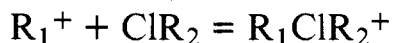


# Binding Energies and Stabilities of Chloronium Ions from Study of the Gas-Phase Equilibria:



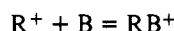
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**Abstract:** Measurement of the temperature dependence of the gas-phase equilibrium constants for the reaction  $C_2H_5^+ + CH_3Cl = C_2H_5ClCH_3^+$  leads, via van't Hoff plots, to  $\Delta H = -30.7$  kcal/mol and  $\Delta S = -30.7$  cal/deg (standard state 1 atm). The temperature dependence for the rate constant of the forward direction of the reaction was determined as  $k = 3.5 \times 10^{-15} T^{-4.575} \text{ cm}^6 \text{ molecules}^{-2} \text{ s}^{-1}$  (for  $CH_4$  as third body). The rate constant for the reaction  $C_2H_5^+ + CH_3Cl = C_2H_4 + CH_3ClH^+$  was found to be considerably slower than the ADO collision rate. This fact was used for an estimate of the proton affinity of  $CH_3Cl$ ,  $PA(CH_3Cl) \approx 158$  kcal/mol. The equilibria  $sec-C_3H_7^+ + CH_3Cl = sec-C_3H_7ClCH_3^+$  were measured and led to  $\Delta H = -22.9$  kcal/mol and  $\Delta S = -44.5$  cal/deg. The enthalpies obtained above lead to the heats of formation:  $\Delta H_f(C_2H_5ClCH_3^+) = 110.8$ ,  $\Delta H_f(sec-C_3H_7ClCH_3^+) = 149.8$ , and  $\Delta H_f(CH_3ClH^+) \approx 189.7$  kcal/mol.

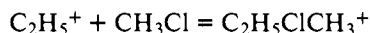
## Introduction

Measurements of ion-molecule reaction equilibria<sup>1</sup> in the gas phase were recently expanded to include the Lewis acid-base equilibria represented by the reaction



$R^+$  is a carbocation and  $B$  a  $\sigma$ ,  $\pi$ , or  $n$  donor base. Measurements of the temperature dependence of the equilibrium constant  $K$  with a pulsed electron beam high-pressure mass spectrometer lead, via van't Hoff plots, to  $\Delta H$  and  $\Delta S$ . In earlier work experiments involving  $R^+ = \text{alkyl}^+$  and the  $\sigma$  bases  $H_2$ ,  $CH_4$ , alkanes were performed, which led to determinations of the binding energies of  $RB^+ = \text{protonated alkanes}$ .<sup>2</sup> Experiments with  $R^+ = \text{alkyl}$  and  $B = OH_2$  provided data on protonated alcohols,<sup>3</sup> while experiments with  $R^+ = \text{acyl cations}$ , i.e.,  $\text{alkylCO}^+$  and  $B = OH_2$ , led to the protonated acids<sup>3,4</sup>  $\text{alkylC(OH)}_2^+$  and heats of formation for  $\text{alkylCO}^+$ .

The present work describes the first results for systems where  $R^+ = \text{alkyl}$  and  $B = \text{alkyl chloride}$ . The resulting  $RB^+$  is a chloronium ion, as illustrated by the reaction of  $C_2H_5^+$  with  $CH_3Cl$ .



Chloronium ions belong to the larger class of halonium ions, whose importance for organic reactions in condensed phases is well recognized. A comprehensive summary of this work can be found in a recent book by Olah.<sup>5</sup> Recently, chloronium ions have been also subjects of theoretical molecular orbital calculations. Jorgensen<sup>6</sup> using MINDO/3 and STO-3G has made calculations for acidic alkyl chloronium ions, i.e., protonated alkyl chlorides =  $\text{alkyl ClH}^+$ . Interested in the effect of solvation on the stability of carbonium ions, Jorgensen<sup>6</sup> also published results on  $\text{alkyl (ClH)}_n^+$  using  $HCl$  as a probe for solvation of the carbonium ions by solvents containing halo atoms. McManus<sup>7</sup> has studied cyclic chloronium ions with MINDO/3.

Halonium ions have been observed also in the gas phase. Cyclic halonium ions  $CH_2(CH_2)_nX^+$  are often postulated as important fragments in the mass spectra of alkyl halides.<sup>8</sup> Beauchamp<sup>9</sup> has made several studies of ion-molecule reactions of alkyl halides. Some of the reactions occurring in these systems lead to formation of halonium ions.

In spite of the great importance of halonium ions, no experimental measurements leading to the enthalpies of formation of these ions have been reported. The present work was aimed to rectify this deficiency.

The thermochemical information obtained for the chloronium ions is discussed in section A of Results and Discussion; section B describes the kinetics of the ion-molecule reaction systems used for the ion equilibria measurements. This second section is addressed primarily to gas-phase ion chemists.

## Experimental Section

The measurements were made with a pulsed electron beam high ion source pressure mass spectrometer which has been described previously.<sup>10</sup> Ultrahigh-purity methane at known pressures in the 1–4 Torr range was passed in slow flow through the temperature controlled ion source-reaction chamber. Known amounts of alkyl chloride and other gases required for the production of  $R^+$  were added to the methane carrier gas. The time dependence of the ions escaping from the ion source after the ionizing electron pulse was obtained after magnetic mass separation and collection of ions of a given mass in a multiscaler.

