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## ICR Mass Spectrometry Study of Gas-Phase Ion Chemistry Between Dimethylchloronium Ions and Alkylamines

### INTRODUCTION

It is well established that the end-product ions formed in the ion/molecule reactions of pure methylchloride are the dimethylchloronium ions,  $(\text{CH}_3)_2\text{Cl}^+$  [1-4]. Since these products are fairly unreactive toward methyl chloride neutrals they are found to accumulate in the system with almost 90% yield at a pressure of one Torr in a high pressure mass spectrometer [5].

Dimethylchloronium ions have been used as alkylating agents in both gas and liquid phase reactions. Such alkylation processes are essentially bimolecular nucleophilic displacement reactions and are usually highly exothermic for bases such as dimethyl ether, ethanol, ammonia, and many aromatic bases [6-10]. The observed relative rates for many of these reactions [8,10] reveal a negative temperature dependence, which strongly supports evidence for a double well potential model as summarized by Magnera and Kebarle [11].

The objective of the present experiments is to measure the rate constants of methylation reactions (1) of  $\text{C}_1$ - $\text{C}_4$  monoalkylamines by dimethylchloronium ions:



in an ion cyclotron resonance (ICR) mass spectrometer. As such, this is an extension of previous work concerning ethylation reactions of alkylamines by diethylchloronium ions [12].

### EXPERIMENTAL

The pulsed ICR mass spectrometer used in this work has already been described [13]. The pulse sequence, the magnetic field and RF frequency conditions are the same as reported in reference [12].

The total pressure at which all experiments are performed is  $(1.0 \pm 0.1) \times 10^{-5}$  Torr ( $1.33 \times 10^{-5}$  mbar), as indicated by an ionization gauge.

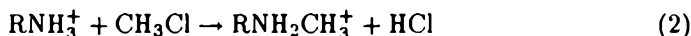
The accuracy of the values of the rate constants determined mainly on the precision of the ionization gauge indications. We expect that the rate constant values are accurate to within 30% for the reactions studied.

Methyl chloride and methylamine from Matheson were of the best available purity ( $\sim 99\%$ ). An analysis of methylamine has shown an impurity of 0.4% of dimethylamine. Ethylamine from Matheson and the propyl-, isopropyl- and butylamines from Aldrich were better than 99% pure and were used without any further purification.

The mixture of methyl chloride with alkylamines were prepared in a known ratio: (1:19) in a separate high vacuum manifold.

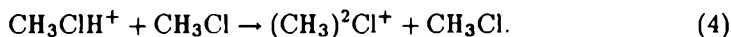
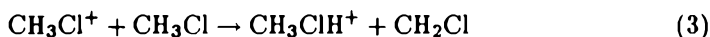
## RESULTS AND DISCUSSION

Since reaction channel (1) is highly exothermic it is expected to be the main reaction pathway. However, a second reaction channel, namely, methyl radical transfer from methyl chloride to protonated alkylamine:



even if exothermic by  $< 40$  kJ/mol, might also contribute to the formation of  $\text{RNH}_2\text{CH}_3^+$  species, especially at low concentration of methyl chloride in the mixture. In order to avoid the interference of this second reaction channel, experiments were performed in mixtures containing 5% of alkylamine. Under these conditions it is reasonable to expect in a first approximation, that immediately after the end of the ionizing electron pulse about 95% of the ions originate from methyl chloride, the remaining coming from alkylamine. Such a distribution of ion species is indeed observed in the mass spectrum at a very short time  $t < 1$  ms after the electron pulse. The subsequent time evolution of the intensities of ions depends of the rate of processes involved between these ion species and the neutrals present in the mixture.

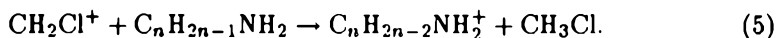
Under the present concentration conditions the abundant molecular  $\text{CH}_3\text{Cl}^+$  ion will react preferentially in the fast reaction (3) ( $k_3 = 12.5 \times 10^{-10}$  cm<sup>3</sup>s<sup>-1</sup> [2]), followed by reaction (4):



The contribution of the charge transfer processes from  $\text{CH}_3\text{Cl}^+$  to alkyloamines, whose rate constants are of the same order as in reaction (3), should not be important in the formation of the amine molecular ions owing to the low concentration of amines in the mixtures.

