Ion-cyclotron Resonance Studies of the Reactions between Ethers and the Trimethylsilyl Cation

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Nucleophilic attack of a dialkyl ether (R–O–R') at the electrophilic silicon centre of the trimethylsilyl cation (Me_3Si^+) produces the 1 : 1 adduct $Me_3Si-\overset{+}{O}RR'$. The adduct generally decomposes by elimination of a neutral fragment. When R > Me, the adduct undergoes characteristic elimination of the olefin (R–H•). When R' > R, the adduct eliminates the larger olefin preferentially. This elimination proceeds by β-hydrogen transfer to oxygen through a four-membered transition state, with the hydrogen transfer being involved in the rate-determining step. When R = Me and R' = CH_2CH_2F, an entirely different decomposition channel is noted, *i.e.* Me_3SiF is eliminated. The adducts from cyclic ethers generally fragment to $Me_3Si-\overset{+}{O}=CH_2$, except for adducts derived from ethylene oxide derivatives, which do not decompose.

TETRAMETHYLSILANE fragments upon electron impact to yield the trimethylsilyl cation.[1] This ion has been advocated as a reagent for c.i. spectroscopy,[2] since a high proportion of the total ion current is carried by the ion (Me_3Si^+ + neutral)$^+$. A number of other studies of alkyl silyl cations have been reported including silyl ions from disiloxanes,[3] ion molecule reactions of tetramethylsilane by time of flight mass spectrometry [1] and ion-cyclotron resonance (i.c.r.) spectroscopy,[4] ion-molecule reactions of fluoromethylsilanes,[5] and c.i. spectra of silanes using methane as reagent gas.[6]


(a) (b)

Alcohols react with Me_3Si^+ in an i.c.r. cell to yield (a).[4] When R ⩾ Et, the decomposing form of (a) undergoes β-H transfer to oxygen with accompanying loss of (R–H•) to yield (b). Here we extend the original study to include ethers, in order to (i) study the fragmentation reactions of adducts formed between ethers and Me_3Si^+, and (ii) extend our work[7] on kinetic isotope effects observed for site-specific hydrogen transfer reactions.

RESULTS AND DISCUSSION

The i.c.r. spectra of tetramethylsilane–ether systems are either listed in Table 1 or recorded in Figures 1 and 2. The genesis of all ion-molecule products has been established by cyclotron ejection experiments. Spectra were determined at 70 eV except in one case (see below) where reactions of ether fragments complicated the interpretation of the spectrum. In general, reactions between Me_3Si^+ and the ether completely dominate the high mass region of the spectrum; reactions between charged ether fragments and neutral ether either do not occur, or are small in comparison.

Dialkyl ethers yield abundant adducts with Me_3Si^+ (see Table 1), and the decomposing form of such species may eliminate an olefin from each side-chain except in the case of a methyl substituent. For example, the ethyl methyl ether and diethyl ether adducts eliminate one and two ethylene units respectively. The corresponding spectrum of [1,1-$^2H_2$]ethyl methyl ether shows

TABLE 1

Ion-cyclotron resonance mass spectra of tetramethyl silane–ether (R–O–R') [a] systems.[b]

(Figures listed are relative power absorptions: pressure of each component = 1×10^{-5} Torr, electron energy = 70 eV; see Experimental section for full details)