## Results and Discussion

**A. Binding Energies and Heats of Formation of Chloronium Ions.** The thermochemical information from the present work is summarized in Table I. Included in Table I, for comparison with the chloronium ions  $R_1ClR_2^+$ , are some oxonium ions  $R_1OHR_2^+$ . The heats of formation for the oxonium ions were calculated from the experimentally measured proton affinities of the ethers<sup>1,18</sup>  $R_1OR_2$ .

The bond energies  $R_1^+ - ClR_2$  may be expected to follow the same trends with changes of substituents  $R_1$  and  $R_2$  as the  $R_1^+ - OHR_2$  bonds; however, the chloronium bonds should be weaker. For substituents  $H$ ,  $CH_3$ ,  $C_2H_5$ ,  $n-C_3H_7$ ,  $sec-C_3H_7^+$ ,  $n-C_4H_9$ ,  $sec-C_4H_9$ , and  $t-C_4H_9$  one expects that the binding energy will decrease with  $R_1$  changing in the above order since the Lewis acidity of  $R_1^+$  decreases with increasing availability of electrons to the "vacant" carbonium ion orbital. Changes of  $R_2$  in the above order, i.e., in order of increasing electron-donating ability of  $R_2$ , will increase the basicity of  $R_2Cl$  and  $R_2OH$  and thus increase the binding energy. (For a semi-quantitative correlation between the LUMO of  $R_1^+$  and HOMO of  $R_2Cl$  see Jorgenson<sup>6</sup>). The expected decrease of the binding energy with change of  $R_1^+$  will be considerably larger than the increase of binding energy with a corresponding change of  $R_2$ .

The limited data in Table I are in line with the above predictions. The binding energies decrease in the order  $R_1 = H$ ,  $CH_3$ ,  $C_2H_5$ ,  $sec-C_3H_7$ . Also the chloronium ions  $R_1^+ - ClR_2$  are seen to have bond energies which are weaker than the oxonium ions. Thus the bond energies  $CH_3^+ - ClH$ ,  $C_2H_5^+ -$

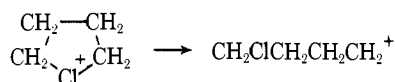
**Table I.** Comparison of Binding Energies in Some Chloronium and Oxonium Ions<sup>a</sup>

RB <sup>+</sup> = R <sup>+</sup> + B	$\Delta H_f(\text{RB}^+)$	$\Delta H$ reaction
CH <sub>3</sub> OH <sub>2</sub> <sup>+</sup> = CH <sub>3</sub> <sup>+</sup> + OH <sub>2</sub>	137 <sup>b</sup>	66.2 <sup>b</sup>
CH <sub>3</sub> ClH <sup>+</sup> = CH <sub>3</sub> <sup>+</sup> + ClH	189.7 <sup>c</sup>	49.2 <sup>c</sup>
C <sub>2</sub> H <sub>5</sub> OHCH <sub>3</sub> <sup>+</sup> = C <sub>2</sub> H <sub>5</sub> <sup>+</sup> + HOCH <sub>3</sub>	120.9 <sup>d</sup>	50.1 <sup>d</sup>
C <sub>2</sub> H <sub>5</sub> ClCH <sub>3</sub> <sup>+</sup> = C <sub>2</sub> H <sub>5</sub> <sup>+</sup> + ClCH <sub>3</sub>	169 <sup>f</sup>	30.7 <sup>e</sup>
<i>sec</i> -C <sub>3</sub> H <sub>7</sub> OHCH <sub>3</sub> <sup>+</sup> = <i>sec</i> -C <sub>3</sub> H <sub>7</sub> <sup>+</sup> + HOCH <sub>3</sub>	110.8 <sup>g</sup>	33.2 <sup>g</sup>
<i>sec</i> -C <sub>3</sub> H <sub>7</sub> ClCH <sub>3</sub> <sup>+</sup> = <i>sec</i> -C <sub>3</sub> H <sub>7</sub> <sup>+</sup> + ClCH <sub>3</sub>	149.8 <sup>f</sup>	22.9 <sup>e</sup>