The relatively abundant  $\text{CH}_2\text{Cl}^+$  species do not react further with methylchloride (endothermic reaction by  $\sim +180$  kJ/mol, [14]) and seem not to interfere

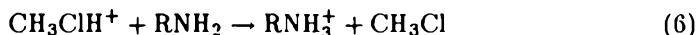
with the methylation processes. On the other hand, the  $\text{CH}_2\text{Cl}^+$  ions react with alkylamines in an exothermic hydrogen abstraction process in which a  $(M - 1)$  alkylamine ion species is formed:



In this way the disappearance of fragment ion  $\text{CH}_2\text{Cl}^+$  can be, in principle, followed by the alkenyl amine ions formation.

The alkylamine molecular ions, their fragment- and product-ions (i.e. those formed in reaction (5)) are observed in the mass spectrum, and the sum of their fractional intensities increases with reaction time. Preliminary results show that such fragment ions as  $\text{CH}_2\text{NH}_2^+$ ,  $\text{CHNH}_2^+$ ,  $\text{CHNH}^+$  seem to be unreactive towards chloro- or bromo- methane [15]. Therefore, we expect that with increasing reaction time the fragment ions from alkylamine will exhibit characteristic ion/molecule reactions with alkylamine neutrals only, leading mainly to the formation of the protonated alkylamine species,  $\text{RNH}_3^+$ .

Finally, the efficient proton transfer from  $\text{CH}_3\text{ClH}^+$  to  $\text{RNH}_2$ , forming protonated alkylamine ions ( $k \approx 10^{-9}$ )  $\text{cm}^3\text{s}^{-1}$ ;



opens another reaction channel for the formation of alkylamine product ions which will accumulate with time in the system.

An example of such behaviour is depicted in Fig. 1 for the system  $\text{CH}_3\text{Cl}/\text{C}_2\text{H}_5\text{NH}_2$  in the ratio 19:1. The time evolution of the main reacted ions,  $\text{CH}_3\text{ClH}^+$  and  $\text{CH}_2\text{Cl}^+$ , may be clearly seen, as well as the formation of product ions of interest:  $(\text{CH}_3)_2\text{Cl}^+$ ,  $\text{C}_2\text{H}_5\text{NH}_2\text{CH}_3^+$ , and those of amine ions accumulating in the system:  $\text{CH}_3\text{NH}_2^+$ ,  $\text{C}_2\text{H}_5\text{NH}_3^+$ ,  $(\text{CH}_3)_2\text{NH}_2^+$  and  $\text{C}_2\text{H}_4\text{NH}_2^+$ .

The rate constants of methylation processes in mixtures of methyl chloride and alkylamines have been calculated from a numerical simulation to find solutions for a system of first- and second-order kinetic differential equations, [16]. However, in order to obviate the evaluation of the rate of dimethylchloronium ions disappearance in reaction (1) from the interference of the proton transfer reaction (6), we started the numerical simulation of the rate for each methyl chloride/alkylamine mixture only after the total disappearance of the  $\text{CH}_3\text{ClH}^+$  species. For instance, in the case of  $\text{CH}_3\text{Cl}/\text{C}_2\text{H}_5\text{NH}_2$  system (Fig. 1) the numerical simulation for dimethylchloronium disappearance rate is started at 0.08 s. Keeping this procedure in mind we will review each system successively.

### 1. The $\text{CH}_3\text{Cl}:\text{CH}_3\text{NH}_2$ Mixture

The observed ions within the experimental time range 80–140 ms are  $\text{CH}_2\text{NH}_2^+$  ( $m/z$  30),  $\text{CH}_3\text{NH}_3^+$  ( $m/z$  32),  $(\text{C}_2\text{H}_6\text{N})^+$  ( $m/z$  44),  $(\text{CH}_3)_2\text{NH}_2^+$  ( $m/z$  46),  $\text{CH}_2\text{Cl}^+$  ( $m/z$  49,51),  $(\text{CH}_3)_3\text{NH}^+$  ( $m/z$  60) and  $(\text{CH}_3)_2\text{Cl}^+$ , (Fig. 2).

