Association Reactions of Trimethylsilyl Ions

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Adduct ions, $[M + (CH_3)_3Si]^+$, were produced by bimolecular association reactions of trimethylsilyl ions, $(CH_3)_3Si^+$, with acetone, cyclohexanone, anisole, dimethyl ether, 2,5-dimethylfuran, 2-methylfuran and furan in ion cyclotron resonance experiments at 300 K and at pressures of $\sim 10^{-7}$ Torr (1 Torr = 133.3 Pa). The rate constants, k_a, for the association reactions varied from 100% to 2% of the collision rate constants, k_c. The rate constants were independent of pressure, except for furan. Measurements were also made of bond dissociation energies for these adduct ions, $D[(CH_3)_3Si^+—X]$, from equilibrium measurements. The association efficiency, k_a/k_c, increased with increasing bond dissociation energy and with increasing numbers of degrees of freedom, in qualitative agreement with theoretical predictions. Observations pertinent to the dependence of k_a on reactant temperature and relative kinetic energy are discussed. The possibility of determining ion–neutral complex binding energies from radiative association rate constants is considered.

INTRODUCTION

Persistent ion–molecule collision complexes, or 'sticky collisions,' were observed relatively early, although infrequently, in the study of ion–molecule reactions.[1–4] The initial observations of persistent complexes or adduct ions involved species with heavy atoms,[1,2] $[(C_2H_5I)_2]^+$, $[(C_2H_5Br)_2]^+$, $[(C_3H_7I)_2]^+$ or unsaturation,[3] $[(C_3H_3N)_2]^+$, $[C_6H_5—C_6H_6]^+$. These ions were observed at low pressures, presumably formed by bimolecular processes. Other experiments on ionic reactions at high pressures showed the formation of detectable intermediate complex ions by termolecular processes, e.g. $[C_4H_8]^+$ in ethylene[4] and $[C_4H_4]^+$ in acetylene.[5]

Adduct ions, MR^+, in which R^+ is the reactant ion and M is the molecule, are frequently observed as product ions in chemical ionization mass spectrometry (CIMS) when $P = 0.1–1$ Torr (1 Torr = 133.3 Pa); for example, $[MC_2H_5]^+$, but not $[MCH_5]^+$, in the methane CI mass spectra of aromatic hydrocarbons[6] and esters,[7] $[MC_4H_9]^+$ in the isobutane CI mass spectra of alcohols[8] and $[MNH_4]^+$ in the ammonia CI spectra of polar compounds.[9] The mechanisms for the formation of these adduct ions have been studied to some extent, but are not well known. It was shown, for example, that the presumed $[MC_3H_3]^+$ ions in the isobutane CI spectra of alcohols were actually $[M + C_4H_9 - H_2O]^+$ ions.[8,10] The proton affinities of the compounds relative to ammonia and the solvation energies of NH_4^+ with the compounds and with ammonia were shown to affect the formation of MNH_4^+ ions in ammonia CIMS of polar compounds.[9,11]

Tetramethylsilane, $(CH_3)_4Si$ (TMS), is a useful CI reagent gas because of the frequently abundant adduct or association ions, $[M + (CH_3)_3Si]^+$ or $[M + 73]^+$, in the CI mass spectra of polar compounds.[12–15] Two mechanisms have been reported for the formation of these adduct ions: a two-step process involving

$(CH_3)_3SiOH_2^+$ or $(CH_3)_3SiOHR^+$ formed by reactions of the dominant reagent ion, $(CH_3)_3Si^+$, with aliphatic alcohols and ethers and a direct association reaction of trimethylsilyl ions with ketones, phenol and anisole, followed by radiative or collisional stabilization.[16–18] Recent ion cyclotron resonance (ICR) experiments with $(CH_3)_3Si^+$ and acetone indicated that radiative association was the dominant process at low pressures and room temperature.[18] The rate constant for the association reaction was large, 70% of the collision limit. No variation of the second-order rate constant was observed as the acetone pressure was changed from 0.5×10^{-7} to 8×10^{-7} Torr.[18]

Radiative association has been reported within the past few years for reactions of low relative molecular mass ions with low relative molecular mass molecules; however, these association reactions are relatively slow and collisional stabilization is significant.[19–23] Recently, other fast radiatively stabilized association reactions have been reported with acetylene.[24] A theoretical analysis has recently been presented for infrared radiative association reactions of polyatomic ions which shows good general agreement with scattered literature data.[25]

We report here recent observations on association reactions of trimethylsilyl ions which appear to be the general reaction with oxygenated compounds for which dissociative addition reactions are endothermic and compare these results with a theoretical model.

EXPERIMENTAL

The experiments were performed with an Extrel FTMS 2000 instrument with a dual cell.[26,27] The experiments were conducted at approximately room temperature, 300 K, as indicated by a thermocouple attached to the source side of the dual cell.

The compounds were introduced from separate

heated inlet systems whose pressures were independently monitored. Experiments lasted 20–60 min, during which period the pressures in the inlet systems were manually adjusted so that the pressures did not vary by more than ±10%. The pressures of the compounds in the source were monitored with an ionization gauge attached directly to the source and were of the order of 10^{-7} Torr. Ionization gauge pressures were converted into actual pressures using sensitivities relative to that of nitrogen, which were calculated from the equation between relative sensitivity and molecular polarizability[28] using calculated values of the molecular polarizabilities.[29] The pressure of TMS was generally low compared with the pressures of the oxygenated compounds, $\sim 1 \times 10^{-7}$–4×10^{-7} Torr (uncorrected), $\sim 0.3 \times 10^{-7}$–1×10^{-7} Torr (corrected). In the absence of other data, it was assumed that the correction factor for TMS was the same as that for neopentane (2,2-dimethylpropane).

The reagents were obtained from several commercial sources and were used without further purification. There were no indications of significant amounts of impurities in the samples from these and other experiments. Very low concentrations of high-basicity impurities from other experiments being done by FT–ICR were sometimes observed as MH^+ product ions at the very long reaction times needed in experiments to determine the rate constants for slow association reactions. These impurities complicated the kinetic analysis of the formation of $[(CH_3)_2CO]_2H^+$, but when they were properly included in the analysis, consistent rate constants for the association process were obtained.