<sup>a</sup> All values in kcal/mol.  $\Delta H_f(\text{R}^+)$  from Lossing and Semeluk:<sup>11</sup> R<sup>+</sup> = CH<sub>3</sub><sup>+</sup> = 261, C<sub>2</sub>H<sub>5</sub><sup>+</sup> = 219, *sec*-C<sub>3</sub>H<sub>7</sub><sup>+</sup> = 192 kcal/mol.  $\Delta H_f(\text{H}^+)$  = 367 kcal/mol.  $\Delta H_f$  neutrals from Cox and Pilcher.<sup>12</sup> <sup>b</sup> From PA(CH<sub>3</sub>OH) = 182, Kebarle.<sup>1</sup> <sup>c</sup> From PA(CH<sub>3</sub>Cl) ≈ 158 kcal/mol, based on present results for reaction 6. Beauchamp<sup>9a</sup> has estimated PA(CH<sub>3</sub>Cl) = 160 kcal/mol. <sup>d</sup> From PA(C<sub>2</sub>H<sub>5</sub>OCH<sub>3</sub>) = 194 kcal/mol, Beauchamp, McIver, Taft, et al.<sup>18</sup> <sup>e</sup> Present work; see Table I. <sup>f</sup> From  $\Delta H$  reaction; see Table I and  $\Delta H_f(\text{R}^+)$ , see footnote a. <sup>g</sup> From PA(*sec*-C<sub>3</sub>H<sub>7</sub>OCH<sub>3</sub>) ≈ 196 kcal/mol (present work) estimate based on PA(CH<sub>3</sub>OCH<sub>3</sub>) = 190 and PA(C<sub>2</sub>H<sub>5</sub>OCH<sub>3</sub>) = 194 kcal/mol.<sup>13</sup>

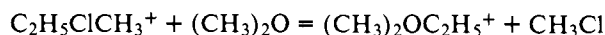
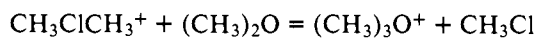
ClCH<sub>3</sub>, and *sec*-C<sub>3</sub>H<sub>7</sub><sup>+</sup>-ClCH<sub>3</sub> are 74, 61, and 69% of the bond energies in the corresponding oxonium ions. One might have expected these percentages to be more uniform; however, a more detailed investigation<sup>14</sup> of the bonding in the dialkyl chloronium ions for R<sub>1</sub> = CH<sub>3</sub>, C<sub>2</sub>H<sub>5</sub>, C<sub>3</sub>H<sub>7</sub>, and *t*-C<sub>4</sub>H<sub>9</sub> based on MINDO/3 calculations and experimental results for a larger variety of chloronium ions indicate that secondary bonding interactions between the Cl atom and hydrogens on the carbon atoms β to the chlorine, as well as steric repulsions between the methyl groups, introduce some small irregularities in the bonding changes. These effects will be discussed in a more comprehensive treatment of the thermochemistry of the alkyl halonium ions.<sup>14</sup>

McManus and Worley<sup>7</sup> have published recently cyclization enthalpies for the formation of cyclic chloronium ions. The results were obtained from MINDO/3 calculated heats of formation and some additional corrections. McManus and Worley were interested in the solvent effect on the cyclization equilibrium:



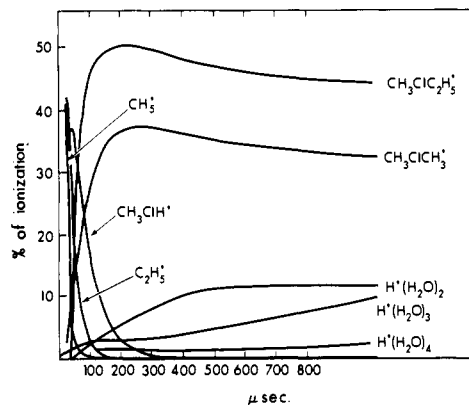
Evidently a solvent consisting of molecules which can donate an electron pair will interact more strongly with the open carbonium ion than with the cyclic chloronium. Therefore such a solvent should shift the equilibrium to the right. These authors predicted a  $\Delta H = +28.3$  kcal/mol for the above reaction. On general grounds one might expect that the  $\Delta H$  for the reaction should be somewhat less than the enthalpy change for the reaction  $n\text{-C}_3\text{H}_7\text{ClCH}_3^+ = n\text{-C}_3\text{H}_7^+ + \text{ClCH}_3$  and somewhat larger than the value for  $\text{sec-C}_3\text{H}_7\text{ClCH}_3^+ = \text{sec-C}_3\text{H}_7^+ + \text{ClCH}_3$ ,  $\Delta H = 22.9$  kcal/mol (Table I). The 28.3 kcal/mol obtained by McManus et al.<sup>7</sup> therefore appears of the right magnitude, i.e., within a few kilocalories per mole of the true value. This result lends support also to the other values calculated by these authors.

Alkyl halonium ions (as fluoroantimonates) in solution are effective alkylating agents. For example, methyl halonium reacting with dimethyl ether leads to the trimethyloxonium ion (see Table 10, ref 5). It is interesting to point out that many of these reactions can be made to occur also in the gas phase. Thus, we have observed with high yield the reactions



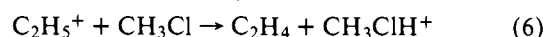
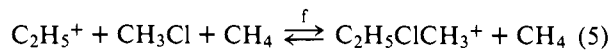
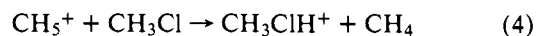
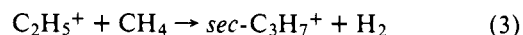
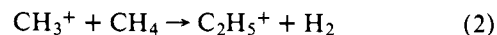
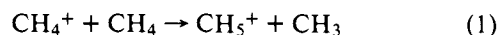
It is interesting to note that C<sub>2</sub>H<sub>5</sub>O(CH<sub>3</sub>)<sub>2</sub><sup>+</sup> cannot be produced in the gas phase by the direct Lewis acid-base reaction between C<sub>2</sub>H<sub>5</sub><sup>+</sup> and dimethyl ether. The dominant yield of this process at pressures in the Torr range is proton transfer leading to the protonated ether and ethylene.

