Ion-Molecule Association in Acrylonitrile

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Abstract

The association reaction of the ions $\text{C}_2\text{H}_2\text{ClCN}^+$ and $\text{C}_2\text{H}_2\text{ClCNH}^+$ with $\text{C}_2\text{H}_2\text{ClCN}$ have been examined using ion cyclotron resonance (ICR) and selected ion flow tube (SIFT) techniques at room temperature. Differences between the results observed by the two techniques for the $\text{C}_2\text{H}_2\text{ClCN}^+/\text{C}_2\text{H}_2\text{ClCN}$ system are accounted for by considerations of the lifetime, $Z(\text{C}_6\text{H}_5\text{N}^+)^*$. In the ICR, the rate coefficient for bimolecular reaction yielding $\text{C}_2\text{H}_2\text{ClCNH}^+ + \text{C}_3\text{H}_2\text{N}$ is $k = 2.5 \times 10^{-9}$ cm$^3$ s$^{-1}$. In the SIFT, the pseudo bimolecular rate coefficient is $k = 2.8 \times 10^{-9}$ cm$^3$ s$^{-1}$, but the major product ion is the association adduct, $\text{C}_6\text{H}_5\text{N}^+$. The $\text{C}_2\text{H}_2\text{ClCNH}^+/\text{C}_2\text{H}_2\text{ClCN}$ system yielded the association adduct in both techniques. The termolecular process measured for the latter association gives a rate coefficient of $k_3 = 1.2 \times 10^{-23}$ cm$^6$ s$^{-1}$ for $\text{M} = \text{C}_2\text{H}_2\text{ClCN}$. 
Introduction

Acrylonitrile (propenonitrile or vinyl cyanide) polymerizes readily via a radical mechanism in solution at room temperature. The propensity to polymerize is sufficiently strong that it is usual to add a radical scavenger to the solution to prevent polymerization when oxygen (an inhibitor) is removed. Polymerization of acrylonitrile is also known to occur via nucleophilic addition of an anion by a Michael-type reaction. * The ion-chemistry of acrylonitrile has also been studied. The negative ions formed by electron attachment to acrylonitrile in the gas phase have been examined\(^2,3\) and the ensuing intracluster anionic polymerization in acrylonitrile clusters formed in a sonic nozzle have also been investigated.\(^4\)

Several studies of the gas phase ion chemistry of positive ions with acrylonitrile have been undertaken. The reaction chemistry of CII\(_2\)CHCN\(^+\), CII\(_2\)CHCNI\(_2\)H\(^+\) and C\(_3\)H\(_2\)N\(^+\) with a number of simple neutrals was reported by Petrie et al.\(^5\) The ion-molecule chemistry of CII\(_2\)CHCN with C\(_n\)\(^+\) (n = 10-18, 20) was reported by Sun et al.\(^6\) and with the fullerene mono-, di- and tri-cations by Javahery et al.\(^7\)

Acrylonitrile is one of the molecules observed using radioastronomy techniques in interstellar clouds.\(^8,9\) Several reactions of positive ions derived from CII\(_2\)CHCN with molecules of relevance to interstellar conditions were reported by Petrie et al.\(^10\) using the selected ion flow tube technique. It was apparent in these earlier ion-molecule studies that just as acrylonitrile will polymerize in solution, so too, the gas phase ions CII\(_2\)CHCN\(^+\) and CII\(_2\)CHCNI\(_2\)H\(^+\) readily associate with the parent gas to form adducts. The product adduct ions formed by association were formed efficiently at close to the collision rate at
flow tube pressures of 0.3 Torr of helium. Efficient association signifies relatively long-lived association complexes which may be stabilized by collision with the bath gas in the flow tube or planetary ionospheric environment (e.g. in Titan's nitrogen atmosphere). In the interstellar cloud environment, stabilization by photon emission is a more likely outcome. It is of interest therefore, to examine further the nature of the association process.

We have previously conducted low pressure-high pressure investigations of several associating systems using the combined techniques of icm cyclotron resonance (l CR) and selected ion flow tube (S11). In this study, we extend these investigations to include association reactions of CH2CN+ and CH3CNH+ with Cl2ClCN over the wide pressure range of 10^-7 Torr to 0.3 Torr.