The numerical simulation is more difficult in this case for the following reasons. Firstly, the reactions of small amounts of dimethylamine and ethylamine impurities in methylamine with  $(\text{CH}_3)_2\text{Cl}^+$  to give  $\text{C}_3\text{H}_9\text{HN}^+$  ( $m/z$  60) species, and secondly,

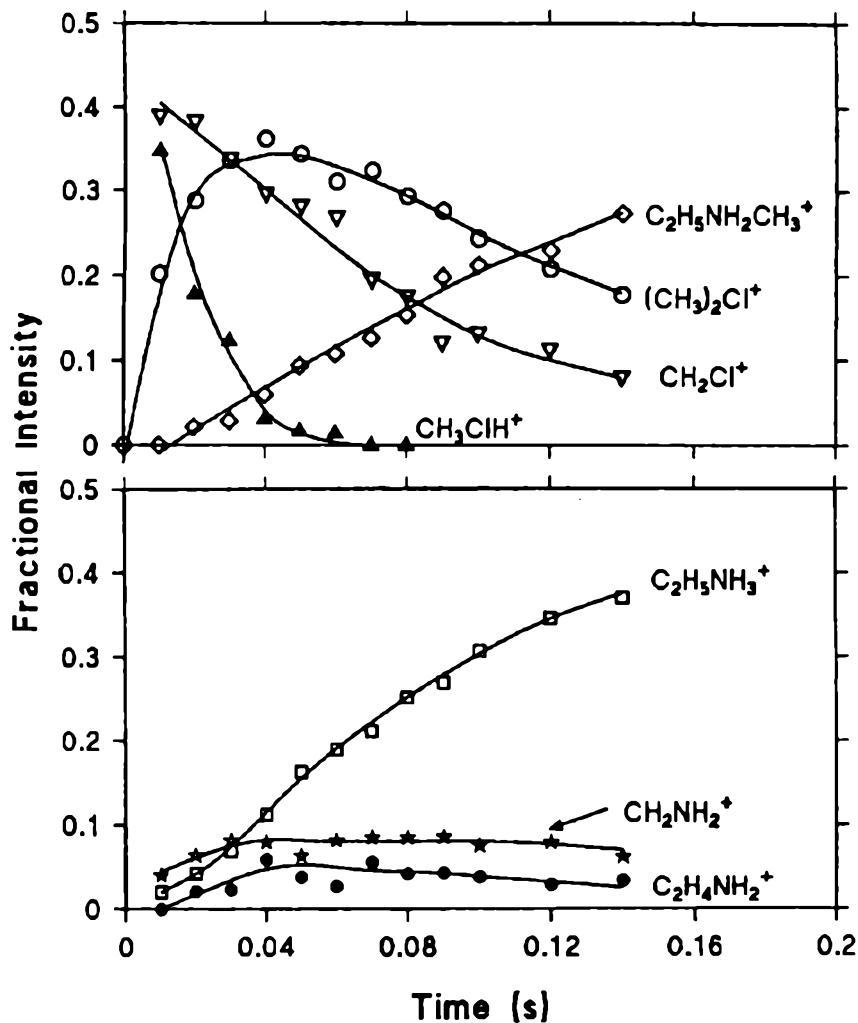


Fig. 1. Temporal variation of ion species formed in the  $\text{CH}_3\text{Cl}/\text{C}_2\text{H}_5\text{NH}_2$  (19:1) mixture. The lines are calculated by assuming known rate constants

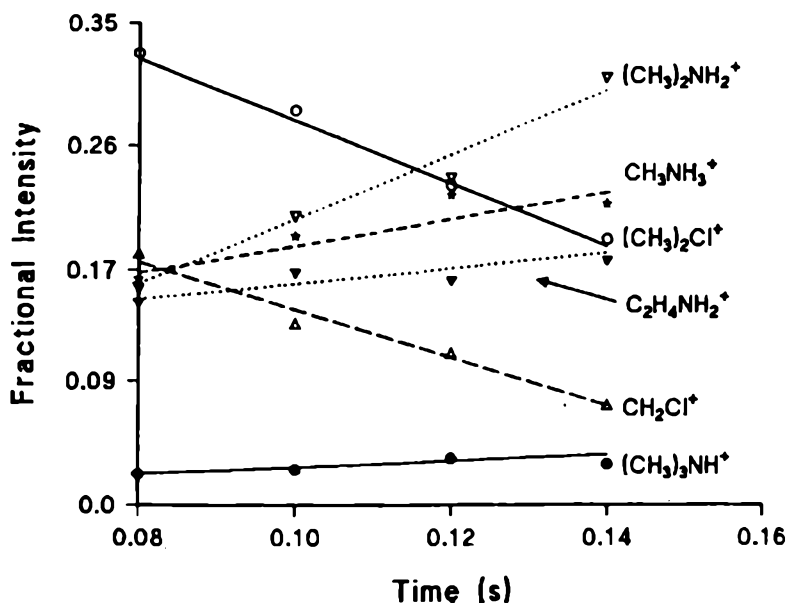
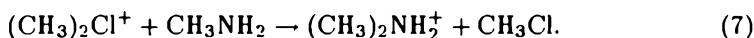