**B. Ion-Molecule Kinetics in Reaction Systems Used to Measure the Equilibrium C<sub>2</sub>H<sub>5</sub><sup>+</sup> + CH<sub>3</sub>Cl = C<sub>2</sub>H<sub>5</sub>ClCH<sub>3</sub><sup>+</sup> and**



**Figure 1.** Time dependence of ions observed in 4 Torr methane containing 0.6 mTorr methyl chloride at 24 °C. Duration of electron pulse 14 μs. Proton hydrates H<sup>+</sup>(H<sub>2</sub>O)<sub>n</sub> due to trace impurities of water.

*sec*-C<sub>3</sub>H<sub>7</sub><sup>+</sup> + CH<sub>3</sub>Cl = *sec*-C<sub>3</sub>H<sub>7</sub>ClCH<sub>3</sub><sup>+</sup>. The reactions of the ethyl cation with methyl chloride were studied using mixtures of methane at known pressures in the 4-Torr range, containing methyl chloride at known pressures between 0.5 and 150 mTorr. The temperature range between 25 and 400 °C was covered in a number of runs. Typical results giving the time dependence of the ion concentrations after the ionizing electron pulse are shown in Figures 1-3. The principal primary ions created by electron impact with methane are CH<sub>4</sub><sup>+</sup> and CH<sub>3</sub><sup>+</sup> with an approximate abundance ratio 55:45. These ions react with methane to produce CH<sub>5</sub><sup>+</sup> and C<sub>2</sub>H<sub>5</sub><sup>+</sup> by the well-known<sup>15</sup> reactions 1 and 2.



At methane pressures in the torr range, reactions 1 and 2 are so fast ( $k_1$  and  $k_2 \approx 10^{-9}$  cm<sup>3</sup> molecules<sup>-1</sup> s<sup>-1</sup>) that they are virtually complete 20 μs after the electron pulse. Therefore, the initial ions observed in Figures 1-3 are CH<sub>5</sub><sup>+</sup> and C<sub>2</sub>H<sub>5</sub><sup>+</sup>. CH<sub>5</sub><sup>+</sup> does not react further with methane; however, C<sub>2</sub>H<sub>5</sub><sup>+</sup> reacts very slowly according to eq 3. Reaction 3 was studied recently<sup>16</sup> and the rate constant was found to be  $k_3 = 6 \times 10^{-13} \exp(-2.5 \text{ kcal/mol}^{-1}/RT)$  cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup>. In 4 Torr methane, this leads to half-lives for reaction 3 of 700 μs at 25 °C and 100 μs at 326 °C. In the presence of CH<sub>3</sub>Cl, CH<sub>5</sub><sup>+</sup> will

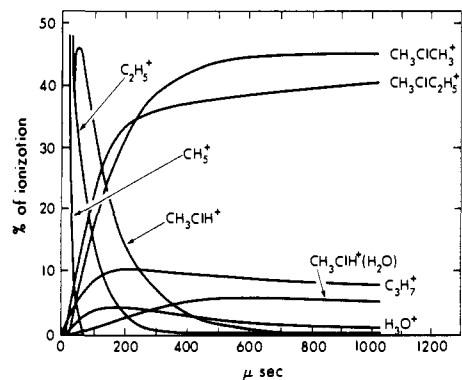


Figure 2. Time dependence of ions observed in 4 Torr methane containing 1.3 mTorr methyl chloride at 130 °C.

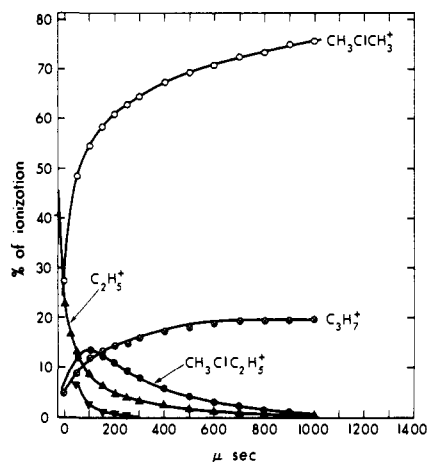


Figure 3. Time dependence of ions observed in 4 Torr methane containing 9.5 mTorr methyl chloride at 319 °C. At this temperature reactions 5f and 5r are fast but  $C_2H_5^+$  produced by 5r reacts also by 3 and 6.  $\blacktriangledown$   $CH_3ClH^+$ .