Ether	$[ROR'-H]^+$	$[ROR']^{+\bullet}$	$[ROR'+H\bullet]^+$	$[Me_3Si]^+$ *m/e* 73	$[Me_4Si]^{\bullet+}$ *m/e* 88	$[Me_2Si=\overset{+}{O}R]$	$[Me_3Si-\overset{+}{O}H_2]$ *m/e* 91	$[Me_3Si-\overset{+}{O}=CH_2]$ *m/e* 103	$[Me_3Si-\overset{+}{O}CH_2\cdot CH_2]$ *m/e* 117	$[Me_3Si-\overset{+}{O}(H)R']$	$[Me_3Si-\overset{+}{O}(H)R']$ [c]	$[Me_3Si-\overset{+}{O}RR']$
Dimethyl ether	35	8	21	100	5							45
Ethyl methyl ether	20	5	26	100	5	6				41		44
Diethyl ether	100 [d]	13	20	100 [d]	3	5	5			23		26
Ethyl n-propyl ether	37	12 [d]	24	100	12 [d]	2	7			45	2	10
Ethylene oxide	15	10	25	100	5				18 [e]			18 [e]
Propene oxide	20	12	22	100	5							15
Oxetan	22	16	25	100	5			32				22
Tetrahydrofuran	35	20	100 [d]	100 [d]	3			35	6			42
Tetrahydropyran	25	18	22 [d]	100	22 [d]			26	4			38
1,4-Dioxan	10	78 [d]	20	100	78 [d]			3	45			80

[a] R–O–R' may represent either a dialkyl ether (R' > R) or a cyclic ether. [b] This table does not include peaks in the spectrum of tetramethylsilane below *m/e* 73, or ether fragment peaks below $[ROR'-H]^+$. [c] Only produced when R' > R > Me, *i.e.* for ethyl n-propyl ether. [d] These two ions have different compositions but the same integral mass; together they produce the relative absorption shown. [e] Both ions are the same in the case of ethylene oxide.

exclusive loss of CH_2CD_2. The general features of such systems are illustrated by specific reference to the spectrum (Figure 1) of di[1,1-$^2H_2$]ethyl ether. The first elimination (of CH_2CD_2) is entirely specific, and the ion so formed undergoes competitive elimination of methane and $C_2H_2D_2$–C_2H_3D (93 : 7). This behaviour is characteristic of (d), the adduct formed between ethanol and Me_3Si^+, which is known [4] to decompose to (e) and (f) as shown in the Scheme. Similar loss of methane occurs from the corresponding fragment derived from ethyl methyl ether (see Table 1). The basic fragmentations of the diethyl ether adduct may therefore be represented as shown in the Scheme. When the two alkyl groups are different, and both larger than methyl, the larger olefin is eliminated preferentially. For example, for ethyl n-propyl ether (Table 1), the adduct eliminates propene followed by ethylene. Initial elimination of ethylene is noted, but it is a minor process.

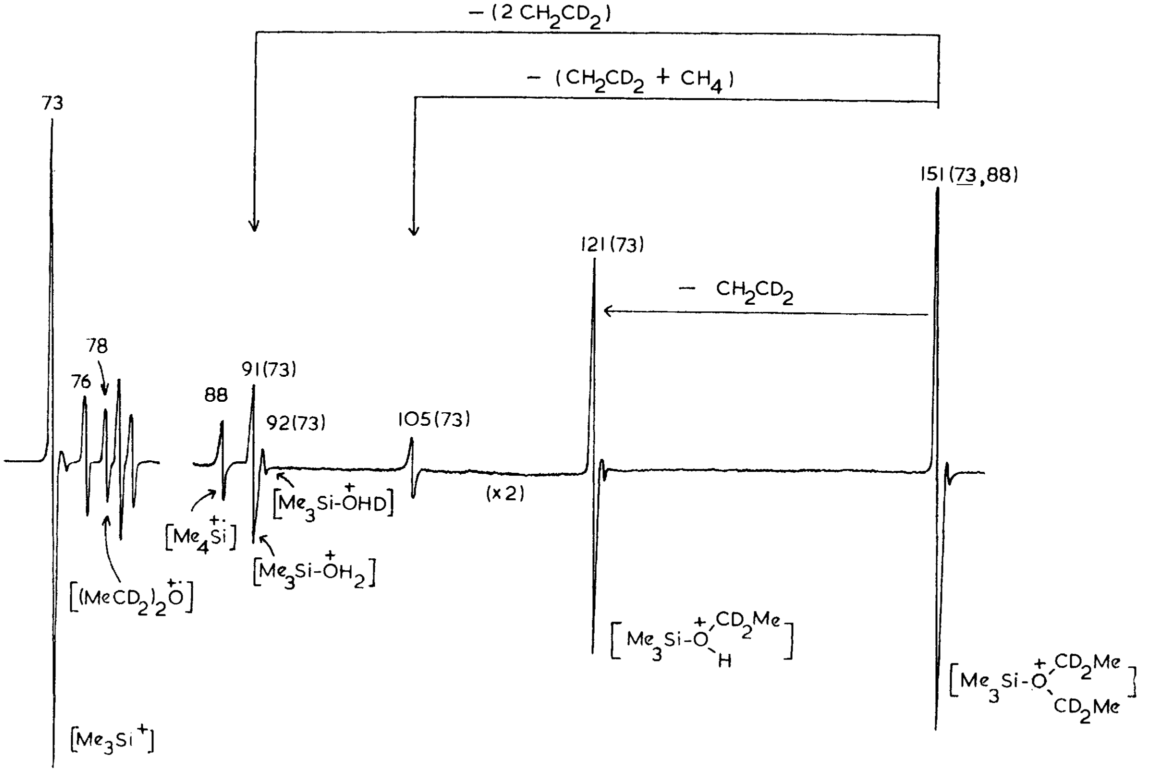
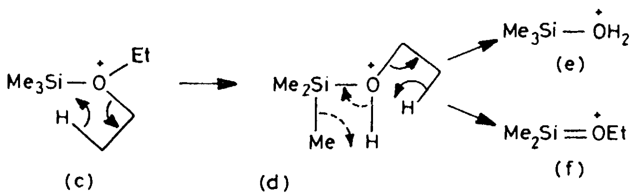