All experimental operations were performed in the source region of the dual-cell Extrel 2000 instrument. The sequence of the pulses for these experiments began with a 1 ms quenching pulse to clear all ions from the source, followed by a 100 ms pulse for the electron

beam, then a delay time of 100 ms, an ion ejection time of 15 ms, a variable reaction time of 2 ms–300 s to study the kinetics of the addition reactions and a detection time of 15 ms. Isolation of the $(CH_3)_3Si^+$ reactant ions was effected by ejection of all other ions from the cell.[26] All of the isotopic peaks of $(CH_3)_3Si^+$ were observed at m/z 73, 74 and 75. The signal-to-noise ratio was large for all of these experiments, being ≥50 for most of the points in most of the experiments. A wide range of excitation and acquisition parameters give satisfactory results, as evidenced by the observations that the signal increases linearly with excitation voltage and that accurate isotopic ratios are obtained. Important parameters in the present study include electron energy, pressures and perhaps trapping voltages.

The ions were generally produced with 10 eV electrons (nominal energy) to reduce the likelihood of significant internal energy in the reacting trimethylsilyl ions. In some experiments, 10–30 eV electrons were used.

At the lowest pressures used in these experiments, $P(TMS)$ and $P(M) \approx 1 \times 10^{-7}$ Torr, the decrease in relative abundance of $(CH_3)Si^+$ with time was not a simple exponential function of time, as indicated by Fig. 1 for the TMS–dimethyl ether system. In this system, the only reaction product is the $[M + 73]^+$ adduct ion from the association reaction

$$(CH_3)_3Si^+ + CH_3OCH_3 \xrightarrow{k_a} [M + 73]^+ \quad (1)$$
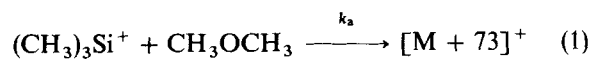
The duration of the introduction period (or the non-exponential decrease in relative abundance of trimethylsilyl ions) decreased with increasing pressure of the reactant compound, as indicated in Fig. 1. Similar observations were made for other association reactions.

Changing the electron energy from 10 to 30 eV had no effect on the apparent induction period or on the
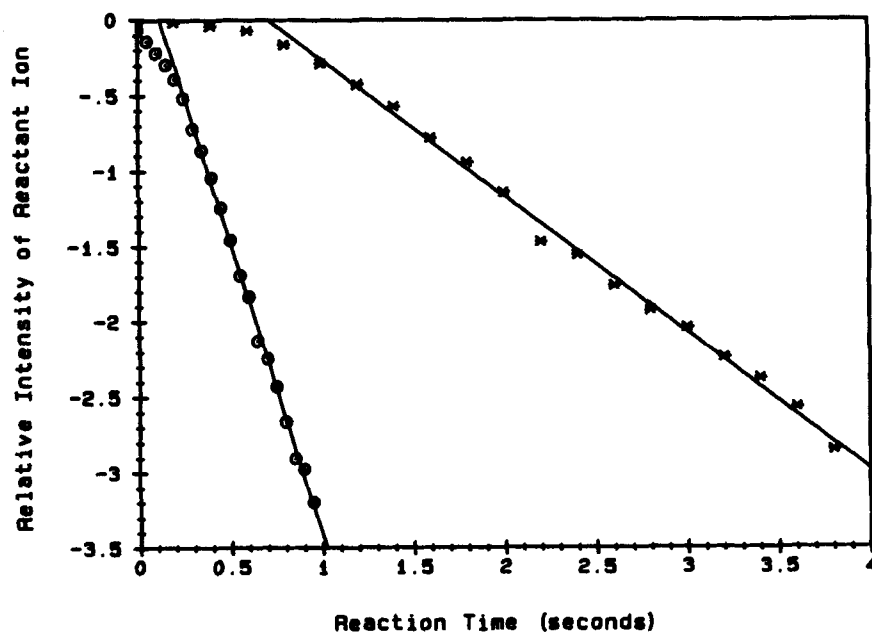

Figure 1. Adduct formation between $(CH_3)_3Si^+$ and CH_3OCH_3. Natural logarithm of relative intensity of $(CH_3)_3Si^+$ vs. time at two different pressures of dimethyl ether at 300 K: (∗) 1.1×10^{-7} Torr; (○) 2.5×10^{-7} Torr. The induction time decreases with increasing pressure.

rate of formation of the adduct ions with acetone, $k_a = (1.8 \pm 0.2) \times 10^{-9}$ cm^3 molecule^{-1} s^{-1} from five experiments at different electron energies. Changing the initial delay time from 5 to 100 ms (which would allow additional collisions for deactivation of electronically or vibrationally excited $(CH_3)_3Si^+$ ions) had no effect on the kinetics of the reaction of trimethylsilyl ions with acetone, $k_a = (2.0 \pm 0.2) \times 10^{-9}$ cm^3 molecule^{-1} s^{-1}.

The induction period increased with increasing kinetic energy of the reacting $(CH_3)_3Si^+$ ions, but the slopes of the disappearance curves for trimethylsilyl ions and, hence, the rate constants for the formation of the adduct ions were independent of the initial excess kinetic energy from 0.03 to 5.0 eV: k_a (m/z 73, anisole) = $(1.8 \pm 0.2) \times 10^{-9}$ cm^3 molecule^{-1} s^{-1}. Similar experiments for the much slower association reaction of $(CH_3)_3Si^+$ with furan also showed that the rate constant for adduct formation was independent of initial kinetic energy of the trimethylsilyl ions: k_a (m/z 73, furan) = $(1.7 \pm 0.1) \times 10^{-11}$ cm^3 molecule^{-1} s^{-1} over the same kinetic energy range. The kinetic energy of the reactant ions was calculated from the amplitude and duration of the r.f. excitation pulse.
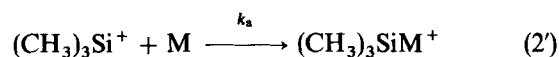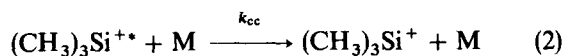
It was noted many years ago that the rate constants for the formation of the persistent ion–molecule complexes decreased rapidly with increasing kinetic energy of the reacting ions.[1-3] It has been reported recently[24] that internal energy in $[C_4H_2]^+$ and $[C_4H_3]^+$ (presumably vibrational energy, ~ 120–130 kJ mol^{-1} (~ 1.23 eV) from formation of these ions by ion–molecule reactions in acetylene) prevents the radiative association reactions with acetylene at pressures of 10^{-7} Torr. An induction period or delay time was necessary to account for the time dependence of the association products, $[C_6H_4]^+$ and $[C_6H_5]^+$. This excess internal energy could be removed by a few non-reactive collisions of $[C_4H_2]^{+\bullet}$ or $[C_4H_3]^{+\bullet}$ with acetylene.