Fig. 2. Temporal variation of ion species formed in the  $\text{CH}_3\text{Cl}/\text{CH}_3\text{NH}_2$  (19:1) mixture after the disappearance of the  $\text{CH}_3\text{ClH}^+$  species. The lines are numerically simulated by assuming known rate constants

the protonated methylamine,  $\text{CH}_3\text{NH}_3^+$ , itself also reacts in a sequence of methylation reactions with methylamine, to give protonated dimethyl- and trimethyl-amine species ( $m/z$  46 and 60). These reactions are of course in competition with the main reaction, namely the methylation of methylamine by dimethylchloronium ions:

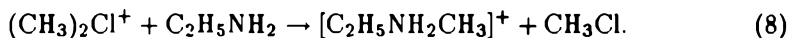


A simulated average value for the rate constant of reaction (7) was found to be  $(5.3 \pm 0.5) \times 10^{-10} \text{ cm}^3\text{s}^{-1}$  in which two extreme alternatives were taken into account: (a) the contribution to the  $m/z$  60 species formation originating from impurities in methylamine, and (b) the contribution to  $m/z$  60 formation from  $\text{CH}_3\text{NH}_3^+$  ions in the methylation reaction sequence. In both cases known reaction rate constants were used [17].

## 2. The $\text{CH}_3\text{Cl}:\text{C}_2\text{H}_5\text{NH}_2$ Mixture

The observed ions and their time evolution are shown in Fig. 1.

In the time interval starting at 70 ms (when the  $\text{CH}_3\text{ClH}^+$  signal has disappeared completely) and ending at 140 ms, the  $(\text{CH}_3)\text{Cl}^+$  species intensity decreases continuously to a final value that is reduced by 14.6%. During the same time interval the intensity of  $[\text{C}_2\text{H}_5\text{NH}_2\text{CH}_3]^+$  ions ( $m/z$  60) increases by 14.7%, indicating that dimethylchloronium ions are consumed in the methylation reaction of ethylamine only:



The rate constant of reaction (8) is, therefore, equal to the disappearance rate of dimethylchloronium ions and is found to be  $(5.3 \pm 1.5) \times 10^{-10} \text{ cm}^3\text{s}^{-1}$ .

### 3. The $\text{CH}_3\text{Cl} : n\text{-C}_3\text{H}_7\text{NH}_2$ Mixture

In addition to the dimethylchloronium ions ( $m/z$  65,67), the  $[\text{C}_3\text{H}_7\text{NH}_2\text{CH}_3]^+$  ( $m/z$  74) species, the protonated propylamine,  $\text{C}_3\text{H}_7\text{NH}_3^+$  ( $m/z$  60), and the  $\text{CH}_2\text{Cl}^+$  fragment ion ( $m/z$  49,51), small intensities of  $\text{C}_3\text{H}_8\text{Cl}^+$  ( $m/z$  58),  $\text{C}_3\text{H}_7^+$  ( $m/z$  43),  $\text{CH}_3\text{NH}_3^+$  ( $m/z$  32) and  $\text{CH}_2\text{NH}_2^+$  ( $m/z$  30) species are found in the mass spectrum.

Following the previously established simulation procedure one sees that within the time interval from 80 to 140 ms the ion/molecule reactions (9) and (10) seem to be the most important (Fig. 3).