FIGURE 1 I.c.r. spectrum of the system $(MeCD_2)_2O$–Me_4Si. Pressure of each component = 1×10^{-5} Torr. Electron beam 70 eV, $\omega_c/2\pi$ = 125 kHz, and ion transit time 2 = 10^{-3} s. Numbers in brackets denote the mass of the precursor ion



SCHEME

The hydrogen rearrangements which accompany the elimination of ethylene from the ethyl methyl ether adduct and the first elimination of ethylene from the diethyl ether analogue are site specific, and these are therefore appropriate systems for the study of possible primary deuterium isotope effects. Deuterium isotope effects can be large for positive ion decompositions,[7] but in general $k_H/k_D < 10$.[8] A maximum estimate of the magnitude of k_H/k_D for loss of ethylene through a four membered transition state can be obtained from theoretical calculations for hydrogen transfer in *symmetrical* systems A · · · H · · · B. The isotope effect decreases as the angle between A · · · H and B · · · H decreases and is calculated to be 2.3 when the angle is 90° (as in four-membered transition state).[9,10] In *unsymmetrical* systems the isotope effect will be even lower.[9,10] The iso-

TABLE 2

A comparison of deuterium isotope effects for the elimination (adduct — C_2H_4) from the ethyl methyl ether and diethyl ether–Me_3Si^+ systems, with changes in pressure, transit time and electron energy

Pressure (Torr)	Transit time (s)	Electron energy (eV)	Isotope effect (k_H/k_D) (±0.05 eV) Ethyl methyl ether	Diethyl ether
2×10^{-5}	2×10^{-3}	70	1.61	1.39
1×10^{-4}	2×10^{-3}	70	1.72	1.43
2×10^{-5}	2×10^{-3}	70	1.61	1.39
2×10^{-5}	1×10^{-4}	70	1.57	1.36
1×10^{-4}	2×10^{-3}	70	1.72	1.43
1×10^{-4}	2×10^{-3}	15	1.78	1.44

tope effects k_H/k_D measured using [2-^{2}H]ethyl methyl ether and di[2-^{2}H]ethyl ether are listed in Table 2 as a function of total pressure (the relative pressures of both components are always 1 : 1), ion transit time, and electron energy. The isotope effect increases with increasing ion transit time and increasing pressure (*i.e.* with decreasing internal energy of the decomposing ion), and with decreasing energy of the electron beam. The upper value of 1.8 obtained for ethyl methyl ether is of the same order as the theoretical value. The hydride ion transfer is therefore involved in the rate-determining step of this reaction; it is not known whether the elimination is concerted or stepwise.