Kinetic studies were made with other systems. Semilogarithmic plots of the relative abundance of trimethylsilyl ions for the dissociative addition reaction of $(CH_3)_3Si^+$ with cyclohexanol to give $(CH_3)_3SiOH_2^+$ were reasonable straight lines (except for the first few points at very short reaction times) under experimental conditions comparable to those in the experiments with TMS and acetone mentioned above. There was no induction period that increased with increasing kinetic energy. The second-order rate constants for the disappearance of trimethylsilyl ions were constant ($\pm 10\%$) and independent of the initial kinetic energy of the ions over a small range of excess kinetic energy, 0.03–5 eV.

Time-dependence experiments were also done on mixtures of TMS with acetone without ion ejection. No induction period was observed for the reaction of trimethylsilyl ions with acetone under these conditions, and semi-logarithmic plots of the relative abundance of trimethylsilyl ions $vs.$ time gave good straight lines with rate constants that were within $\pm 10\%$ of the average values given in Table 2.

These observations are consistent with a model of $(CH_3)_3Si^+$ ions which are unreactive for adduct ion formation when they are translationally excited and reactive when they have been translationally cooled by collisions. This model is similar to that proposed for the reactions of vibrationally excited $[C_4H_2]^{+\bullet}$ and

$[C_4H_3]^{+\bullet}$.[24] The procedure which accelerates the higher and lower mass ions to the point of ejection apparently also accelerates the trimethylsilyl ions. These reactant ions must then be collisionally cooled before they can react by radiative association. Assuming only two states of $(CH_3)_3Si^+$, viz. a translationally hot state (unreactive for association) that is collisionally cooled with rate constant k_{cc} and a translationally cold state that reacts (by association) with a rate constant, k_a, we can write a two-step mechanism:

$$(CH_3)_3Si^{+\bullet} + M \xrightarrow{\ k_{cc}\ } (CH_3)_3Si^+ + M \qquad (2)$$

$$(CH_3)_3Si^+ + M \xrightarrow{\ k_a\ } (CH_3)_3SiM^+ \qquad (2')$$

Such a mechanism gives a double exponential time dependence for the decrease in total trimethylsilyl ion concentration.

A good fit can be obtained from such a double exponential function for the experimental time dependence data on the relative abundance of the trimethylsilyl ions: $A \exp(-k_{cc}[M]t) + B \exp(-k_a[M]t)$. The data were analysed with a standard curve-fitting routine,[30] fitting the disappearance of the trimethylsilyl ions to the double exponential equation above to obtain $k_{cc}[M]$ and $k_a[M]$. No efforts were made to obtain precise values for the rate constants for the collisional cooling of translationally excited trimethylsilyl ions with the samples, k_{cc}. However, these rate constants paralleled the rate constants for the adduct formation reactions of $(CH_3)Si^+$, k_a, being largest with anisole and cyclohexanone and smallest with furan.

Values of $k_a[M]$ were obtained from curve fitting to the double exponential equation and from the slope of the linear portion of the disappearance curve of a semilogarithmic plot of the relative abundance of trimethylsilyl ions $vs.$ time for most of the compounds. In some cases values of $k_a[M]$ were also obtained from the formation of the association ion. Values of $k_a[M]$ (and hence k_a) obtained by the different routines were similar, but not identical, and all values are used to give an indication of the reliability of the rate constant determinations.

Previous experiments gave the same value for the association rate constant for $(CH_3)_3Si^+$ with acetone with tenfold change in pressure of TMS.[18] These data also showed no dependence of the rate constant for the association reaction on the pressure of acetone.[18] The increase in the association rate constant, $k_a((CH_3)_3Si^+,$ furan), with increase in furan pressure was established in two sets of experiments done 3 months apart. A similar increase with increasing TMS pressure was noted for $k_a((CH_3)_3Si^+,$ furan).

The second-order rate constants for the formation of the $[M + 73]^+$ adduct ions are reproducible to within ± 10–20% and the relative values for the same compound at different pressures should be reliable. However, there is some concern about the absolute accuracy of the rate constants, since direct measurements of the pressures could not be made.

The rate constant for the reaction of CH_3CO^+ with $(CH_3)_2CO$ was measured to be $(2.8 \pm 0.1) \times 10^{-10}$ cm^3 molecule^{-1} s^{-1} at pressures of $\sim 2 \times 10^{-7}$ Torr, calculated using the literature value for the correction factor

for ionization gauge readings for acetone relative to nitrogen.[28] This value was the average of four replicate determinations done within 1 h. Six months later the rate constant for this reaction was measured to be $(2.17 \pm 0.09) \times 10^{-10}$ cm^3 molecule^{-1} s^{-1} (average of four replicate determinations within 1 h $\pm$ the standard deviation) using the same correction factor, but with a different ionization gauge. The short-term precision of the measurements is very good and the long-term precision is $\sim \pm 15\%$.

A recent compilation of ion–molecule rate constants[31] includes eight values for this rate constant, ranging from 2.0×10^{-10} to 4.6×10^{-10} cm^3 molecule^{-1} s^{-1}, with an average value of $(3.1 \pm 1.0) \times 10^{-10}$ cm^3 molecule^{-1} s^{-1}. There are four ICR values: 2.0×10^{10}, $(2.33 \pm 0.10) \times 10^{-10}$, $(2.30 \pm 0.10) \times 10^{-10}$ and $(4.3 \pm 0.3) \times 10^{-10}$ cm^3 molecule^{-1} s^{-1}, which give an average of $(2.7 \pm 1.0) \times 10^{-10}$ cm^3 molecule^{-1} s^{-1}.[31] Our average value $((2.5 \pm 0.4) \times 10^{-10}$ cm^3 molecule^{-1} s$^{-1})$ agrees well with the average value of all of the ICR measurements or with the average value of the three relatively consistent (low) ICR values, $k = (2.2 \pm 0.2) \times 10^{-10}$ cm^3 molecule^{-1} s^{-1}.