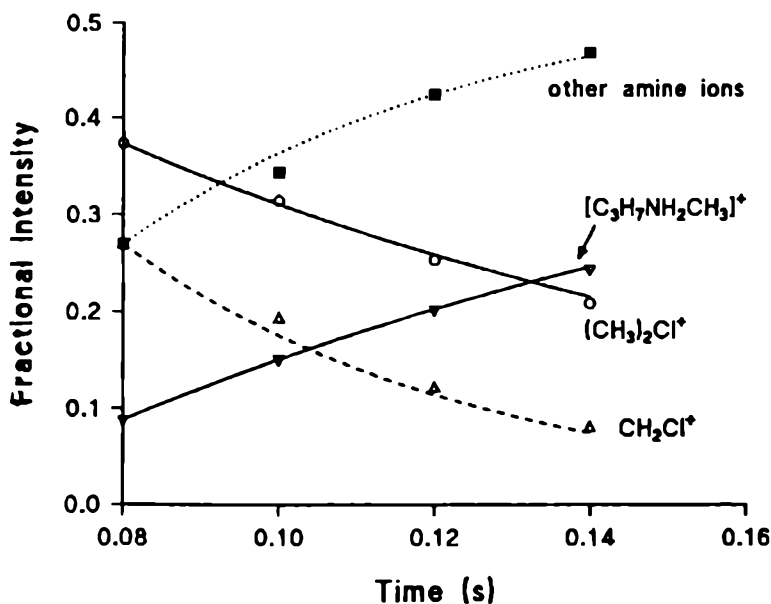


Fig. 3. Temporal variation of ion species formed in the  $\text{CH}_3\text{Cl}/n\text{-C}_3\text{H}_7\text{NH}_2$  (19:1) mixture after the disappearance of the  $\text{CH}_3\text{ClH}^+$  species. The lines are numerically simulated by assuming known rate constants

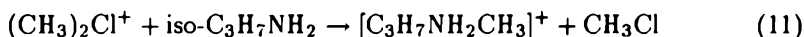


The experimental results show that during this 60 ms time interval the fractional intensity of dimethylchloronium ions has decreased by 16%, while that of the

product ions,  $[\text{C}_3\text{H}_7\text{NH}_2\text{CH}_3]^+$ , has increased by the same amount. This suggests strongly that the only disappearance reaction channel for dimethylchloronium ions is reaction (9) for which the rate constant is found to be  $(5.7 \pm 1.6) \times 10^{-10} \text{ cm}^3\text{s}^{-1}$ .

#### 4. The $\text{CH}_3\text{Cl}:\text{iso-C}_3\text{H}_7\text{NH}_2$ Mixture

The ion species and the ion/molecule processes observed in this mixture are similar to those in the methyl chloride/n-propylamine system. However, the iso-propylamine being more reactive, the total fractional intensity of corresponding amine ion species is higher than in the  $\text{CH}_3\text{Cl}/\text{n-C}_3\text{H}_7\text{NH}_2$  mixture (Fig. 4). The numerical simulation of the rate constant for the methylation reaction (11).



within the time interval 60 to 180 ms, yield a value of  $(7.1 \pm 2.3) \times 10^{-10} \text{ cm}^3\text{s}^{-1}$ .

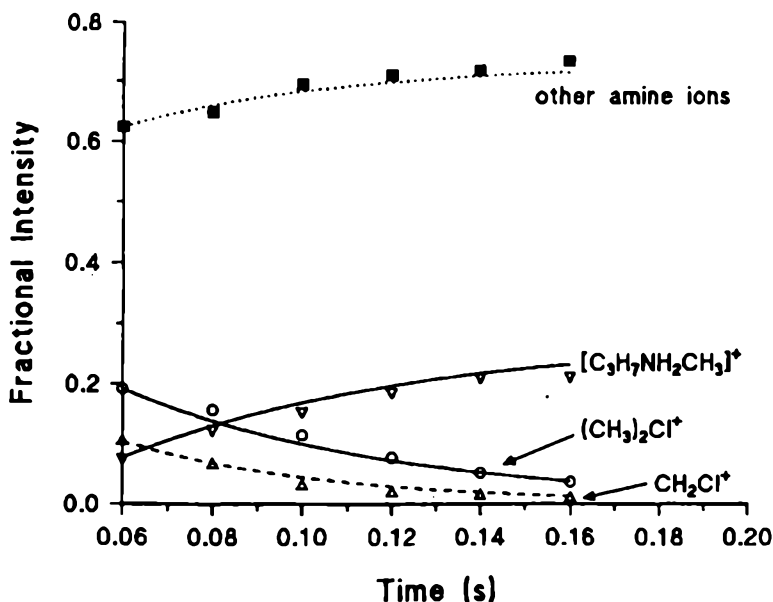


Fig. 4. Temporal variation of ion species formed in the  $\text{CH}_3\text{Cl}/\text{iso-C}_3\text{H}_7\text{NH}_2$  (19:1) mixture after the disappearance of the  $\text{CH}_3\text{ClH}^+$  species. The lines are numerically simulated by assuming known rate constants

