction is given by $100 \times k_{bi}/k_{col}$, where the collision rate constant k_{col} was calculated by using the method of Su and Chesnavich [16].

To investigate the further reactions of primary product ions with the reagent gas in multistep ion/molecule reactions, these ions were generated by the appropriate bimolecular ion molecule reaction in the FTICR cell. At an adequate reaction time (about 1–4 s) the ions were isolated as described previously adding a thermalization step by collisions with argon. This was admitted by a pulsed valve after a primary reaction time and removed after a delay time of 0.8–1.5 s. Subsequently the ion under investigation was selected by broad ejection and single shots prior to further reaction with the neutral reactant.

2.4. Computations

Semiempirical (PM3) and ab initio calculations (RHF/6-31g(d)) were performed by using the GAUSSIAN 98w programs [17]. The search for possible minima on the hypersurface and the geometry optimization of the species of interest was performed first by the semiempirical method PM3. The structures found were re-optimized using RHF/6-31g(d). It has been shown that this level of theory is sufficient to reproduce structures obtained with a much larger basis set [23]. Harmonic vibrations were

computed to characterize the stationary points as minima and to estimate the zero-point vibrational energy. In the calculations of the isodesmic reactions (1) and (2) the frequencies obtained were used without a scaling factor to correct for thermal energy. This is justified in view of the moderate reliability of the calculated energies at the level of theory used and the fact, that systematic errors nearly cancel in isodesmic reactions.

3. Results and discussion

The EI and CI mass spectra of MTBE (**1**) and MTSE (**2**) are known. As expected the molecular ions of both ethers give rise to only exceedingly small peaks in the EI mass spectra. If the vapor pressure of these compounds is raised to get more abundant molecular ions, only "self-CI" of the ether is observed producing the protonated species **1H$^+$** and **2H$^+$** and some other secondary ions. Consequently, the bimolecular reactions of the radical cations **1$^{\cdot+}$** and **2$^{\cdot+}$** were not studied. Further, it proved to be rather difficult to obtain "pure" CI-mass spectra of MTBE and MTSE. Under all conditions used, these spectra displayed always some more or less intense signals which could be attributed to EI fragment ions.

The main fragment ion in the EI mass spectrum of MTBE and of MTSE arises from loss of a methyl radical from the molecular ions to produce ion **1a**, $(CH_3)_2C^+–OCH_3$, *m/z* 73, and **2a** $(CH_3)_2Si^+–OCH_3$, *m/z* 89, respectively. The further fragmentations of these ions were investigated by means of their MIKE spectra (Table 1). The ion **1a** fragments mainly by loss of $CH_2=O$ yielding an ion $C_3H_7^+$, *m/z* 43, but additionally distinct peaks are observed at *m/z* 41, *m/z* 45, and *m/z* 55. The ions *m/z* 41 are due to loss of CH_3OH from the ion **1a**, but remarkably the ions *m/z* 45 and *m/z* 55 are generated from **1a** by loss of C_2H_4 and H_2O. Both processes require considerable rearrangement of the precursor ion and possibly indicate the admixture of an ion 89 of different structure to the ions $(CH_3)_2C^+–OCH_3$. Thus, the elimination of H_2O indicates ions containing a free hydroxy group formed

Table 1
MIKE spectra of ions derived from MTBE (**1a**, **1H$^+$**) and MTSE (**2a**; **2H$^+$**)

Fragment lost	1a	2a	1H$^+$	2H$^+$
–CH_4	7	. . .	. . .	40
–H_2O	34	. . .	. . .	. . .
–C_2H_4	23	9	. . .	. . .
–$CH_2=O$	100	100	. . .	. . .
–CH_3OH	17	. . .	100	100

by loss of the O-methyl group in the first fragmentation step of **1$^{\cdot+}$**. To get more information about this fragmentation, the EI mass spectrum of *tert*-butyl trideuteromethyl ether **1-d$_3$** (MTBE-d$_3$) has been obtained. In this spectrum the peak originally at *m/z* 73 is completely shifted to *m/z* 76, confirming the specific loss of a methyl radical from the *tert*-butyl group. This eliminates the possibility that the ions **1a** in the MTBE mass spectrum are a mixture of ions arising by methyl loss from different positions of **1$^{\cdot+}$**. The MIKE spectrum of the ion **1a-d$_3$**, *m/z* 76, $(CH_3)_2C^+–OCD_3$, exhibits an intense signal at *m/z* 44 and a smaller one at *m/z* 41 corresponding to the losses of $CD_2=O$ and CD_3OH, respectively. This confirms the proposed structure $(CH_3)_2C^+–OCD_3$ of **1a-d$_3$** and the absence of any H/D exchange prior to these fragmentations, in contrast to the extensive H/D exchange observed in protonated MTBE. However, the signals for the loss of water and ethylene are split into peaks for losses of H_2O, HDO, and (some) D_2O, and for losses of C_2H_4 and $C_2H_2D_2$. The intensity distributions within each group of these signals is far from that expected for H/D scrambling between the methyl groups of **1a-d$_3$**, but clearly all three methyl groups participate in these fragmentations.

The MIKE spectrum of the ion **2a**, $(CH_3)_2Si^+–OCH_3$, *m/z* 89, is dominated by the signal at *m/z* 59 arising from **2a** by loss of $CH_2=O$. Again a small peak at *m/z* 61 for the elimination of C_2H_4 is observed, requiring again an interaction between the two methyl groups at the Si atom. No indication for the loss of H_2O from this precursor ion is found, however.