Uncertainties of ± 15–25% are not uncommon for rate constants of ion–molecule reactions obtained in different laboratories, with different instruments and/or by different techniques. From the 15 reported values for the rate constant for the reaction of $[C_2H_2]^+$ with C_2H_2, one obtains an average value of $(1.20 \pm 0.27) \times 10^{-9}$ cm^3 molecule^{-1} s^{-1} after discarding the discordant high and low values.[31] Similarly, the six reported values for the rate constant for the reaction of $CH_3COCH_3^{+\cdot}$ with CH_3COCH_3 give $(6.1 \pm 1.3) \times 10^{-10}$ cm^3 molecule^{-1} s^{-1}.[31] Other reactions for which several rate constants are reported from different laboratories give similar relative uncertainties.[31] Consequently, we believe that the uncertainties in the present rate constant measurements are reflected in the standard deviations of the measurements, that there are no obvious systematic errors in the measurements and that reliable values of rate constants can be obtained from appropriately corrected ionization gauge pressures.

Experiments were also done on the formation of the protonated acetone dimer ion:

$$(CH_3)_2COH^+ + (CH_3)_2CO \rightarrow [(CH_3)_2CO]_2H^+ \quad (3)$$

over the pressure range 1×10^{-7}–20×10^{-7} Torr at 300 K. Significant contributions occur from both radiative and collisional stabilization, since the apparent second-order rate constant is a pressure-dependent function, $k_a = (13.0 \pm 0.5) \times 10^{-12} + (2.6 \pm 0.2) \times 10^{-22}[M]$ cm^3 molecule^{-1} s^{-1}, calculated using the literature value for the correction of ionization gauge pressures of acetone to actual pressures.

The present results are in reasonable agreement with previously reported values for this system, $k_a = 9.2 \times 10^{-12} + 1.8 \times 10^{-22}[M]$ cm^3 molecule^{-1} s^{-1}.[22] The presence of trace impurities of high proton affinity materials in the ICR cell complicated the determination of this very small rate constant. The rate constant for the disappearance of $(CH_3)_2COH^+$ was significantly larger than that for the formation of $[(CH_3)_2CO]_2H^+$, because of the competing fast proton transfer reaction

from $(CH_3)_2COH^+$ to the trace impurities. However, including proton transfer in the kinetic analysis of the time dependences of all of the reactants and products gave a consistent value for k_a.

Using the experimental association efficiency, $k_a/k_c = 8.4 \times 10^{-4}$, for adduct formation at zero pressure, $D[(CH_3)COH^+—OC(CH_3)_2] = 30$ kcal mol^{-1} (Ref. 32) and Dunbar's equation,[25] we calculate that a difference of $\sim 15\,°C$ would account for the observed difference in association efficiencies between the present results and those reported previously.[22] Similarly, RRKM calculations show that a temperature increase of $15\,°C$ is sufficient to increase the dissociation rate constant for $[(CH_3)_2CO]_2H^+$ by 30% near room temperature.[33] Other experiments in this laboratory have shown that the formation of $[(CH_3)_2CO]_2H^+$ is very sensitive to temperature. A small temperature difference between the two experimental conditions can explain most of the discrepancy between these two measurements.

Relative bond dissociation energies were obtained from equilibrium measurements made at room temperature between pairs of trimethylsilyl adduct ions:

$$[73 + B_1]^+ + B_2 \rightleftharpoons [73 + B_2]^+ + B_1 \quad (4)$$
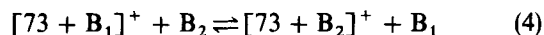
Measured pressures of TMS and two compounds were each introduced through a separate heated inlet system into the ion source. The source pressures were determined from ionization gauge pressures as discussed above.

A quenching pulse was applied to remove all ions from the source. After a short (100 ms) pulse for electron ionization (10 eV) and a 100 ms delay pulse, a 15 ms ion ejection sequence was applied to remove all ions except the trimethylsilyl ions. A variable, but long, reaction time (as much as 300 s) was required to ensure equilibrium between $[73 + B_1]^+$ and $[73 + B_2]^+$.

Typical data are plotted in Fig. 2 as relative intensities vs. reaction time, with a monotonic increase for the more strongly bonded species, a maximum for the less strongly bonded species, and constancy of the ionic ratio $[73 + B_2]^+/[73 + B_1]^+$ at long reaction times. The relative intensity for $(CH_3)_3Si^+$ was virtually zero for times greater than ~ 5 s. Values of $\Delta G°$ were calculated from $\Delta G° = -RT \ln K_{eq}$. The $\Delta G°$ values are the averages of three replicates with standard deviations of $\sim \pm 0.5$ kJ mol^{-1}. Since it has been shown previously that $\Delta S°$ for equilibrium among the trimethylsilyl adducts of alcohols and esters is approximately zero,[34] we have taken $\Delta G° = \Delta H°$.

Several pairs of compounds were studied with TMS to establish a ladder of dissociation energies and the data are given in Table 1. The data are consistent within ± 1.2 kJ mol^{-1}. Values of the dissociation energies, $D[(CH_3)_3Si^+—X]$, or E_b, are calculated using the value of 188 kJ/mol (1.95 eV) for the trimethylsilyl–acetone adduct.[34] When multiple values of $\Delta H°$ are available from different pairs, the average value is taken.