**Experimental**

The flow tube experiments were made using a SIFT operating at room temperature (300 ± 5 K) located at the University of Canterbury and which has been described previously. The ICR experiments were made using an ICR, which has not been described before, located at Canterbury University. This ICR is similar in principle and design to the ICR at the Jet Propulsion Laboratory (JPL) which has been described elsewhere. The instrument utilizes a McMahan-Beauchamp type cell design with separate trapping plates in the source and resonance regions. The only significant difference between the ICR at Canterbury and the instrument at JPL is that the Canterbury instrument has a nine inch electromagnet with a two inch gap between the pole faces. The cell was operated in both trapped and drift modes of operation and all measurements were made with a magnetic field of 1.3 T.
A trace of the radical inhibitor 4-methoxyphenol was added to the acrylonitrile to prevent its polymerization in the absence of oxygen.

Results and Discussion

in many ion-molecule systems where association reactions occur, significant differences in rate coefficients and product distributions are found between low pressure (ICR) and higher pressure (SIFT) techniques. Quite often, the nature of the reaction is different in different pressure regimes. This is particularly apparent when the system undergoing association has a tertiary reaction rate $\geq 1 \times 10^{-6}$ cm$^3$/sec.

$\text{CH}_2\text{ClCN}^+ + \text{Cl}_2\text{CICN}$

At low pressure, the ICR investigation showed the bimolecular Reaction (1)

$$\text{ClH}_2\text{ClCN}^+ + \text{ClH}_2\text{ClCN} \rightarrow \text{ClH}_2\text{ClCNH}^+ + \text{Cl}_2\text{N}_2$$  \hspace{1cm} (1)

occurring with a rate coefficient $k = 2.5 \times 10^{-9}$ cm$^3$/s $\pm 10\%$ and $\text{ClH}_2\text{ClCNH}^+$ was the only ion product found. The reaction was studied in both trapped and drift mode of operation of the ICR cell over the pressure range $8 \times 10^{-7}$ Torr to $3 \times 10^{-5}$ Torr of $\text{ClH}_2\text{ClCN}$ with the same result from each mode of operation. The rate coefficient observed at these low pressures is slightly less than the capture rate coefficient for the reaction of $k_{\text{coll}} = 3.6 \times 10^{-9}$ cm$^3$/s.$^{18}$

An earlier study using a SIFT reported the association adduct $\text{C}_6\text{H}_6\text{N}_2^+$ as the only product of the reaction and the measured rate coefficient was similar to the ICR result above, viz. $k_{\text{SIFT}} = 2.0 \times 10^{-9}$ cm$^3$/s.$^{15}$ A re-examination of this reaction in the SIFT showed two products of reaction: $\text{ClH}_2\text{ClCNH}^+$ and $\text{C}_6\text{H}_6\text{N}_2^+$
\[ \text{Cl}_2\text{C}_2\text{H}_4\text{CN}^+ + \text{Cl}_2\text{C}_2\text{H}_4\text{CN} \rightarrow \text{Cl}_2\text{C}_2\text{H}_4\text{CN}^+ + \text{C}_3\text{H}_2\text{N} \quad (2a) \]
\[ \rightarrow \text{C}_6\text{H}_6\text{N}_2^+ \quad (2b) \]

with a rate coefficient of \( k = 2.8 \times 10^{-9} \text{ cm}^3 \text{s}^{-1} \). In the earlier measurement, the product channel \( \text{Cl}_2\text{C}_2\text{H}_4\text{CN}^+ + \text{C}_3\text{H}_2\text{N} \) was discounted due to \( \text{Cl}_2\text{C}_2\text{H}_4\text{CN}^+ + \) being present in the flow tube as an impurity ion in the injection. Because both ions, \( \text{Cl}_2\text{C}_2\text{H}_4\text{CN}^+ \) and \( \text{Cl}_2\text{C}_2\text{H}_4\text{CN}^+ \), are injected together, it was not possible to obtain an accurate measure of the branching ratio of reaction (2) in both the present and previous studies. From the known mass discrimination of the instrument and the relative magnitude of the mass peak corresponding to \( \text{C}_6\text{H}_6\text{N}_2^+ \), we estimate reaction (2b) represents \( \geq 60\% \) of reactive collisions. This uncertainty is a consequence of the presence of \( \text{Cl}_2\text{C}_2\text{H}_4\text{CN}^+ \) in the flow tube, from sources other than Reaction (2a).