The CI (isobutane) mass spectra of MTBE and the unimolecular decomposition of protonated MTBE,

Table 2
Rate constants, k_{bi}, and reaction efficiencies, eff, of the reactions of the ions $(CH_3)_2C^+–OCH_3$, **1a**, $(CH_3)_2Si^+OCH_3$, **2a**, protonated MTBE, **1H$^+$**, and protonated MTSE, **2H$^+$**, with MTBE or MTSE, with CH_3COCH_3, and with NH_3

	1a		**2a**		**1H$^+$**		**2H$^+$**	
Reactant	k_{bi}[a]	Eff[b]	k_{bi}[a]	Eff[b]	k_{bi}[a]	Eff[b]	k_{bi}[a]	Eff[b]
MTBE/MTSE	0.020	0.13	8.53	60	5.05	35	5.69	40
CH_3COCH_3	0.020	0.08	7.88	32	12.1	48	13.4	56
NH_3	$\ll 0.002$	$\ll 0.01$	1.51	7.2	7.46	36	11.1	54

[a] $\times 10^{-10}$ [cm^3 molecules^{-1} s^{-1}].

[b] $= k_{bi}/k_{collision} \times 100$ [%].

1H$^+$, has been studied before [5a]. The CI spectrum displaces an intense peak for **1H$^+$**, and this protonated ether molecule fragments solely by formation of the ion $(CH_3)_3C^+$, *m/z* 57. MTSE exhibits also an intense signal for the protonated molecule **2H$^+$** in the CI mass spectrum. As mentioned previously the spectrum also contains a peak for the ion $(CH_3)_2Si^+–OCH_3$, *m/z* 89, which is usually the second most intense signal in the spectrum, but which may be due to EI fragmentation. However, besides an intense signal for the formation of the ion $(CH_3)_3Si^+$, *m/z* 73, the MIKE spectrum of **2H$^+$** shows a flat topped peak of moderate intensity at *m/z* 89 which arises from loss of CH_4 from the precursor ion **2H$^+$**. So at least a fraction of the ions **2a**, *m/z* 89, in the CI (isobutane) mass spectrum of MTSE are fragment ions of the protonated ether. An analogous fragmentation is detected neither in the MIKE spectrum nor in the CA mass spectrum of **1H$^+$**.

This short discussion of the EI and CI mass spectra of MTBE and MTSE shows that the bimolecular gas phase ion chemistry of these ethers should arise primarily from the reactions of the fragment ions **1a**, $(CH_3)_2C^+–OCH_3$, *m/z* 59 and **2a**, $(CH_3)_2Si^+–OCH_3$, *m/z* 89, formed by EI from MTBE and MTSE, and by the protonated molecules **1H$^+$**, *m/z* 89, and **2H$^+$**, *m/z* 105, and the fragment ions $(CH_3)_3C^+$, *m/z* 57, and $(CH_3)_3Si^+$, *m/z* 73, formed in the CI mass spectra of MTBE and MTSE. The reactions of the latter ions with organic molecules are well known from CI mass spectrometry using isobutane [18] and tetramethylsilane [19] as the reactant gas. Therefore, these ions have not been studied again. The results of a study of

the other four principal ions in the EI and CI mass spectra of MTBE and MTSE with some selected organic molecules by using FTICR are discussed in the following section.

3.1. Reaction of ions $(CH_3)_2C^+–OCH_3$ and $(CH_3)_2Si^+–OCH_3$

The ions **1a**, $(CH_3)_2C^+–OCH_3$, and **2a**, $(CH_3)_2Si^+–OCH_3$, are expected to be stable. In particular, **1a** gains stability from a resonance stabilization by the methoxy substituent [20]. In fact, this ion can be visualized as an acetone cationized by a methyl cation at the O atom or as a C-protonated 2-isopropenyl methyl ether. As a consequence **1a** is expected to react as a very weak electrophile possibly forming adducts with *n* bases and transferring either a proton or a methyl cation to suitable bases. The silicenium ion **2a** is expected to be much less stabilized by a resonance effect of the methoxy substituent [6,21], and since the formation of Si–C– and Si–O double bonds is energetically not favored, neither proton nor methyl cation transfer is expected but only the addition reactions of a typical electrophile.

These expectations are born out by the gas phase reactions of the ions **1a** and **2a** with the respective ether molecules MTBE and MTSE, with acetone and with ammonia. The kinetic data for these reactions are collected in Table 2. The kinetic plots for the reactions of **1a** and **2a** with MTBE and MTSE are shown in Fig. 1. The only reaction observed in the system **1a**/MTBE is a very slow proton transfer to MTBE
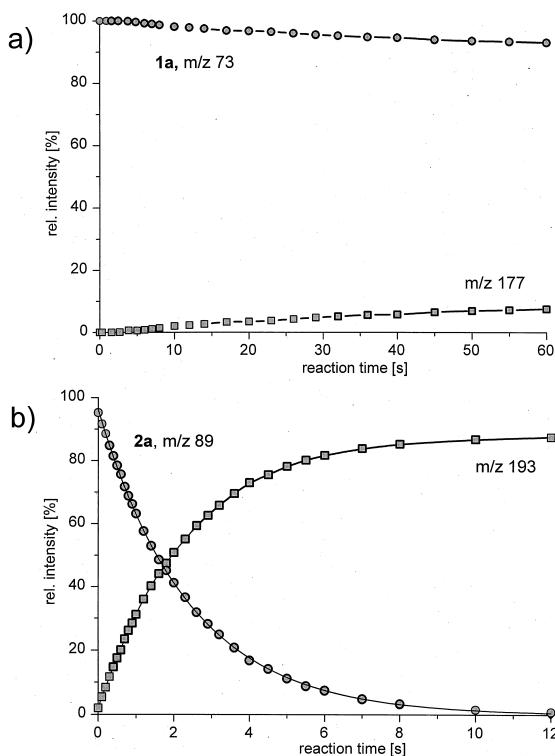
Fig. 1. Reaction of (a) ions **1a** with MTBE and (b) ions **2a** with MTSE.