proton transfer to  $CH_3Cl$  by reaction 4 and the  $C_2H_5^+$  will engage in the Lewis acid-base process 5f. The exothermic reaction 5f proceeds via an excited intermediate  $(C_2H_5ClCH_3^+)^*$  which must be stabilized by third-body collisions. Such reactions are generally third order at total pressures in the Torr range. The formation of  $CH_3ClH^+$  and  $C_2H_5ClCH_3^+$  is clearly observed at room temperature (see Figure 1). The methylethylchloronium ion does not react further; however,  $CH_3ClH^+$  is seen to decrease rapidly, while at the same time  $CH_3CICH_3^+$  increases. This must be due to reaction 7. Reaction 7 belongs to a general class of acid-catalyzed self-condensation reactions leading to dialkyl halonium ions. It is well known in solution<sup>5</sup> and is formally analogous to the acid-catalyzed condensation of alcohols to ethers. Reaction 7 was observed earlier in the gas phase by Beauchamp.<sup>9</sup> The occurrence of reaction 6, which represents proton transfer from  $C_2H_5^+$  to methyl chloride, is not directly indicated in Figure 1. However, this reaction is clearly observed at higher temperatures as will be seen later.

As evident from Figure 1,  $C_2H_5ClCH_3^+$  and  $CH_3CICH_3^+$  are the major products at room temperature. It is interesting to note that the final concentration of  $CH_3CICH_3^+$  is somewhat lower than that for  $C_2H_5ClCH_3^+$  even though  $CH_5^+$ , which is the precursor of  $CH_3CICH_3^+$ , has an initial concentration which is somewhat larger than the  $C_2H_5^+$  concentration. This difference must be due to the proton transfer reactions 8 and 9 to water impurity. While the rate constants  $k_8$  and  $k_9$  should be of very similar magnitude,  $CH_3ClH^+$  disappears more slowly by reaction 7 (see Figure 1) and therefore has more time to proton transfer to water by reaction 8.

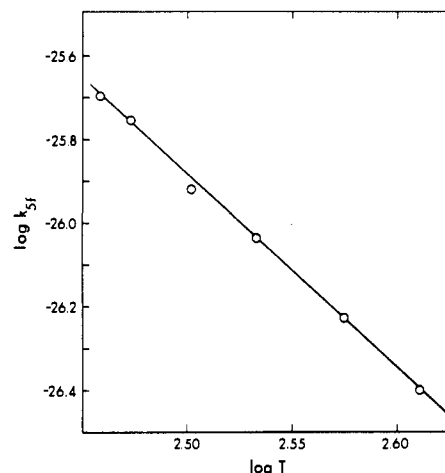
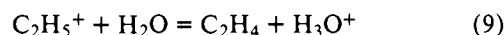


Figure 4. Temperature dependence of rate constant  $k_{5f}$  for reaction 5f:  $C_2H_5^+ + CH_3Cl + CH_4 = C_2H_5ClCH_3^+ + CH_4$ . Straight line obtained from log plot leads to relationship  $k_{5f} = 3.55 \times 10^{-15} T^{-4.575}$  ( $cm^3$  molecules<sup>-1</sup> s<sup>-1</sup>).



The reactions observed at the higher temperature of 130 °C can be discussed on the basis of Figure 2. The  $CH_3Cl$  concentration in this run is 1.3 mTorr, which is twice as high as that in Figure 1. Still the disappearance of  $C_2H_5^+$  is slower at the higher temperature. The cause for this is the negative temperature coefficient of the association reaction of  $C_2H_5^+$  with methyl chloride, i.e., reaction 5f. Third-body reactions like 5f generally have a negative temperature coefficient. Determinations of the rate constant  $k_{5f}$  were possible for temperatures in the range 20–135 °C. The procedure used is described in the Appendix. A plot of  $\log k_{5f}$  vs.  $\log T$  is shown in Figure 4. The straight line obtained defines the relationship  $k_{5f} = cT^n$  with  $c = 3.55 \times 10^{-15}$  and  $n = -4.575$  for  $k_5$  in  $cm^6$  molecules<sup>-2</sup> s<sup>-1</sup>.

The slower disappearance of  $C_2H_5^+$  by 5f and the higher value of  $k_3$  at higher temperatures lead to more abundant formation of  $C_3H_7^+$  (see Figure 2). The longer persistence of  $C_2H_5^+$  leads also to noticeable proton transfer to  $CH_3Cl$  by reaction 6. Thus in Figure 2  $CH_3ClH^+$  tails to longer reaction times because it is produced by  $C_2H_5^+$  via 6. The effect of reaction 6 is also seen in the final products: the  $CH_3CICH_3^+$  is now the major product since it is produced by both  $CH_5^+$  and  $C_2H_5^+$  via reactions 4, 6, and 7.