#### 5. The $\text{CH}_3\text{Cl}:\text{n-C}_4\text{H}_9\text{NH}_2$ Mixture

With lengthening of the carbon atom chain in alkylamines, the mass spectrum of the mixture increases in complexity. Within the time interval 80 to 200 ms the main ions are  $(\text{CH}_3)_2\text{Cl}^+$  ( $m/z$  65,67),  $[\text{C}_4\text{H}_9\text{NH}_2\text{CH}_3]^+$  ( $m/z$  88),  $\text{C}_4\text{H}_9\text{NH}_3^+$  ( $m/z$  74) and  $\text{CH}_2\text{Cl}^+$  ( $m/z$  49,51). Much smaller amounts of ions having  $m/z$  102, 72, 57,

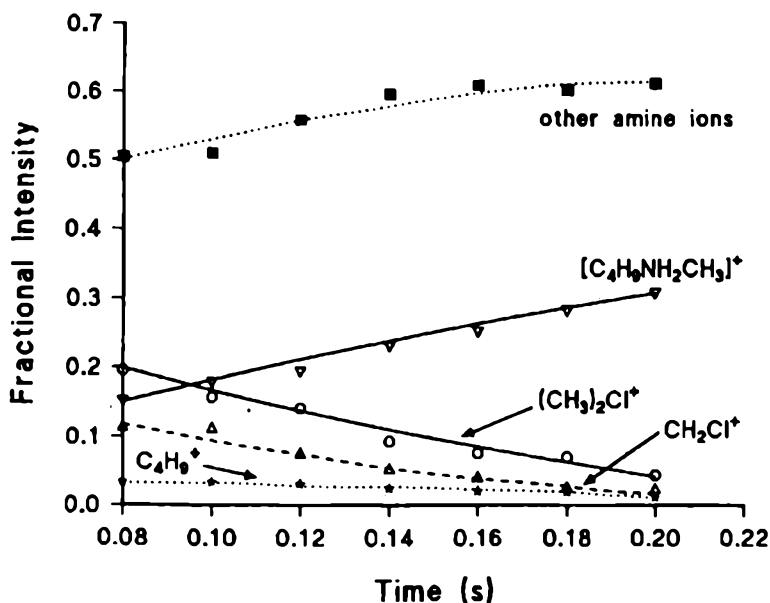


Fig. 5. Temporal variation of ion species formed in the  $\text{CH}_3\text{Cl}/n\text{-C}_4\text{H}_9\text{NH}_2$  (19:1) mixture after the disappearance of the  $\text{CH}_3\text{ClH}^+$  species. The lines are numerically simulated by assuming known rate constants

47, 44, 41, 32 and 30 are observed in this mixture. Fortunately, the methylation reaction of butylamine by dimethylchloronium ions:



seems to be balanced with the decrease in fractional intensity of the reactant ion being compensated by an equal increase in the product ion  $m/z$  88, Fig. 5. The rate constant for reaction (12) was found to be  $(6.9 \pm 2.2) \times 10^{-10} \text{ cm}^3\text{s}^{-1}$ .

In the case of the  $\text{CH}_3\text{Cl}/\text{sec-C}_4\text{H}_9\text{NH}_2$  mixture the complexity of the mass spectrum and its time evolution makes it difficult to unravel the ion/molecule reactions. Such behaviour could be expected owing to the higher reactivity of *sec*-butylamine. The decrease by 16% of relative intensity of the reactant ion,  $(\text{CH}_3)_2\text{Cl}^+$ , is not compensated by the increase in methylated butylamine,  $[\text{C}_4\text{H}_9\text{NH}_2\text{CH}_3]^+$ , species. The missing balance of ion intensities is not easily attributed to another specific ion product, owing to the existence of several competing methylation processes in this system. Due to this difficulty we have not attempted to simulate the experimental results, although they are reproducible.

Summing up, the rate constants of the methylation reactions (7), (8), (9), (11) and (12) are essentially of the same magnitude; approximately  $(6 \pm 2) \times 10^{-10} \text{ cm}^3\text{s}^{-1}$ . Compared with the collision rate ( $k_{\text{coll}} \approx 16 \times 10^{-10} \text{ cm}^3\text{s}^{-1}$ ) [18], on the average every third collision is a reactive one. This average rate constant



value is close to the rate constant for the reaction between dimethylchloronium ions and ammonia ( $k = 7.5 \times 10^{-10} \text{ cm}^3\text{s}^{-1}$ ) [8]. Perhaps the rate coefficients for the methylation reaction increases slightly with the lengthening of the carbon chain and the presence of tertiary carbon atoms, but the experimental error margin is too high to accredit this observation. In comparison with ethylation reactions of the same alkylamines the methylation reactions are faster, as expected, by at least a factor 2, [12]. Steric effects are probably responsible for this observed difference.

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