Fig. 2. Reaction of (a) ions **1a** with acetone and (b) ions **2a** with acetone.

with subsequent formation of the proton bound dimer of MTBE, m/z 177 [Fig. 1(a)] The proton affinity (PA) of MTBE (PA 841.6 kJ/mol [22]) is definitely below that of 2-isopropenyl methyl ether (PA 894.9 kJ/mol [22]), and its methyl cation affinity (MCA) should be distinctly below that of acetone, so that both transfer reactions are endothermic and slow. However, adduct formation is also not observed. Similarly, the dominant reaction of **1a** with acetone (PA 812 kJ/mol [22]) by far is a slow proton transfer followed by formation of the proton-bound homodimer of acetone at m/z 117 [Fig. 2(a)]. A formation of proton bound homodimers of the base is often observed for an endothermic proton transfer. Only at long reaction times the formation of adducts ions at m/z 147 is observed with low intensity. A transfer of a methyl cation from **1a**, $(CH_3)_2C^+–OCH_3$, to acetone has been checked by the reaction of the deuterated ion **1a-d₃**, $(CH_3)_2C^+–OCD_3$. This reaction would be thermoneutral, but
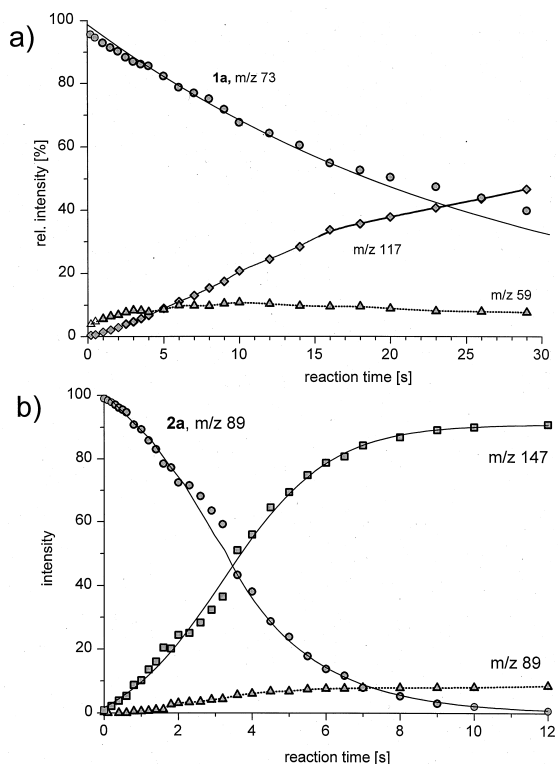
nonetheless it is not observed experimentally. No reaction, and in particular no adduct formation or proton transfer, could be detected for the system **1a**/ammonia. This is surprising because NH_3 (PA 853, 6 kJ/mol [22]) is more basic than MTBE and acetone. In summary, the ion **1a** must be either a rather weak electrophile, or the adducts dissociate back to products quickly because of the lack of stabilization by collision or by radiation under the conditions of FTICR spectrometry. In contrast to this, **2a**, $(CH_3)_2Si^+–OCH_3$, forms easily an adduct ion, m/z 193, with MTSE [Fig. 1(b)], an adduct ion m/z 147 with acetone [Fig. 2(b)], and an adduct ion m/z 106 with ammonia as the only product ions. Evidently, $(CH_3)_2Si^+–OCH_3$ is not only a better electrophile than $(CH_3)_2C^+–OCH_3$, but the adduct ions are also quite effectively stabilized by emission of radiation.

Table 3
Structure parameters and stabilization energies, ΔE_{stab}, of *tert*-butyl carbenium ion, **1a**, trimethylsilicenium ion, and **2a**, and of their adducts with H_2O $(CH_3)_2O$, and NH_3

Ion	d(E–A)[a,b] (pm)	d(E–C)[a] (pm)b	$\langle$CEA[a,b] (deg)	ΔE_{stab} (expt) (kJ/mol)	ΔE_{stab} (calc) (kJ/mol)
$(CH_3)_3C^+$	. . .	147.5	. . .	324.8	283
+ H_2O	166.5	150.8	101.5	. . .	. . .
+ $(CH_3)_2O$	158.1	152.9	106.9/93.6	. . .	. . .
+ NH_2	154.4	151.9	106.3	. . .	. . .
1a	. . .	148.9	. . .	429.3	393
+ H_2O	263.7	148.8	88.1/96.68	. . .	. . .
+ $(CH_3)_2O$	268.0	148.5	89.6/96.0	. . .	. . .
+ NH_2	157.1	152.0	106.4	. . .	. . .
$(CH_3)_3Si^+$	. . .	184.7	. . .	. . .	95
+ H_2O	191.0	185.9	99.4	. . .	. . .
+ $(CH_3)_2O$	185.1	186.4	103.8	. . .	. . .
+ NH_2	186.5	194.4	102.9	. . .	. . .
2a	. . .	184.2	. . .	. . .	117
+ H_2O	190.9	185	99	. . .	. . .
+ $(CH_3)_2O$	184.2	185	104	. . .	. . .
+ NH_2	191.5	185.7	95	. . .	. . .