The rate constant of reaction 6 was measured by following the decrease of the  $C_2H_5^+$  concentration and the increase of  $[CH_3ClH^+] + [CH_3CICH_3^+]$  product (see Appendix). The constants could be determined only above 300 °C, where the competition by reaction (5f) was not so dominant. The rate constant  $k_6 \approx 3 \times 10^{-11}$   $cm^3$  molecules<sup>-1</sup> s<sup>-1</sup> was obtained near 300 °C. The rate constant appeared to increase with temperature but the experimental scatter was rather large and did not permit a meaningful Arrhenius plot of  $k_6$  to be made. If reaction 6 was exothermic by more than a few kilocalories per mole, one could expect that the rate constant  $k_6$  would be close to the value  $2 \times 10^{-9}$   $cm^3$  molecule<sup>-1</sup> s<sup>-1</sup> predicted by the ADO (average dipole orientation) theory<sup>17</sup> ( $\alpha_{CH_3Cl} = 4.5 \times 10^{-26}$   $cm^3$ ,  $\mu_D = 1.9$  D). Bohme<sup>18</sup> has shown that at pressures below  $\sim 0.1$  Torr and at room temperature, exothermic proton transfer proceeds with rate constant values close to those predicted by the ADO theory, i.e., close to the ion-molecule collision rates. At higher pressures one must consider the possibility that collisional stabilization of the reaction intermediate,  $C_2H_5ClCH_3^+$  in the present case, might

suppress the proton transfer reaction. In earlier work, we have observed that even at higher pressures ( $p \approx 5$  Torr) the proton transfer rate constant is near ADO if the reaction is strongly exothermic. For example,<sup>3</sup> proton transfer by  $C_2H_5^+$  to  $H_2O$  is in the ADO range and completely dominates over the reaction  $C_2H_5^+ + OH_2 = C_2H_5OH_2^+$ . The proton affinity of water is about 9 kcal/mol higher than that of ethylene.<sup>1</sup> Therefore the low value for  $k_6$  suggests a proton affinity of  $CH_3Cl$  which is somewhat lower than  $PA(C_2H_4) = 160$  kcal/mol. The above proton affinity value for ethylene can be obtained from the heat of formation of  $C_2H_5^+ = 219$  kcal/mol determined by Lossing and Semeluk.<sup>11</sup> A lower limit of  $PA(CH_3Cl)$  can be obtained if one assumes that  $k_6$  obeys the relationship  $k_6 = k_{ADO} \exp(-E_6/RT)$ . The present determination  $k_6 \approx 3 \times 10^{-11}$   $cm^3$  molecule<sup>-1</sup> s<sup>-1</sup> at 300 °C leads to  $E_6 \approx 4.8$  kcal/mol. Assuming that the activation energy  $E_6$  is due to the endothermicity of reaction 6, i.e.,  $\Delta H_6 \approx E_6$ , one obtains  $PA(CH_3Cl) = PA(C_2H_4) - \Delta H_6 \approx 160 - 4.8 = 155.2$  kcal/mol. The above value is a lower limit since, as mentioned above, eq 5 and 6 must proceed through the same collision complex and are therefore competitive. Beauchamp<sup>9a</sup> in earlier work estimated  $PA(CH_3Cl) \approx 160$  kcal/mol. The present results suggest that the most likely value is at least a couple of kilocalories per mole lower.

The rate constant for reaction 7 leading to the dimethyl chloronium ion could be determined, approximately, at several different temperatures between 25 and 150 °C. The rate constant was found to decrease gradually with temperature. Thus  $k_7 \approx 6 \times 10^{-10}$  at 25 °C gradually decreased to  $\approx 2 \times 10^{-10}$   $cm^3$  molecules<sup>-1</sup> s<sup>-1</sup> at 150 °C. Unfortunately the results were somewhat scattered, and did not permit a good determination of the temperature dependence of  $k_7$ . Beauchamp<sup>9</sup> using ICR obtained  $k_7 \approx 1.4 \times 10^{-10}$   $cm^3$  molecules<sup>-1</sup> s<sup>-1</sup> at  $\sim 25$  °C. This value corresponds to the upper temperature range of the present determinations. It is possible that the ICR results<sup>9</sup> were affected by presence of excitation in the reactants.

The reactions observed at the higher temperature 319 °C are shown in Figure 3. The methyl chloride concentration in this run is 9.5 mTorr, which is very much higher than the concentrations used for the lower temperature runs (Figures 1 and 2). In spite of this the ethyl cation is seen to persist right to the end of the observational period. An examination of the rates for reactions 5 and 6, which can be calculated on basis of the extrapolated  $k_{5f}$  and  $k_6$  to 319 °C, shows that these would have removed  $C_2H_5^+$  rapidly. The persistence of  $C_2H_5^+$  is therefore due to the decomposition of  $C_2H_5ClCH_3^+$  to  $C_2H_5^+$  and  $CH_3Cl$ , i.e., to the reverse reaction 5r. This is supported by the observation that the ethylmethylchloronium ion goes through a maximum. It can be noticed, in Figure 3, that the ratio  $[C_2H_5ClCH_3^+]/[C_2H_5^+]$  becomes constant above  $\sim 250$   $\mu s$ . Such constant ratios were observed in runs made in the temperature range 250–400 °C. The concentrations of  $C_2H_5ClCH_3^+$  and  $C_2H_5^+$  decrease with time (at constant ratio) because the ethyl cation is drained by reactions 3 and 6. The observed constant ratio could be the equilibrium ratio for reaction 5 if the forward 5f and reverse 5r rates were