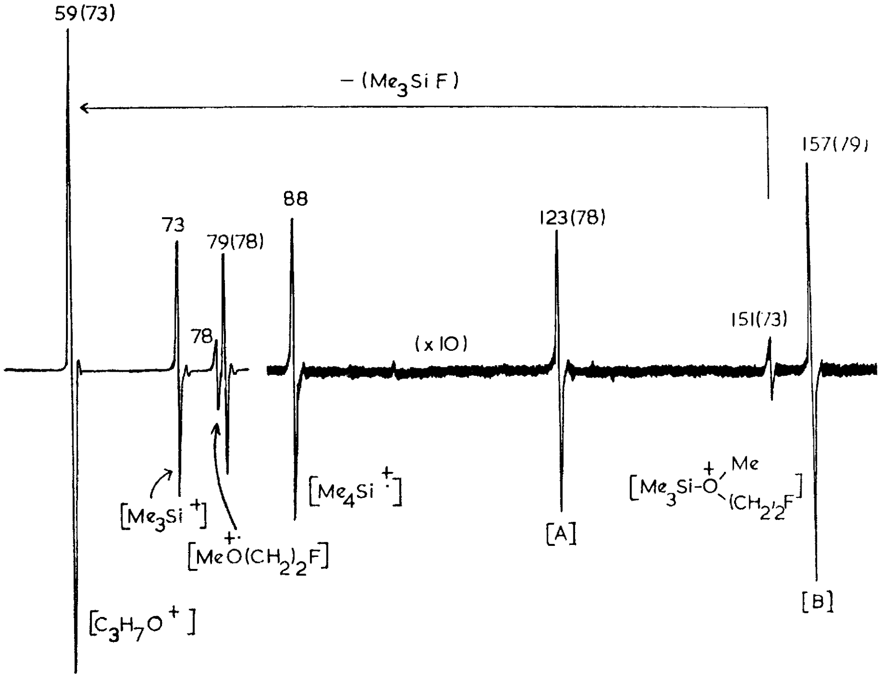
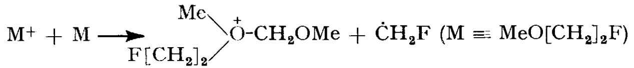


FIGURE 2 I.c.r. spectrum of the system MeOCH$_2$CH$_2$F–Me$_4$Si. Electron beam 11.5 eV, other details as for Figure 1. [A] produced by the reaction

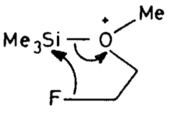


$$M^+ + M \longrightarrow \underset{F[CH_2]_2}{\overset{Me}{\ }}\!\!>\overset{+}{O}\text{-}CH_2OMe + \dot{C}H_2F \ (M \equiv MeO[CH_2]_2F)$$

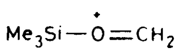
$$[B]\ MH^+ + M \longrightarrow M_2H^+$$

It was our intention to study the change in isotope effect with the changing electronic character of the transition state. To this end we studied 2-fluoroethyl methyl ether, but in this case the usual adduct does not eliminate fluoroethylene. In addition, many reactions occur between ether fragments and the neutral ether when the spectrum is measured at 70 eV. In order to remove such species, the spectrum was determined at 11.5 eV; even so it was still complex, and is described in detail in Figure 2. The usual adduct is detected as a very small peak, whereas the decomposing form of this adduct eliminated trimethylsilyl fluoride [see (g)], certainly the most facile loss noted during this investigation.*

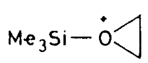
Cyclic ethers also form 1 : 1 adducts with Me$_3$Si$^+$ (see Table 1), which, in turn, eliminate neutral molecules to produce stable fragments whenever possible. The adduct from ethylene oxide does not decompose, those from oxetan, tetrahydrofuran, and tetrahydropyran eliminate C_2H_4, C_3H_6, and C_4H_8 respectively to form (h). The tetrahydrofuran and tetrahydropyran adducts eliminate, to a lesser extent, C_2H_4 and C_3H_6 to give (i), whereas the 1,4-dioxan adduct preferentially loses ethylene oxide to form (i). Of particular interest are the isomeric adducts produced from oxetan and propene oxide, since the propene oxide adduct does not decompose, whereas the oxetan adduct readily eliminates ethylene. This shows that structural integrity of the two ethers is retained upon adduct formation.