[a] E = central C atom for cabenium ions and central Si atom for silicenium ions.
[b] A = O atom of H_2O or $(CH_3)_2O$ or N of NH_3.

3.2. Computational results

To further illustrate the different reactivities of ions **1a** and **2a** [and their analogues $(CH_3)C^+$ and $(CH_3)_3Si^+$], the structures and stabilities of these ions and their adducts to H_2O, $(CH_3)_2O$, and NH_3 as nucleophiles have been characterized by semiempirical (PM3) and ab initio [RHF/6-31g(d)] methods. The results (Table 3) demonstrate clearly the different electrophilicity of these ions. Adduct formation between the *tert*-butyl cation $(CH_3)_3C^+$ and H_2O has been investigated before [5], and recently Uggerud and Bache-Andreassen studied in detail the reactions of simple protonated alcohols with water by FTICR spectrometry and ab initio methods [23]. In the case of protonated *tert*-butanol it has been shown [5] that there are two stable structures, one covalently bonded structure with a C–O bond length of 147 pm, and one corresponding to a complex (termed "α-complex" [5]) of the *tert*-butyl cation and water with a C–O distance of 285 pm. We did not specifically search for all stable structures in the system $[(CH_3)_3C–O^+H_2]/$
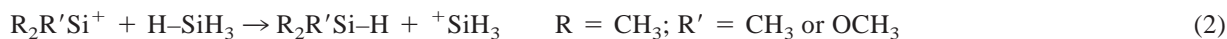
$[(CH_3)_3C^+; OH_2]$, and our computational result corresponds to a covalently bonded structure with a C–O bond length of 163.0 (PM3) and 166.5 pm [RHF/6-31g(d)], respectively. This is considerably longer than that reported in the literature (147 pm [5b]; 161.1 pm [23]), but the *tert*-butyl group in this structures exhibits a definite pyramidalization which indicates covalent bonding to the O atom. The structures calculated for the adduct of $(CH_3)_2O$ to $(CH_3)_3C^+$ by the semiempirical method PM3 and by ab initio RHF/6-31g(d) differ substantially. The PM3 structure exhibits a planar *tert*-butyl group and a C–O bond length of 302.4 pm from the central C atom to the ether O atom. Thus, this structure corresponds clearly to an INC of the *tert*-butyl cation and dimethyl ether. It has been shown before that steric crowding in an oxonium ion leads to dissociation into an INC [5a]. However, the ab-initio structure is clearly that of a covalently bonded oxonium ion, although the C–O bond length are different: 145.7 pm for the bonds to the methyl groups and 158.1 pm for the bond to the *tert*-butyl ligand. Values about 158 pm have been calculated before for the C–O bond of *tert*-butyl

oxonium ions [5a], and it should be noted that the C–O bond length in the ether adduct is shorter than in the adduct with water. This effect can be due to the greater nucleophilicity of the ether O atom. Finally, the adduct of NH_3 to $(CH_3)_3C^+$ exhibits a C–N bond length of 154.2 pm (PM3) and 154.4 ppm [RHF/6-31g(d)], respectively, only slightly longer than the 151 pm found usually in aliphatic ammonium ions. The significant covalent nature of the bond between the central C atom of the *tert*-butyl group and the heteroatom of the nucleophile in all these adducts of the *tert*-butyl cation is suggested by a distinct pyramidalization at the central C atom, as compared to the free planar *tert*-butyl carbenium ion. In contrast to this, the ion **1a** retains the planar geometry with respect to the two methyl groups and the methoxy substituent at the central C atoms as in the free carbenium ion in the adducts with O nucleophiles. In fact, the bond lengths and angles within the $(CH_3)_2C^+$–OCH_3 moiety of the adducts do not differ significantly from the free carbenium ion **1a**. Further, H_2O or $(CH_3)_2O$ is attached quite distantly with "bond" lengths of 264 pm (H_2O) and 268 pm [$(CH_3)_2O$] in reasonable agreement with the 285 pm reported for the stable INC of the *tert*-butyl cation and H_2O [5]. Thus, these adducts are better portrayed as an ion $(CH_3)_2C^+$–OCH_3 solvated by H_2O, $(CH_3)_2O$. This result can be well understood if one recalls that the structure of the *covalently* bonded adducts would correspond to a O-protonated hemiketal or ketal which are known to be labile species in solution. Only the adduct of the much stronger nucleophile ammonia exhibits significant pyramidalization at the central C atom of **1a** and indicates covalent bonding. The C–N distance in this adduct of 157.1 pm is slightly larger than the 154 pm calculated for the adduct $(CH_3)_3C^+$/

NH_3, but still in the range of C–N bonds of alkyl ammonium ions.