These values for dissociation energies of the trimethylsilyl adduct ions are consistent with the dissociation energies of trimethylsilyl ions with oxygen-containing bases reported previously.[34] Recent reports indicate that $(CH_3)_3Si^+$ ions add to the ring, not the O atom, in furan;[35] however, it is the bond dissociation energy, not the site of addition, which is impor-
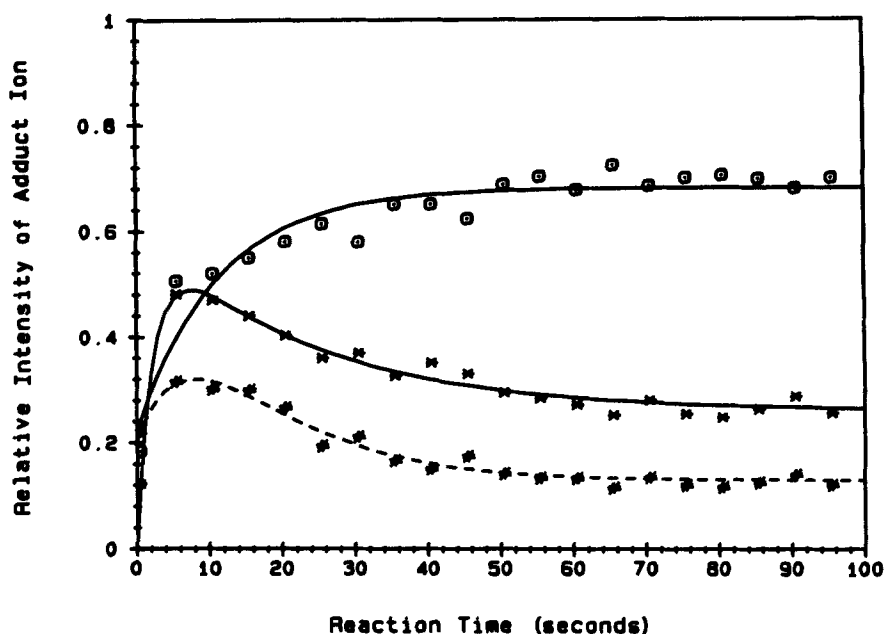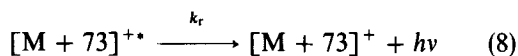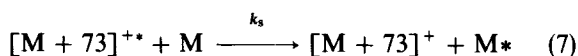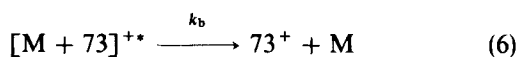
Figure 2. Displacement equilibrium between adduct ions, $[(CH_3)_3Si—DMF]^+ + 2MF \rightleftharpoons [(CH_3)_3Si—2MF]^+ + DMF$. (O) $[(CH_3)_3Si—DMF]^+$, m/z 169; (*) $[(CH_3)_3Si—2MF]^+$, m/z 155; (#) $I(155) \times P(DMF)/I(169) \times P(2MF)$ at 300 K. 2MF = 2-methylfuran; DMF = 2,5-dimethylfuran.

tant in the subsequent discussions of association efficiencies.

RESULTS AND DISCUSSION

The dominant, if not the exclusive, reaction of the trimethylsilyl ions with all of these compounds is adduct formation without the involvement of any stable intermediates. The mechanism of the reaction is the following:

$$73^+ + M \xrightarrow{k_f} [M + 73]^{+*} \qquad (5)$$

$$[M + 73]^{+*} \xrightarrow{k_b} 73^+ + M \qquad (6)$$

$$[M + 73]^{+*} + M \xrightarrow{k_s} [M + 73]^+ + M* \qquad (7)$$

$$[M + 73]^{+*} \xrightarrow{k_r} [M + 73]^+ + h\nu \qquad (8)$$
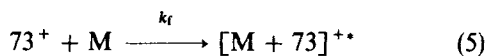
In this analysis, collisional stabilization of the excited complex by reaction with TMS can be neglected, since previous experiments gave the same rate constant for adduct formation between $(CH_3)_3Si^+$ and acetone with TMS pressures which differed by a factor of ten and because the pressure of TMS was generally significantly less than that of the oxygenated compounds, M. Applying the steady-state analysis to the excited intermediate, one obtains the usual expression for the pressure dependence of k_a, the overall second-order rate constant for the disappearance of $(CH_3)_3Si^+$ or the formation of the detectable $[M + 73]^+$ ions (Reaction (1)),[18,19,22] which has been rearranged to give the association efficiency, k_a/k_f:

$$k_a/k_f = (k_r + k_s[M])/(k_b + k_r + k_s[M]) \qquad (9)$$

If the extent of collisional stabilization is relatively small, this equation may be approximated[22] by

$$k_a/k_f = k_r/(k_b + k_r) + k_b k_s[M]/(k_b + k_r)^2 \qquad (10)$$

One may make the standard assumption about the stabilization rate constant, k_s, for the deactivation of the excited intermediate, $[M + 73]^{+*}$, by collision with M, (Reaction (7)), that $k_s = Bk_c' = k_c'$ (strong collision assumption, $B = 1$, and k_c' is the collision rate constant for the excited intermediate complex, $[M + 73]^{+*}$, with M).[19,22] In addition, one may make the reasonable assumption that k_f, the forward rate constant for formation of the excited intermediate complex, is k_c, the collision rate constant for the reaction of $(CH_3)_3Si^+$ with M. One then obtains the equation for the possible

Table 1. Thermochemistry of trimethylsilyl adducts

Compound	$-\Delta G° = -\Delta H°$ (kJ mol^{-1})[a]	E_b (kJ mol^{-1})[b]
Cyclo-hexanone		199
Acetone	11	188
2,5-Dimethylfuran	8 / 14	180
Dimethyl ether	4 / 15	175
Anisole	1 / 5	174
2-Methylfuran	3 / 4	172
Furan	13	159

[a] For reaction $(CH_3)_3SiB_1^+ + B_2 = (CH_3)_3SiB_2^+ + B_1$.
[b] Bond dissociation energy $D[(CH_3)_3Si^+—B]$. All values relative to E_b (acetone) = 188 kJ mol^{-1} from Ref. 32.

Table 2. Rate constants for association: $(CH_3)_3Si^+ + M \rightarrow (M + (CH_3)_3Si)^+$

Compound, M	k_a [a]	Range [b]	k_c [c]	k_a/k_c [d]	P [e]	k_c' [f]
Anisole	21 ± 3	16–27	18.3	1.2 ± 0.2	0.4–1.4	14.7
Cyclohexanone	25 ± 3	20–27	24.1	1.0 ● 0.1	0.4–2	19.6
Acetone	18 ± 3	12–22	26.1	0.69 ± 0.07	0.3–3	23.4
DME [g]	4 ± 1	2–5	15.7	0.26 ± 0.06	0.9–13	14.5
DMF [g]	5 ± 1	4–7	13.7	0.37 ± 0.07	0.9–3	11.3
2MF [g]	2.2 ± 0.4	2–3	13.1	0.17 ± 0.03	0.8–4	11.1
Furan [h]	0.18 ± 0.04	0.1–0.4	12.5	0.014 ± 0.003	1–10	10.9

[a] k_a = Average value of association rate constant, 10^{-10} cm^3 molecule^{-1} s^{-1}.
[b] Range of rate constants from all experiments under several different experimental conditions, 10^{-10} cm^3 molecule^{-1} s^{-1}.
[c] k_c = Collision rate constant, 10^{-10} cm^3 molecule^{-1} s^{-1}, $(CH_3)_3Si^+ + M \rightarrow$, calculated from Refs 36 and 37.
[d] k_a/k_c = Average value of association efficiency.
[e] P = Pressure range of experiments, 10^{-7} Torr.
[f] k_c' = Collision rate constant for intermediate complex $[M + 73]^{+*}$ with M, calculated from Refs 36 and 37.
[g] DME = dimethyl ether; DMF = 2,5-dimethylfuran; 2MF = 2-methylfuran.
[h] Data for furan show a small linear increase with pressure; the k_a reported is the value at zero pressure from a least-squares analysis of the k vs. P data.