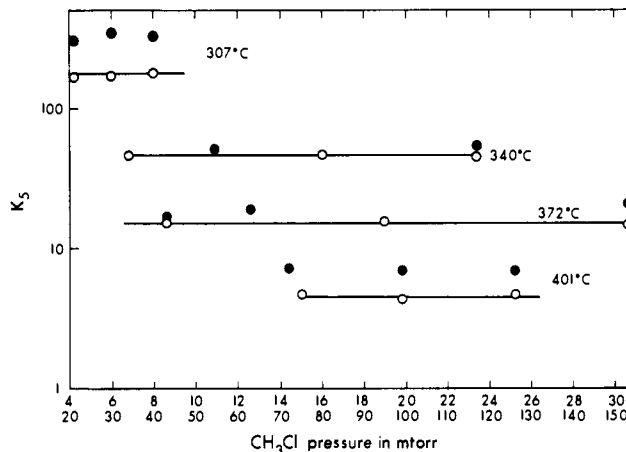


Figure 5. Equilibrium constant  $K_5$  for reaction 5:  $C_2H_5^+ + CH_3Cl = C_2H_5ClCH_3^+$  vs. methyl chloride pressure: ●, equilibrium quotient  $Q_5$  evaluated from stationary ratio  $[C_2H_5ClCH_3^+]/[C_2H_5^+]$  at longer reaction times; ○, equilibrium constant from analog computer simulation of reaction system. Bottom pressure range for data at 401 °C.

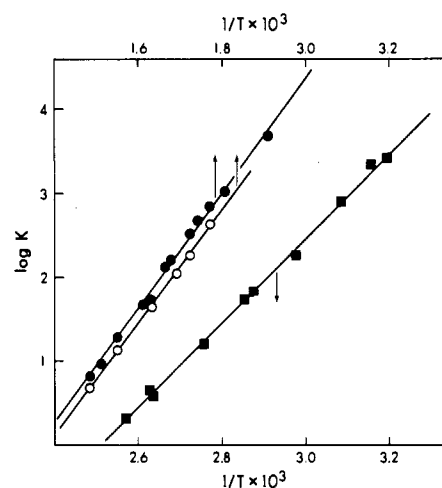


Figure 6. van't Hoff plots of equilibrium constants for reaction 5,  $C_2H_5^+ + CH_3Cl = C_2H_5ClCH_3^+$ : ●, equilibrium quotients from stationary ratio  $[C_2H_5ClCH_3^+]/[C_2H_5^+]$  at longer reaction times; ○, equilibrium constants from analog computer simulation of reaction system.  $1/T$  for reaction 5 on top of figure. van't Hoff plot of equilibrium constants for reaction 12:  $i-C_3H_7^+ + CH_3Cl = i-C_3H_7ClCH_3^+$  ■ (standard state 1 Torr).

much faster than the  $C_2H_5^+$  draining rates 3 and 6. On this assumption equilibrium constants quotients

$$Q_5 = \frac{[C_2H_5ClCH_3^+]}{[C_2H_5^+][CH_3Cl]}$$

were calculated from the kinetically stationary ion ratios observed over the temperature range 250–400 °C at various methyl chloride pressures. The plots in Figure 5 show that the equilibrium quotients  $Q_5$  are essentially independent of methyl

Table II. Summary of Experimental Measurements

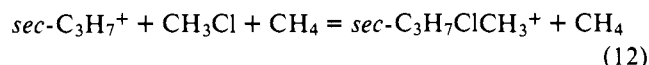
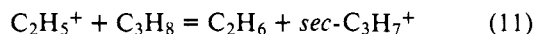
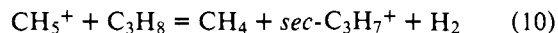
$C_2H_5^+ + CH_3Cl = C_2H_5ClCH_3^+$	$k^a = 3.55 \times 10^{-15} T^{-4.575}$	$\Delta H^\circ = -30.7$ kcal/mol <sup>b</sup>	$\Delta S^\circ = -30.7$ cal/deg
$sec-C_3H_7^+ + CH_3Cl = sec-C_3H_7ClCH_3^+$		$\Delta H^\circ = -22.9$ kcal/mol <sup>b</sup>	$\Delta S^\circ = -44.5$ cal/deg
$C_2H_5^+ + CH_3Cl = C_2H_4 + CH_3ClH^+$	$k \approx 3 \times 10^{-11}$ (300 °C) <sup>c</sup>	$\Delta H \approx +2 + 2$ kcal/mol <sup>e</sup>	
$CH_3ClH^+ + CH_3Cl = CH_3ClCH_3^+ + HCl$	$k \approx 6 \times 10^{-10}$ (25 °C) <sup>d</sup> $\approx 2 \times 10^{-10}$ (150 °C) <sup>d</sup>		

<sup>a</sup> Third-order rate constant in  $cm^6$  molecules<sup>-2</sup> s<sup>-1</sup> third body methane. <sup>b</sup> Standard deviation from least-squares treatment  $\sim 0.5$  kcal/mol; however, error in absolute value probably considerably larger, believed to be in the range  $\pm 2$  kcal/mol. <sup>c</sup> Values for rate constant in  $cm^3$  molecules<sup>-1</sup> s<sup>-1</sup>. Measurement difficult because of interference from competitive reactions. Rate constant showed small positive temperature coefficient. <sup>d</sup> In  $cm^3$  molecules<sup>-1</sup> s<sup>-1</sup>. <sup>e</sup> Estimate based on slow rate of reaction. See text.

chloride pressure. A van't Hoff plot of the equilibrium quotients  $Q_5$  obtained with the kinetically stationary ion ratios is shown in Figure 6.