If one takes pyramidalization at the central Si atom as the criterion, all the adducts of the silyl cations $(CH_3)_3Si^+$ and **2a**, $(CH_3)_2Si^+$–OCH_3, with H_2O, $(CH_3)_2O$, and NH_3 represent covalently bonded structures with a tetravalent central Si atom. However, in the case of the adducts of **2a** and the O nucleophiles the two Si–O bonds are clearly different with about 160 pm for the bond to the methoxy ligand and 190.9 pm (H_2O) or 184.2 pm [$(CH_3)_2O$] to the O atom of the nucleophile added. Note also that in the adduct to the silicenium ions the C–O bond to the ether–O atom is the shorter one. Further, almost identical bond lengths are observed for the adduct of $(CH_3)_3Si^+$, indicating that the methoxy group of **2a** has no strong effect on its electrophilicity. From these computational results it is expected that **2a**, $(CH_3)_2Si^+$–OCH_3, as well as $(CH_3)_3Si^+$, will generate adducts with a broad variety of nucleophiles, whereas **1a**, $(CH_3)_2C^+$–OCH_3, will exhibit a much lower proclivity for adduct formation than even $(CH_3)_3C^+$ and will react with stronger and more basic nucleophiles by proton transfer. This is born out by the experiments discussed above. Interestingly, in the system **1a**/NH_3, where ab initio calculation predict the formation of a stable covalent adduct, no reaction at all is observed. One possible explanation could be that the incoming NH_3 molecule is directed to a fast and reversible adduct formation without the chance to abstract a proton, while the O nucleophiles are bound in a loose INC and can pickup a proton before dissociation.

Finally, the stabilization energy E_{stab} of the carbenium ions and silicenium ions by their ligands were analyzed as usual by calculating the enthalpy change of the isodesmic reactions (1) and (2)

$$R_2R'C^+ + H–CH_3 \rightarrow R_2R'C–H + {}^+CH_3 \qquad R = CH_3; R' = CH_3 \text{ or } OCH_3 \qquad (1)$$

$$R_2R'Si^+ + H–SiH_3 \rightarrow R_2R'Si–H + {}^+SiH_3 \qquad R = CH_3; R' = CH_3 \text{ or } OCH_3 \qquad (2)$$

In the case of the carbenium ions experimental heats of formation [22] as well as enthalpies calculated by RHF/6-31g* can been used to calculate E_{stab}, since the heat of formation of the relevant species are explicitly tabulated [22] with the exception of $\Delta H_f(\mathbf{1a})$, which can be calculated from the PA(2-propenyl methyl ether) [22]. For the Si species involved in isodesmic reaction (2), only experimental values for the silanes and the corresponding silicenium ions can be found, but no experimental data are available for the Si–O species, so that only the ab initio values can be used to calculate E_{stab}. The results (Table 3) for the carbenium ions $(CH_3)_3C^+$ and $\mathbf{1a}$ show the expected large stabilization of the *tert*-butyl cation and a considerable further stabilization of $\mathbf{1a}$. It is seen that RHF/6-31g(d) underestimates the stabilizing effect of the methyl groups substantially, but the experimental value of 105 kJ/mol for the difference in ΔE_{stab} of both carbenium ion is correctly reproduced by this ab initio method. In the case of the silicenium ions $(CH_3)_3Si^+$ the RHF/6-31(d) value deviates even more from the experimental E_{stab}. Obviously, the basis set 6-31g(d) is not sufficient to reliably calculate the absolute energies of silicenium ions. Nonetheless it is clear that the stabilizing effect of the methyl groups is quite small for the trimethylsilicenium ion, as expected [21], and the additional stabilizing effect of the methoxy group of $\mathbf{2a}$ is also rather small. If it is assumed that the RHF/6-31g(d) calculation again reproduces the relative stabilities correctly, the increase in ΔE_{stab} owing to the methoxy substituent amounts to only 22 kJ/mol. This agrees very well with the experimental observation, that the silicenium ions $(CH_3)_3Si^+$ and $\mathbf{2a}$ do not differ very much in their reactivity toward nucleophiles, in contrast to the carbenium ions $(CH_3)_3C^+$ and $\mathbf{1a}$.

3.3. Reaction of ions $(CH_3)_3C–O^+(H)CH_3$ and $(CH_3)_3Si–O^+(H)CH_3$

The protonated molecules $\mathbf{1H}^+$ and $\mathbf{2H}^+$ of MTBE and MTSE, respectively, were also reacted with their neutral ethers, with aceton, and with NH_3, and the kinetic data of these reactions are included in Table 2.
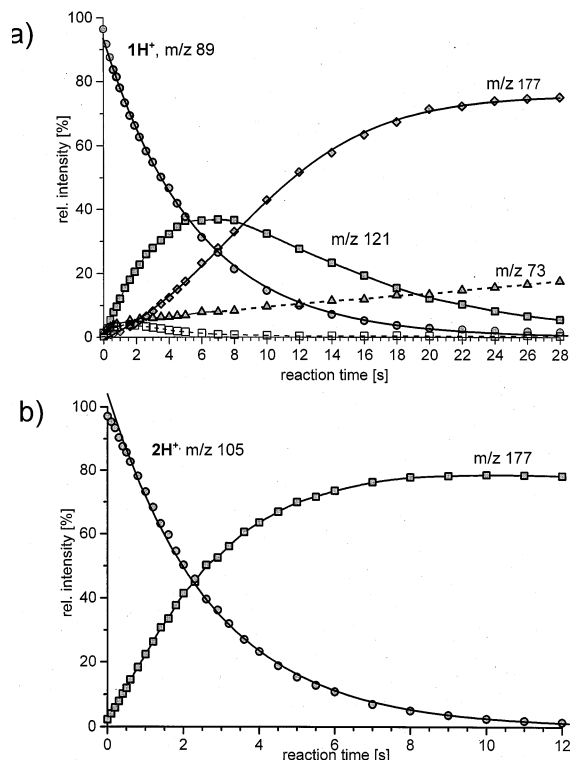

Fig. 3. Reaction of (a) ions $\mathbf{1H}^+$ with MTBE and (b) ions $\mathbf{2H}^+$ with MTSE.