What do these observations tell us about the lifetime of the \( (\text{C}_6\text{H}_6\text{N}_2^+)^* \) complex? As no collision-stabilized product is observed in the ICR, the mean lifetime of the complex, \( \tau(\text{C}_6\text{H}_6\text{N}_2^+)^* \), is much less than the time between collisions at \( 3 \times 10^{-5} \text{ Torr} \) of \( \text{Cl}_2\text{C}_2\text{H}_4\text{CN} \); i.e. \( \tau \ll 430\mu \text{s} \). Furthermore, in the ICR approximately 30\% of all collisions undergo unimolecular dissociation back to reactants since the measured rate coefficient of \( k = 2.5 \times 10^{-9} \text{ cm}^3 \text{s}^{-1} \) is about 70\% of the collision rate. Writing the sequence of reactions that occur in this system in their general form, we have:

\[
\begin{align*}
\text{A}^+ + \text{B} & \xrightleftharpoons[{k,}]{k,} (\text{AB}^+)^* & (3) \\
(\text{AB}^+)^* & \xrightarrow[k^{-2}]{k^{-2}} \text{A}^+ + \text{D} & (4) \\
(\text{AB}^+)^* & \xrightarrow[k^{-r}]{k^{-r}} \text{AB}^+ + \text{hv} & (5)
\end{align*}
\]
(AB\textsuperscript{+})\textsuperscript{*} + M \xrightarrow{\beta k_{\text{coll}}} AB\textsuperscript{+} + M \quad (6)

In the Cl\textsubscript{2}CHCN\textsuperscript{+}/CH\textsubscript{2}CHCN system in the ICR, reaction (5) is too slow to compete with reactions (3) and (4).

The behavior exhibited by this reaction is very similar to that displayed by the CH\textsubscript{3}\textsuperscript{+}/CH\textsubscript{2}CHCN association system discussed recently\textsuperscript{19} where no association product was observed in the ICR at pressures of 1 x 10\textsuperscript{-4} Torr but which exhibited a collision rate coefficient for bimolecular reaction. In the SIFT, both CH\textsubscript{3}\textsuperscript{+} and CH\textsubscript{2}CHCN\textsuperscript{+} yielded the association adduct as the main product of their reaction with acrylonitrile.

Estimates for the rate coefficients $k_1, k_2$ and the function $\beta \tau$ for (AB\textsuperscript{+})\textsuperscript{*} are obtained by fitting the model expressed in equations (3) through (6) to the experimental data. The observed ICR bimolecular rate coefficient $k_{2\text{obs}}$ is defined by\textsuperscript{12}

$$k_{2\text{obs}} = k_f(k_2 + \beta k_{\text{coll}}[M])/(k_1 + k_2 + \beta k_{\text{coll}}[M]) \quad (7)$$

where the coefficient $\beta$ is a number between 0 and 1 that gives a measure of the efficiency of stabilization of (AB\textsuperscript{+})\textsuperscript{*} by the bath gas. With the assumptions: $k_f = k_{\text{SIFT}} = 2.8 \times 10^{-9}$ cm$^3$s$^{-1}$; the branching ratio for association in the SIFT $\geq 60\%$ association (Reaction (2b)); $\beta k_{\text{coll}} = 3.2 \times 10^{-9}$ cm$^3$ s$^{-1}$ and equating the rates at the cross over points between bimolecular and termolecular kinetics as described elsewhere,\textsuperscript{19} we obtain the results summarized in Table 1. The fit of the model to the ICR and SIFT experimental data is shown in Figure 1.
A pressure dependent reaction was observed in the ICR instrument for this reaction corresponding to collisional stabilization of the \([(\text{CH}_2\text{CHCN})_2\text{H}^+]*\) complex to yield the proton-bound dimer.

\[
\text{CH}_2\text{CHCNH}^+ + \text{CH}_2\text{CHCN} + \text{M} \rightarrow (\text{CH}_2@\text{ICN})_2\text{H}^+ + \text{M} \quad (8)
\]

The termolecular rate coefficient we observe for this process is \(k_3 = 1.2 \times 10^{-23}\text{cm}^6\text{s}^{-1}(\text{M} = \text{CH}_2\text{CHCN})\) and \(k_3 = 1.5 \times 10^{-24}\text{cm}^6\text{s}^{-1}(\text{M} = \text{He})\).