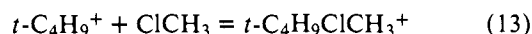
In order to check the assumption that the ion concentration ratio is close to the equilibrium ratio, a kinetic analysis was performed. The reactions 3, 5f, 5r, and 6 involving the  $C_2H_5^+$  ion were programmed into an analog computer. Numerical values for the rate constants 3, 5f, and 6 were introduced into the computer for each given temperature. The values for  $k_3$  in function of temperature were taken from Hiraoka.<sup>16</sup> The values for 5f were taken from extrapolations based on Figure 4. The value  $k_6 = 3 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  was used for reaction 6. The value of  $k_{5f}$  was treated as a variable parameter and adjusted until the analog computer reproduced the concentration changes and particularly the stationary ratio  $[C_2H_5ClCH_3^+]/[C_2H_5^+]$  observed at long reaction times. The  $k_{5f}$  obtained in this manner together with  $k_{5r}$  were used to evaluate the equilibrium constant  $K_5 = k_{5f}/k_{5r}$ . These values of the equilibrium constant are shown in Figures 5 and 6. The  $K_5$  is somewhat smaller than  $Q_5$  as expected, since the  $C_2H_5^+$  in the kinetically controlled ratio  $[C_2H_5ClCH_3^+]/[C_2H_5^+]$  is lower owing to removal of  $C_2H_5^+$  by reactions 3 and 6. However, the van't Hoff plots of  $Q_5$  and  $K_5$  are very similar. The  $\Delta H^\circ_5$  and  $\Delta S^\circ_5$  obtained from the plots are given in Table II, which contains a summary also of the other reactions discussed in this section. Considering that the correction is small, we think that the neglect of the unknown and small (positive) temperature coefficient of  $k_6$  in the analog simulation is not serious.

The measurement of the equilibrium between the *sec*-propyl cation, methyl chloride, and the *sec*-propylmethylchloronium ion was achieved without difficulties in methane containing some propane and known pressures of  $CH_3Cl$  in the milliTorr range. In methane containing small amounts of propane, the well-known<sup>15</sup> reactions 10 and 11 occur.



These reactions lead to *sec*- $C_3H_7^+$  as the only final ion. In the presence of  $CH_3Cl$ , the propyl cation forms the *sec*-propylmethylchloronium ion via reaction 12. Proton transfer from *sec*-propyl to methyl chloride does not occur since the proton affinity of methyl chloride is much lower than that of propylene. The equilibria 12 were observed and measured without interference from other reactions. Measurements of  $K_{12}$  at different pressure showed  $K_{12}$  to be independent of the  $CH_3Cl$  pressure. The van't Hoff plot of  $K_{12}$  is shown in Figure 6. The  $\Delta H^\circ_{12}$  and  $\Delta S^\circ_{12}$  obtained from this plot are given in Table II.

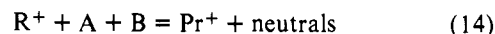
Some experiments towards measuring the equilibria



were performed with isobutane containing traces of methyl chloride. The principal final ion resulting from ion-molecule reactions in electron irradiated pure isobutane is  $t\text{-}C_4H_9^+$ . In the presence of  $CH_3Cl$  the formation of the *tert*-butylmethylchloronium ion via eq 13 could be expected. However, this ion was not observed even at the lowest temperature ( $\sim 25^\circ\text{C}$ ) accessible with the ion source used. Evidently the bonding in the *tert*-butylchloronium ion is too weak so that this ion is not stable above room temperature. We expect to be able to measure the equilibria 13, with our low-temperature ion source, at some later date.<sup>14</sup>

## Appendix

**Determination of Rate Constants.** The rate constant  $k$  for a given reaction involving an ionic reactant  $R^+$  and an ionic product  $Pr^+$  reacting as in eq 14 was obtained from eq 15.



$$\nu \int_{t_0}^t R^+ dt = [Pr^+]_t - [Pr^+]_{t_0} \quad (15)$$

The time integral of the ionic reactant  $R^+$  was obtained by graphic evaluation of the area under  $R^+$  from normalized ion intensity-time dependence plots like those in Figures 1-3. Plots of  $[Pr^+]_t - [Pr^+]_{t_0}$ , where  $t_0$  is constant and  $t$  is increased, taken from the time dependence curves, vs. the integral give straight lines with slope  $\nu$ . The (pseudo)-first-order rate constant  $\nu = k[A][B]$  for a third-order reaction like eq 14. As an example a plot of eq 15 for reaction 5f,  $C_2H_5^+ + CH_3Cl + CH_4 = C_2H_5ClCH_3^+ + CH_4$ , leads to a straight line whose slope  $\nu_{5f} = k_{5f}[CH_3Cl][CH_4]$ , which leads to  $k_{5f}$  since the concentrations of  $CH_3Cl$  and  $CH_4$  are known.

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