The kinetic plots for the reactions with the ethers and with acetone are shown in Figs. 3 and 4.

The reactions of the protonated silyl ether $\mathbf{2H}^+$ with these reactants are straightforward. In the case of MTSE [Fig. 3(b)] and acetone [Fig. 4(b)] as the neutral reaction partner the only reaction observed is the transfer of a trimethylsilyl cation to the nucleophile, giving rise to the product ion $[(CH_3)_3Si]_2O^+$–CH_3, m/z 177, and $(CH_3)_3Si–O^+=C(CH_3)_2$, m/z 131, respectively. In both cases the transfer of the trimethylsilyl group is efficient, and a competition by transfer of the O methyl group of $\mathbf{2H}^+$ is not observed. It should be remembered that efficient silyl group transfer by silylation reagents is a well known reaction in solution, so that this outcome of the gas phase reactions of $\mathbf{2H}^+$ is unspectacular. From the reactants chosen, only NH_3 (PA 853.6 kJ/mol [22]) is a stronger base than MTSE (PA 847.0 kJ/mol [22]). Hence, a fast exothermic proton transfer is expected as the predominant reaction of $\mathbf{2H}^+$
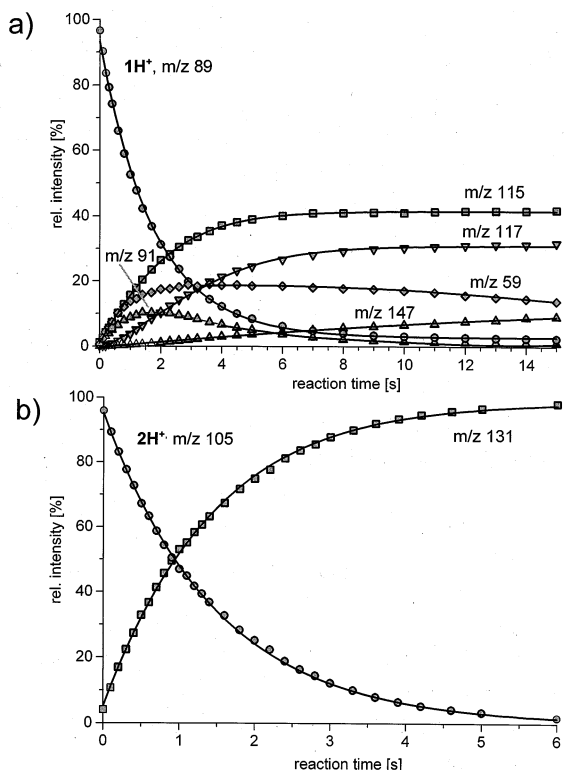
Fig. 4. Reaction of (a) ions $1H^+$ with acetone and (b) ions $2H^+$ with acetone.

with NH_3. Formation of NH_4^+ is indeed the main process in the system $2H^+/NH_3$, but surprisingly the transfer of the trimethylsilyl group competes efficiently (branching ratio $[NH_4^+]/[(CH_3)_3Si–NH_3^+] = 1.2$).

The reactions of the protonated *tert*-butyl ether $1H^+$ with its neutral precursor MTBE, acetone, and NH_3 exhibit a broader variety, as can be seen from Figs. 3(a) and 4(a). Again, a high total efficiency is observed for all three reactions studied. In the case of

MTBE as reactant the main product ion, m/z 177, which accounts for more than 70% of the product ions, corresponds the proton bound homodimer $[(CH_3)_3C–O(CH_3)··H^+··(H_3C)O–C(CH_3)_3]$. However, the kinetic plot shows unambiguously that this is a *secondary* product ion arising from a primary product ion, m/z 121. This latter product ion corresponds to the proton bound heterodimer $[CH_3O(H)··H^+··(H_3C)OC(CH_3)_3]$ of methanol and MTBE. Thus, the reaction (Scheme 1) is initiated by the elimination of C_4H_8 (very likely isobutene) and capture of the protonated methanol by the attacking MTBE molecule and proceeds by fast ligand exchanging of the methanol by a molecule MTBE present in excess in the FTICR cell. Further minor primary reactions observed are the formation of the *tert*-butyl cation, m/z 57, and formation of ion $1a$. However, both-reactions appear to be due to some excited $1H^+$ still present in the cell.

The reactions of $1H^+$ with acetone are summarized in Scheme 2. The three primary product ions generated at m/z 59, m/z 91, and m/z 115 correspond to protonated acetone, to the proton bound heterodimer $[CH_3O(H)··H^+··O=C(CH_3)_2]$ of methanol and acetone, and to addition product of the *tert*-butyl cation to acetone. In particular the proton bound heterodimer $[CH_3O(H)··H^+··O=C(CH_3)_2]$ undergoes a fast ligand switching with the excess acetone present in the FTICR cell yielding the proton bound homodimer of acetone $[(CH_3)_2C=O··H^+··O=C(CH_3)_2]$ at m/z 117. It is not possible to decide positively from the kinetic plot whether the adduct m/z 115 also generates the proton bound homodimer of acetone at m/z 117 by exchange of C_4H_8 against an acetone molecule. To examine secondary reactions of the ion m/z 115, this
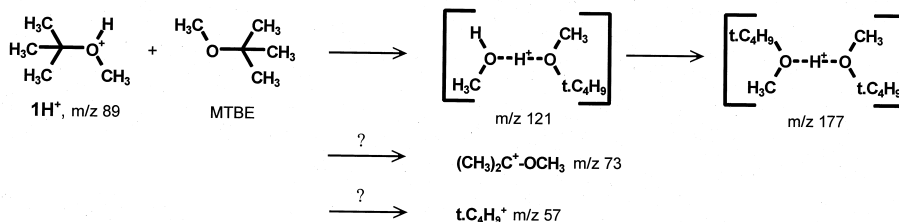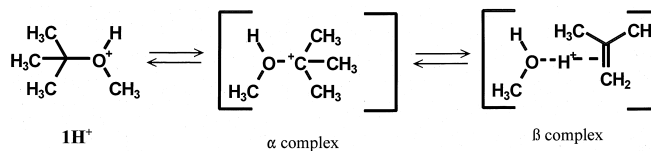