pressure variation of k_a, the second-order rate constant for adduct formation, or the association efficiency, k_a/k_c:

$$k_a/k_c = k_r/(k_b + k_r) + k_b k_c'[M]/(k_b + k_r)^2 \quad (11)$$

Table 2 lists values of the second-order rate constants, k_a, for the reactions of $(CH_3)_3Si^+$ with a series of oxygenated organic compounds. Adduct ions, $[M + 73]^+$, are the dominant or exclusive reaction products with all of these compounds. Dissociative addition reactions with these compounds forming the obvious $(M + 73 - X)^+$ products are endothermic, as has been discussed previously for the reaction between $(CH_3)_3Si^+$ and acetone.[18] The average value for the rate constant for the addition of $(CH_3)_3Si^+$ to acetone from the present experiments is in excellent agreement with the average value obtained previously in this laboratory obtained from experiments with the present FTMS-

2000 and with a laboratory made ICR instrument: $(18 \pm 3) \times 10^{-10}$ cm^3 molecule^{-1} s^{-1} in these experiments vs. $(18 \pm 3) \times 10^{-10}$ cm^3 molecule^{-1} s^{-1}.[18]

The association efficiencies, k_a/k_c, where k_a is the experimental second-order association rate constant and k_c is the calculated collision rate constant for trimethylsilyl ions with the compound,[35,36] for anisole and for cyclohexanone are unity, within experimental error. Within the experimental precision of the data, there is no variation with pressure over this range; no increase in k_a/k_c is expected for these very fast association reactions.

Figure 3 shows pressure plots of the association efficiencies for three other compounds studied: acetone, dimethyl ether and furan. Within the precision of the data there is no pressure variation of the rate constants for the reactions of $(CH_3)_3Si^+$ with acetone or with

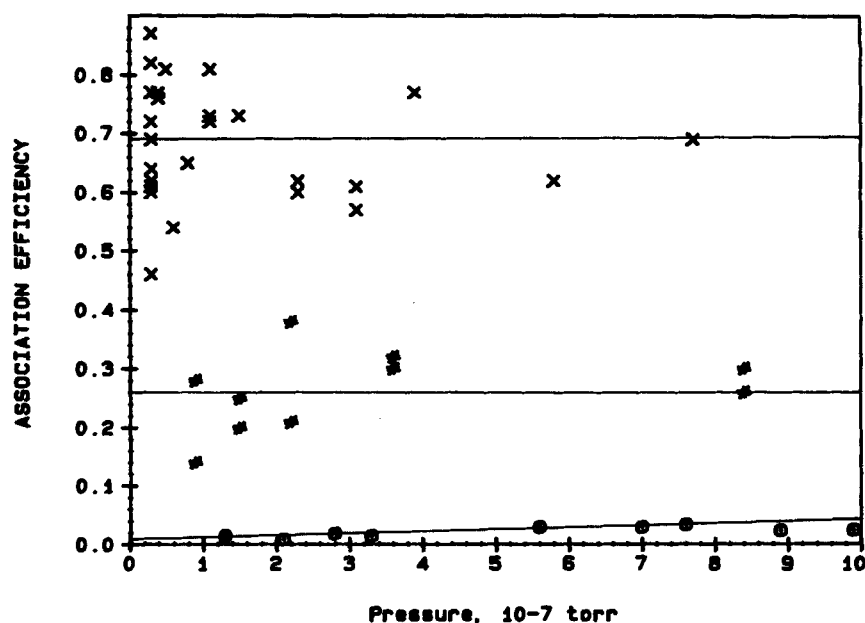Figure 3. Association efficiency, k_a/k_c, vs. $P(M)$ at 300 K for $(CH_3)_3Si^+ + M \rightarrow [M + (CH_3)_3Si]^+$. M = acetone, including data from Ref. 18; (#) M = dimethyl ether; (○) M = furan.

dimethyl ether. The data for acetone include previously reported measurements[18] with the corrected pressures. The large number of points at the lowest pressure, 0.3×10^{-7} Torr, reflects the large number of experiments showing the lack of effects of experimental parameters. The association efficiencies for reactions of $(CH_3)_3Si^+$ with 2,5-dimethylfuran and with 2-methylfuran are also independent of pressure, over the range 1×10^{-7}–4×10^{-7} Torr. The average association efficiencies vary widely for these compounds, from 0.01 to 0.7.

The increase with increasing pressure predicted by Eqn (11) for collisional stabilization is observed only for the slowest association reaction with furan. The slope of the curve of the association rate constant vs. pressure is significantly larger than the standard deviation of the measurements. Collisional stabilization of a similar magnitude by TMS was also noted for the formation of the trimethylsilyl ion–furan adduct ion. For this system, therefore, Eqn (10) must be modified to give

$$k_a/k_f = k_r/(k_b + k_r)$$
$$+ k_b(k_s(F) + k_s'[TMS])/(k_b + k_r)^2 \quad (12)$$

where [F] and [TMS] refer to the concentrations of furan and tetramethylsilane, respectively. A more detailed analysis of these slow association reactions of trimethylsilyl ions will be given subsequently.

The association efficiency depends on the competition between decomposition and radiative stabilization of the excited intermediate complex ions. From the essentially unit efficiency for $(CH_3)_3Si^+$ with anisole and cyclohexanone, one can estimate from Eqn (11) that radiation must be much more rapid than dissociation: k_r/k_b must be greater than about 10. If $k_r \approx 10$–100 s^{-1}, as appears to be the case for IR radiation,[25] then $k_b < 1$–10 s^{-1}. Another interpretation of these data from Eqn (9) is that k_b and k_r may be approximately the same, but are significantly smaller than $k_s[M] = k_c'[M] = 2$–3 s^{-1}, at the lowest pressures of these experiments; therefore, $k_b < 0.5 \text{ s}^{-1}$. In any event, at room temperature these are long-lived complexes with respect to dissociation.