In the SIFT, as in the ICR instrument, only one reaction product, \((\text{CH}_2\text{CHCN})_2\text{H}^+\), was formed with a rate coefficient \(k \geq 1.3 \times 10^{-9}\text{cm}^3\text{s}^{-1}\). The lower limit on this rate coefficient is a consequence of the fact that some \(\text{CH}_2\text{CN}^+\) was injected into the flow tube with the reactant ion \(\text{CH}_2\text{CHCNH}^+\). In the SIFT the rate of reaction is determined by the rate of decrease of \(\text{CH}_2\text{CHCNH}^+\) with \(\text{CH}_2\text{CHCN}\) flow and because \(\text{CH}_2\text{CHCNH}^+\) is formed from \(\text{CH}_2\text{CHCN}^+\) via reaction (2a), then the rate of removal of \(\text{CH}_2\text{CHCN}^+\) is determined by the rate of reaction (8) in the SIFT to be closer to the capture rate coefficient of \(3.6 \times 10^{-9}\text{cm}^3\text{s}^{-1}\).

The measurement of the rate coefficient for termolecular association in the ICR allows us to place constraints on the lifetime \(\tau\) of the complex \((\text{C}_6\text{H}_7\text{N}^4)^*\) with respect to unimolecular dissociation. Using the scheme shown in reactions (3) through (6) as discussed previously and assuming \(k_f \approx 3.6 \times 10^{-9}\text{cm}^3\text{s}^{-1}\), then the results summarized in Table 1 represent the best fit of the model to the experimental data. \(\beta \star \tau[(\text{CH}_2\text{CHCN})_2\text{H}^+]*\) lies in the range 0.4 ps to 14 ps. The comparison between the model and the data is shown in Figure 2.

A summary of the experimental results is given in Table 2.
Collision Efficiency $\beta$ and Lifetime $\tau$

The values of $k_3$ measured in the ICR for $M = \text{He}$ and $M = \text{Cl}_2\text{H}_2\text{CHCN}$ enable the relative efficiencies for collisional stabilization of $(\text{C}_3\text{H}_7\text{N}_2^+)^*$ by a helium bath gas compared to $\text{Cl}_2\text{H}_2\text{CHCN}$, to be found such that $\beta_{\text{He}}/\beta_{\text{Cl}_2\text{H}_2\text{CHCN}} = 0.66$. This value is unexpectedly large but follows the trend that complexes formed with molecules having large dipole moments appear to give larger $\beta_{\text{He}}/\beta_{\text{PG}}$ ($1^G = \text{parent gas}$) ratios than complexes with molecules without dipole moments. Values of $\beta_{\text{He}}/\beta_{\text{PG}}$ ratios found in other systems lie mainly in the range 0.2 - 0.4. Why this ratio should be so large in this system is not clear. More data in similar systems needs to be obtained before any trends can be firmly established.

The absolute value for $\beta$, as opposed to the relative $\beta$ value ($\beta_{\text{He}}/\beta_{\text{Cl}_2\text{H}_2\text{CHCN}}$) deduced here, is significantly less than unity because weak collisions with the bath gas occur. Values of $\beta_{\text{PG}} - 0.1$ have been found for collisions of $(\text{AB}^+)^*$ with parent gas molecules in systems where bimolecular channels compete with collisional stabilization. Similar competition occurs with the $\text{Cl}_2\text{H}_2\text{CHCN}^+/\text{Cl}_2\text{H}_2\text{CHCN}$ system, but not with $\text{Cl}_2\text{H}_2\text{CHCN}^+/\text{Cl}_2\text{H}_2\text{CHCN}$.

In the present experiments, it is not possible to obtain a value for $\tau(\text{AB}^+)^*$ independently of $\beta$. However assuming $\beta - 0.1$ for the $\text{Cl}_2\text{H}_2\text{CHCN}^+/\text{Cl}_2\text{H}_2\text{CHCN}$ association, the mean lifetime of $(\text{C}_6\text{H}_6\text{N}_2^+)^*$ - 16 $\mu$s. Slightly larger values of $\beta$ are to be expected in systems such as $\text{Cl}_2\text{H}_2\text{CHCN}^+/\text{Cl}_2\text{H}_2\text{CHCN}$ because of the absence of other channels competing with collisional stabilization for depletion of $(\text{AB}^+)^*$.  