Scheme 1.
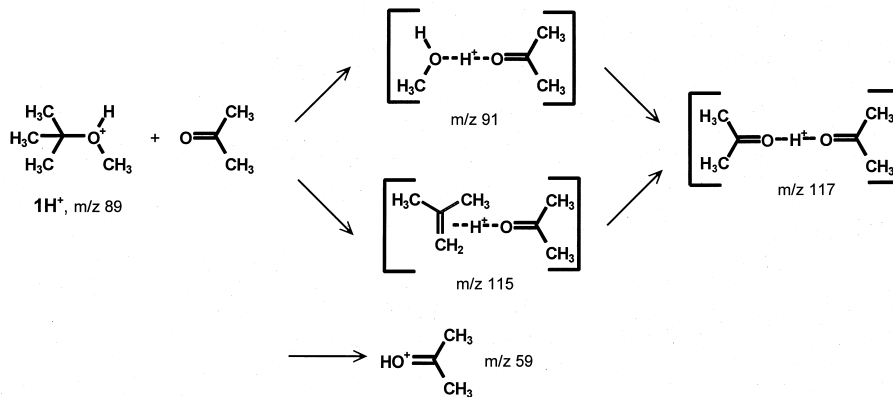
Scheme 2.

ion was isolated in a separate experiment from the reaction mixture of **1H**[+] and acetone after an appropriate reaction time delay. Only a very slow secondary reaction yielding the proton-bound homodimer of acetone, *m/z* 117, was observed with an efficiency <0.5%. This result is significant, since the primary product ion *m/z* 115 may correspond to an *O-tert-tertbutylated* acetone, [(CH_3)_3C–[+]O=C(CH_3)_2] or to a *proton bound heterodimer* [C_4H_{10}··H^{+}··O=C(CH_3)_2] of isobutene and acetone. In this latter case an efficient ligand exchange reaction is expected, as in the case of the other proton bound heterodimers. NH_3 (PA 853.6 kJ/mol [22]) is significantly more basic than MTBE (PA 841.6 kJ/mol [22] so that a fast exothermic proton transfer is predicted for the reaction of **1H**[+] with NH_3. Indeed, NH_4^{+} is the main product ion, but the kinetic plot displays also the formation of a product ion *m/z* 50 as a significant competing reaction. This product ion is converted into the proton bound homodimer [H_3N··H^{+}··NH_3] of NH_3 at *m/z* 35. Thus, the primary product ion *m/z* 50 corresponds obviously to the proton bound heterodimer [CH_3O(H)··H^{+}··NH_3] of methanol and am-

monia, and all three nucleophilic reagents induce the elimination of butene from the protonated ether **1H**[+] with capture of the remaining protonated methanol in a proton bound heterodimer. It is of particular interest, that this reaction path can compete even with exothermic proton transfer as in the case of NH_3 as the nucleophile.

Audier et al. have examined the structure(s) of protonated MTBE **1H**[+] in much detail by MIKE spectrometry and ab initio calculations [5a]. The stimulus for their study was that in specifically deuterated derivatives of **1H**[+] an extensive exchange of all nine H/D atoms of the *tert*-butyl group and the extra H/D atoms at the O atom is observed prior to the fragmentation of metastable **1H**[+]. Their more detailed analysis of this exchange revealed that two populations of **1H**[+] are produced by chemical ionization of MTBE, one minor fraction decomposes to the *tert*-butyl cation without H/D exchange, whereas the major fraction undergoes complete randomization prior to dissociation. This result indicates that metastable ions **1H**[+] represent a system of interconverting structures as shown in Scheme 3: the protonated ether

Scheme 3.

$1H^+$, an INC designated as α complex $[(CH_3)_3C^+\cdot\cdot(H)OCH_3]$ of a *tert*-butyl cation with methanol, and an INC termed β complex $[(CH_3)_2C=CH_2\cdot\cdot H^+\cdot\cdot(H)OCH_3]$ corresponding to a proton bound heterodimer of isobutene and methanol. This was confirmed by ab initio calculations, which showed however, that the α complex is not a stable species, and that the covalent $1H^+$ is the most stable structure with the β complex lying 70 kJ/mol below the energy level defined by the dissociation products $(CH_3)_2C=CH_2$ and $CH_3O^+H_2$.