For acetone and dimethylfuran, for which the association efficiencies with trimethylsilyl ions are slightly larger and slightly smaller than 0.5, respectively, one estimates from Eqn (10) that radiation and dissociation occur at nearly the same rates: $k_r/k_b = 2$ for acetone and 0.7 for dimethylfuran. For dimethyl ether and 2-methylfuran, dissociation is 3–5 times faster than radiation. The association efficiency is fairly low, ~ 0.01, for furan and $k_b \gg k_r$.

One notes from the data in Table 2 that the association efficiency increases with increasing molecular complexity or degrees of freedom: cyclohexanone > acetone and 2,5-dimethylfuran > 2-methylfuran > furan. No adduct ions (<0.5%) and, indeed, no reactions were observed in similar experiments between $(CH_3)_3Si^+$ and H_2O or CH_3OH. However, $(CH_3)_3SiOH_2^+$ is observed in mixtures of TMS with traces levels of water under CI conditions[15,38] and $(CH_3)_3SiOHCH_3^+$ ions are easily observed with the addition of small amounts of methanol to TMS mixtures under CI conditions.[38,39]

One also observes that the association efficiency increases with increasing values of the dissociation energy, $D[(CH_3)_3Si^+$—X], since $D[(CH_3)_3Si^+$—c-$C_6H_{10}O] > D[(CH_3)_3Si^+$—$OC(CH_3)_2]$ and $D[(CH_3)_3Si^+$—$OC(CH_3)_2] > D[(CH_3)_3Si^+$—$O(CH_3)_2]$. No adduct ions (efficiency <0.5%) were observed between $(CH_3)_3Si^+$ and benzene, for which the trimethylsilyl cation affinity, $D[(CH_3)_3Si^+$—X] is much lower than that for acetone, 100 vs. 188 kJ mol^{-1}.[34] Increasing molecular complexity and increasing $(CH_3)_3Si^+$—X bond dissociation energies are expected to increase the lifetime of the excited intermediate complex.

Dunbar[25] has recently given an approximate theoretical model for infrared radiative stabilization in association reactions of ions with polyatomic molecules. With a series of reasonable assumptions to define average properties of the intermediate complex ions, the following equation[25] was obtained which relates $R = k_r/k_b$, the ratio of the radiative stabilization rate constant and the dissociation rate constant ot reactants for the excited intermediate complex, $[M + 73]^{+*}$, N, the number of vibrational degrees of freedom in the intermediate complex, T, the temperture of the separated ions and molecules (in K), presumed to be equal and the same as the equilibrium temperature of the system, and the bond dissociation energy, $D[((CH_3)_3Si^+$—X] $= E_b$, in eV:

$$E_b = \left(\frac{1.26}{\log N - 1.076} + 0.001\,86(T - 300)\left(1 + \frac{30}{N}\right) \right)$$
$$\times (1 + 0.098 \log R) \quad (13)$$

Table 3 compares the experimentally observed association efficiencies with the efficiencies calculated from the values of R obtained from Eqn (12), $k_a/k_c = k_r/(k_b + k_r) = R/(1 + R)$. The fourth column in Table 3 shows the association efficiencies calculated assuming $T = 300$ K, the temperature of the ion source. The calculated results are systematically too high, but the qualitative trends are correct: both the calculated and experimental values of the association efficiency increase with increasing bond dissociation energy and with increasing number of degrees of freedom. The theoretical model explains the large differences in association efficiencies for the formation of adduct ions with approximately the same bond dissociation energies but different vibrational degrees of freedom: anisole ($E_b = 1.80$ eV; $N = 81$) $\gg$ dimethyl ether ($E_b = 1.81$ eV; $N = 60$) and dimethyl ether ($E_b = 1.81$ eV; $N = 60$) $\gg$ furan ($E_b = 1.64$ eV; $N = 60$).

The uncertainties in the calculated values for association efficiencies in Table 3 represent the effects of an uncertainty of ± 0.05 eV ($\sim \pm 3\%$) in each bond dissociation energy. The effect of the uncertainty in bond dissociation energy on the association efficiency depends on both the dissociation energy and the number of degrees of freedom. For complex molecules, with large N, the calculated association efficiency is not particularly sensitive to uncertainties in the bond dissociation energy as with anisole, 2,4-dimethylfuran and cyclohexanone.

Two possible explanations can be suggested for the fact that the theoretical association efficiencies are too

Table 3. Theoretical and experimental association efficiencies

Compound	E_b[a]	N[b]	Exptl	Association efficiency (k_a/k_c) 300 K[c]	352 K[d]
Cyclohexanone	2.06	84	1.0 ± 0.1	1.00 ± 0.001	0.998 ± 0.001
Acetone	1.95	63	0.69 ± 0.07	0.94 ± 0.03	0.69 ± 0.13
2,5-DMF[e]	1.85	78	0.37 ± 0.07	0.99 ± 0.01	0.92 ± 0.05
DME[e]	1.81	60	0.26 ± 0.06	0.55 ± 0.15	0.17 ± 0.08
Anisole	1.80	81	1.2 ± 0.02	0.99 ± 0.01	0.90 ± 0.06
2-MF[e]	1.78	69	0.17 ± 0.03	0.86 ± 0.07	0.46 ± 0.15
Furan	1.64	60	0.014 ± 0.003	0.11 ± 0.06	0.025 ± 0.015

[a] $D[(CH_3)_3Si^+$—M] (eV) from Table 1.
[b] Number of vibrational degrees of freedom.
[c] Calculated from Eqn (12) at 300 K.
[d] Calculated from Eqn (12) at 352 K, the temperature at which the theoretical and experimental efficiencies for acetone were the same (0.69).
[e] Abbreviations as in Table 2.

high. One is that the effective temperature of the reactants is greater than 300 K. Consequently, the intermediate complex may have a higher internal temperature than that assumed by the model: $E = E_b + KE + E_{rot} + E_{vib}$.[25] The last column in Table 3 gives theoretical values for the association efficiencies calculated by adjusting the temperature for the TMS–acetone system to obtain agreement between the experimental and theoretical results. This 'effective' temperature is 79 °C (352 K). With this adjustment of temperature, there is excellent agreement between the theoretical and experimental association efficiencies.

The actual temperature of the source itself cannot be this high. This increase in temperature corresponds to an increase in average kinetic energy ($\frac{3}{2}kT$) of only 0.005 eV, an amount of kinetic energy that might be retained by the trimethylsilyl cations in the efficient association reactions. In the case of furan, however, reaction occurs in only one in forty collisions, enough to remove any excess translational energy. The fact that the reactant ion decays exponentially over several half-lives as the furan adduct is formed eliminates the possibility that translationally excited ions are affecting that rate constant.