(g)



(h)



(i)

In conclusion, we have shown that the reaction between an ether and the trimethylsilyl cation yields an abundant adduct, and that subsequent elimination of a neutral molecule from this species may provide valuable

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* The analogous loss of trimethylsilane from the other adducts does not occur. The product ion from this reaction would be [(ROR') – H$^\cdot$]$^+$. Such ions are observed in all spectra but they are not coupled to Me$_3$Si$^+$. They are produced by loss of an α hydrogen from the ether molecular ion (see, *e.g.* Figure 1, where only an [(MeCD$_2$)$_2$O – D$^\cdot$]$^+$ peak is observed.

structural information. While this is also true for adducts formed with alcohols,[4] it should be stressed that not all adducts formed between organic compounds and Me_3Si^+ fragment, *e.g.* the stable adducts formed from amines, ketones, and aldehydes do not eliminate neutral molecules.

EXPERIMENTAL

I.c.r. spectra were measured at a nominal 70 eV (unless otherwise specified) with a Dynaspec ICR 9 spectrometer, modified to allow direct reading of the ion-transit time.[11] Typical operating conditions were $\omega_c/2\pi = 153.57$ kHz (range 0—150 a.m.u.) or 125.0 kHz (0—200 a.m.u.), emission current 0.2 μA, ion current in the range 10^{-11}—10^{-12} A, and ion transit time 2×10^{-3} s (unless otherwise specified). Cyclotron ejection experiments were carried out as described previously.[4] Isotope effects were calculated from peak abundances after the ^{13}C contribution had been subtracted. Each value listed in Table 2 is a mean of ten measurements.

All unlabelled compounds were either purified commercial products or were prepared by reported procedures.

Di[1,1-$^2H_2$]*ethyl Ether*.—A mixture of sodium [1,1-$^2H_2$]-ethoxide (0.51 g, from [1,1-$^2H_2$]ethanol which was prepared by treatment of acetyl chloride with lithium aluminium deuteride), [1,1-$^2H_2$]ethyl toluene-*p*-sulphinate (1.5 g; prepared [12] from [1,1-$^2H_2$]ethanol, and [1,1-$^2H_2$]ethanol (3.0 g) was heated under reflux for 30 min. The crude product was collected by distillation and fractionated to give the labelled ether, b.p. 34—35 °C (0.21 g, 38%; $^2H_4$ = 100%).

[2-^2H]*Ethanol*.—Ethylene oxide (2.1 g) was added dropwise to a stirred slurry of lithium aluminium deuteride (1 g) in diethyl ether (40 cm^3) maintained at 0 °C. The mixture was stirred at 0 °C for 1 h, and at 20 °C for 3 h. Water (1 cm^3), aqueous sodium hydroxide (15%; 1 cm^3), and water (3 cm^3) were added dropwise, and the liquid decanted from the precipitate and dried ($MgSO_4$). Fractional distillation afforded [2-^2H]ethanol, b.p. 77—78 °C (2.15 g, 94%; $^2H_1$ = 100%).

Di[2-^2H]*ethyl Ether*.—This was prepared [13] from sodium [2-^2H]ethoxide and [2-^2H]ethyl bromide (from [2-^2H]-ethanol [14]); yield 78%, $^2H_2$ = 100%.

[1,1-$^2H_2$]*Ethyl Methyl Ether*.—This was prepared [15] from [1,1-$^2H_2$]ethyl bromide and sodium methoxide in 35% yield ($^2H_2$ = 100%).

[2-^2H]*Ethyl Methyl Ether*.—This was prepared [15] from [2-^2H]ethyl bromide and sodium methoxide in 40% yield ($^2H_1$ = 100%).

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