If these results are used for the interpretation of the ion/molecule reactions studied here one has to recall that metastable ions in an ion beam mass spectrometer contain an appreciable amount of excess energy, just enough to produce fragmentation within a reaction time frame of microseconds. In contrast, ions within a FTICR cell are supposed to be "cool" with a thermal energy corresponding to the temperature of the wall of the FTICR cell. Therefore it is expected that ions in the FTICR cell exhibit the most stable structure, in the case of $1H^+$ the covalently bonded structure of O-protonated MTBE. However, during an ion/molecule reaction in the diluted gas phase of a FTICR spectrometer the ions are "electrostatically" activated by ion/dipole and ion/induced dipole interactions within the collision complex. This may indeed activate fast interconversion between isomeric structures of the reacting ion. In view of this possibility the reactions of $1H^+$ are most effortlessly explained by the reactions of the INC $[(CH_3)_2C=CH_2\cdot\cdot H^+\cdot\cdot(H)OCH_3]$, which is either already transferred as a stable species [5a] from the external ion source into the FTICR cell or, more likely, which is generated from $1H^+$ by the electrostatic activation within the collision complex. This β complex is a proton bound heterodimer, and it is known that these dimers undergo fast exothermic ligand exchanges. Of the two components in the β complex $[(CH_3)_2C=CH_2\cdot\cdot H^+\cdot\cdot(H)OCH_3]$, isobutene (PA 802.1 kJ/mol [22]) is more basic than methanol (PA 754.3 kJ/mol [22]). Nonetheless, during the ligand exchange reaction with MTBE isobutene is exchanged first because methanol is the better partner in a proton bound complex owing to its dipole moment. It should be noted that this reaction step is formally an elimination reaction, but it is difficult to perceive that an E_2 elimination mechanism of O-protonated MTBE yields exclusively the proton bound heterodimer of the attacking base and the leaving group CH_3OH. This would require a *syn*-elimination process and a preorientation of the attacking molecule of the sterically demanding MTBE. In the second step the reactant present in large excess induces exchange of the methanol ligand of the initial proton bound heterodimer. The analogous reaction sequence proceeds with NH_3 as the reactant, but in this case a complete decomposition of the β complex by proton abstraction of the more basic NH_3 is the main process. At first sight the reaction with acetone appears to be an exception since substitution of isobutene by ligand exchange seems to compete with ligand exchange of methanol to generate the product ion *m/z* 115. However, this ion is not a proton bound heterodimer but an oxonium ion arising by *tert*-butylation at the carbonyl-O atom. This looks like the product of a S_N2_B reaction, but in view of the steric hindrance of the back-side attack by the *tert*-butyl group the efficiency of this process appears too high. An alternative mechanism which has been proposed for the reaction of protonated *tert*-butanol with H_2O is a S_N2_F reaction with front side attack of the nucleophile [23]. The PA of isobutene and acetone are not very different. In view of the fast interconversion between $1H^+$ and its INC isomers α complex and β complex [5a] one has also to take into account that during the encounter of the β complex with acetone the proton first accepted by the acetone molecule returns to the isobutene, and that the resulting *tert*-butyl cation is captured by O alkylation by a S_N1 mechanism by the acetone. Similar mechanisms have been shown to occur during *tert*-butylation of benzene (the "Crafts-Friedel" alkylation of Cacace and co-workers [24]).

4. Conclusion

The results of the study of the ion/molecule reactions of each of the most abundant ions in the EI mass spectrum and CI mass spectrum of MTBE and MTSE,

respectively, provide a clear example of the difference in the reactivity of carbenium ions and silicenium ions. In the case of the fragment ions $(CH_3)_2E^+-OCH_3$ (**1a**, E = C, **2a** E = Si) the methoxy substituted carbenium ion **1a** is considerably more stable and less reactive toward a nucleophile than is the *tert*-butyl cation. In fact, no electrophilic reaction has been observed for carbenium ion **1a**. Slow deprotonation of **1a** is observed and may become more efficient with bases stronger than 2-propenyl methyl ether, the conjugated base of **1a**. In contrast to this, the gas phase reactivity and stability of the trimethylsilicenium ion and the silicenium ion **2a** are not very different, each forming easily a stable adduct with nucleophiles even in the dilute gas phase of the FTICR spectrometer, obviously by efficient radiative stabilization. Since the 2-silapropenyl methyl ether is not a stable compound because of the energetic unfavorable Si–C double bond, no deprotonation is expected or observed.

Similarly, the ion/molecule reactions of the protonated ether **1H**$^+$ and **2H**$^+$ reflect the different chemistry of main group elements of the first and second row of the PS. The protonated silyl ether **2H**$^+$ turns out to be a rather strong silylation reagent, since even in the case of the reaction with NH_3 which is more basic than MTSE by almost 7 kJ/mol, the branching of 1.2 between proton transfer and silyl group transfer is found. The present result does not answer the question, however, if the fast silyl group transfer is due to a structure of stable **2H**$^+$ corresponding to an α complex consisting of a trimethyl silicenium ion and methanol, or due to the fact that hypervalent Si derivatives with a trigonal bipyrimidal structure are not a transition state but a stable structure [25]. This would favor S_N2_B reactions with back-side attack. Preliminary ab initio calculation with the 6-31g(d) basis set give no indication of a stable α complex. In the case of **1H**$^+$ the results corroborate the suggestion [5] that protonated MTBE easily converts to a stable β complex consisting of proton-bound isobutene and methanol. With this structure the fast elimination of isobutene observed in all systems can be described as a fast ligand switching reaction which does not require an additional activation energy. Of course, an analogous β complex is not energetically accessible for protonated MTSE, because this would require formation of the unstable silaisobutene.

Acknowledgements

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