A second possible explanation of the large theoretical association rate constants is that the binding energies are too high. Absolute values of the binding energies are related to the value of 1.95 eV for the acetone–trimethylsilyl cation binding energy.[34] Results nearly

identical with those obtained by adjusting the temperature, as described above, can be obtained for the association efficiencies by using a value of 1.80 eV for $D((CH_3)_3Si^+$—$OC(CH_3)_2)$. It may be possible, then, that measurement of radiative rate constants in conjunction with Dunbar's theoretical approach[25] would provide a method of measuring ion–neutral complex binding energies complementary to existing methods.

We have approximated the association efficiency, k_a/k_f, by k_a/k_c, in which k_f is the forward rate constant for the formation of the excited intermediate complex and k_c is the collision rate constant for the reaction of $(CH_3)_3Si^+$ with M. No data are available for k_f values for the different compounds. If k_f is less than k_c, then the experimental association efficiencies will be less than the calculated association efficiencies, $k_r/(k_b + k_r)$. We note that the ratios of experimental to theoretical association efficiencies at 300 K are significantly lower for the furans (0.2–0.4) than for dimethyl ether and acetone (0.5–0.7). These differences may result from different k_f values related to the bonding of $(CH_3)_3Si^+$ to the different classes of compounds: O-bonding for dimethyl ether and acetone and C-bonding for the furans.[35]

Acknowledgement

REFERENCES

1. R. F. Pottie, R. Barker and W. H. Hamill, *Radiat. Res.* **10**, 644 (1959).
2. R. F. Pottie and W. H. Hamill, *J. Phys. Chem.* **63**, 877 (1959).
3. A. Henglein, *Z. Naturforsch., Teil A* **17**, 41 (1962).
4. F. H. Field, *J. Am. Chem. Soc.* **83**, 1523 (1961).
5. M. S. B. Munson, *J. Phys. Chem.* **69**, 872 (1965).
6. M. S. B. Munson and F. H. Field, *J. Am. Chem. Soc.* **89**, 1047 (1967).
7. M. S. B. Munson and F. H. Field, *J. Am. Chem. Soc.* **88**, 4337 (1966).
8. F. H. Field, *J. Am. Chem. Soc.* **92**, 2672 (1970).
9. T. Keough and A. J. DeStefano, *Org. Mass Spectrom.* **16**, 537 (1981).
10. B. L. Jelus, R. K. Murray, Jr, and B. Munson, *J. Am. Chem. Soc.* **97**, 2362 (1975).
11. P. Rudewicz and B. Munson, *Anal. Chem.* **58**, 2903 (1986).
12. T. J. Odiorne, D. J. Harvey and P. Vouros, *J. Phys. Chem.* **76**, 3217 (1972).
13. T. J. Odiorne, D. J. Harvey and P. Vouros, *J. Org. Chem.* **38**, 4274 (1973).
14. R. N. Stillwell, D. I. Carroll, J. C. Nowlin and E. C. Horning, *Anal. Chem.* **55**, 1313 (1983).
15. D. Clemens and B. Munson, *Org. Mass Spectrom.* **20**, 360 (1985).
16. R. Orlando, F. Strobel, D. P. Ridge and B. Munson, *Org. Mass Spectrom.* **22**, 597 (1987).
17. R. Orlando, D. P. Ridge and B. Munson, *Org. Mass Spectrom.* **23**, 527 (1988).
18. R. Orlando, D. P. Ridge and B. Munson, *J. Am. Soc. Mass Spectrom.* **1**, 144 (1990).

19. C. R. Herd and L. M. Babcock, *J. Phys. Chem.* **91**, 2372 (1987).
20. C. R. Herd and L. M. Babcock, *J. Phys. Chem.* **93**, 245 (1989).
21. T. C. Pentecost and L. M. Babcock, paper presented at the 37th ASMS Conference on Mass Spectrometry and Allied Topics, Miami Beach, FL, May 21–26, 1989.
22. P. Kofel and T. B. McMahon, *J. Phys. Chem.* **92**, 6174 (1988).
23. J. J. Fisher and T. B. McMahon, paper presented at the 37th ASMS Conference on Mass Spectrometry and Allied Topics, Miami Beach, FL, May 21–26, 1989.
24. V. G. Anicich, A. D. Sen and M. J. McEwan, paper presented at the 38th ASMS Conference on Mass Spectrometry and Allied Topics, Tucson, AZ, June 3–8, 1990.
25. R. C. Dunbar, *Int. J. Mass Spectrom. Ion Processes* **100**, 423 (1990).
26. R. B. Cody, J. A. Kinsinger, S. Ghaderi, I. J. Amster, F. W. McLafferty and C. E. Brown, *Anal. Chim. Acta* **178**, 46 (1985).
27. Y. Pan and D. P. Ridge, *J. Phys. Chem.* **93**, 3375 (1989).

28. J. E. Bartmess and R. M. Georgiadis, *Vacuum* **33**, 149 (1983).
29. K. J. Miller and J. A. Savchik, *J. Am. Chem. Soc.* **101**, 7206 (1979).
30. J. H. Noggle, *F-Curve*. LEDS, Research Triangle Park, NC.
31. Y. Ikezoe, S. Matsuoka, M. Takebe and A. Viggiano, *Gas Phase Ion–Molecule Reaction Rate Constants Through 1986*. Maruzen, Tokyo (1987).
32. D. S. Bomse and J. L. Beauchamp, *J. Phys. Chem.* **85**, 488 (1981).
33. W. Forst and Z. Prasil, *J. Chem. Phys.* **51**, 3006 (1968).
34. A. C. M. Wojtyniak and J. A. Stone, *Int. J. Mass Spectrom. Ion Processes* **74**, 59 (1986).
35. M. E. Crestoni, S. Fornarini and M. Speranza, *J. Am. Chem. Soc.* **112**, 6929 (1990).
36. T. Su and W. Chesnavich, *J. Chem. Phys.* **76**, 5183 (1982).
37. D. P. Ridge, in *Structure/Reactivity and Thermochemistry of Ions*, ed. by P. Ausloos and S. G. Lias, p. 1. Reidel, Boston (1987).
38. D. Clemens, MS Thesis, University of Delaware (1983).
39. D. Clemens and B. Munson, *Anal. Chem.* **57**, 2022 (1985).