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Conclusions

There is a competition in each collision complex between dissociation and stabilization. The dissociation can be back to reactants or on to products that are different from the reactants. The stabilization of \((AB^+)^*\) can be by either by radiative energy loss or by a loss to the bath gases by a collision process. In the systems that have been studied both here and elsewhere there are examples that exhibit both forms of stabilization. There are also examples of the domination of each process and also examples of various combinations of them.

Observation of stabilization of the complex in the present instrumentation, i.e. ICR and SII-T, requires that either (1) the collision complex have a lifetime long enough to allow collisions with the bath gases before dissociation occurs or (2) the radiative lifetime of the collision complex be of the same order of magnitude or shorter than the collision complexes lifetime, \(\tau(AB^+)^*\).

The literature suggests that competition between dissociation to reactants \((k.1)\) or dissociation on to products \((k.2)\) is determined by the energy barrier in the product channel. As this energy barrier approaches the energy of the reactants, the product channel dissociation rate becomes smaller and eventually becomes much smaller than the dissociation rate back to reactants. This barrier results from the fact that to get to a place on the energy surface of the reaction corresponding to product formation, some rearrangement of the atoms or bonding from that of the reactants must occur. Any rearrangement is generally associated with a higher energy transition state, thus forming a barrier toward dissociation on to products. An exception to this would be a charge transfer reaction.
The competition between dissociation of the collision complex and stabilization of the collision complex seems largely dependent on the lifetime of the collision complex. The longer the complex lives, the greater the chances that a stabilizing collision will occur or a stabilizing photon will be emitted. Our only absolute stabilizing efficiency measurement gives a $\beta$ of 0.093.12 With only one data point it is very difficult to determine how the collision efficiency is affected by either the nature of the collision complex or by the nature of the third body. Many studies have provided evidence of the relative efficiency of different bath gases in stabilizing the complex.

It is not believed that the collision efficiency will change much during the initial stabilization process. A collision complex formed from reactants at thermal energies will have, on average, several hundredths of an CV of internal energy above the dissociation limit toward the reactant channel. If this energy is removed, then the rate of dissociation of the collision complex back to reactants will be reduced to nearly zero. This small amount of internal energy is about the amount that can be removed in a few stabilizing collision with the bath gases and also the size expected for one photon of a low frequency bending mode quanta. Thus the minimum number of collisions or emitted photons required to stabilize the collision complex from dissociating back towards the reactants will not be sufficient to stabilize it from dissociation to products in cases where the barrier to product formation is less than the reactant energy. After one or two collisions or one photon emitted, there will still remain a competition between dissociation on toward products and stabilization. This competition will continue until the energy of the collision complex is below the barrier in the product channel. While the stabilizing efficiency (or the average energy removal) will remain fairly constant during
this competition, the rate of dissociation toward products will be reduced as the barrier energy is approached. The present numerical model of association dots not include this property.

There is a general trend in the available data showing that the lifetime of the collision complex increases with its chemical complexity as predicted by statistical theories. Since the absolute collision efficiency has been measured in only one system, the data we have presented cannot separate between $\beta$ and $\tau$, and we have included the lifetimes and collision efficiency as a product. We note that this $\beta \cdot \tau$ product increases from 1.6 $\mu$s for the $\text{CH}_3\text{II}^+\text{CN}^+$ collision complex to 13 $\mu$s for the $\text{CH}_3/\text{CH}_3\text{CN}^+$ collision complex. The present study falls within this range.

It is generally assumed that the most important effects controlling the lifetime of the collision complex are the number of internal degrees of freedom and the well depth. The more internal degrees of freedom, the more dispersed the internal energy of the collision complex becomes. The thinking is that by dispersing the energy, in the internal degrees of freedom, the less likely they will be centerd in a mode that will cause the dissociation of the complex.

Modeling of the intrared radiative lifetimes shows that the lifetime is very dependent on the dipole moment in the collision complex. Laboratory measurements of radiative lifetimes have been on the first few vibrational levels and these lifetimes have been measured from 0.7 ms to $>11$ ls. Correlation with known physical properties have been slow. Modeling of the process has also been with the first few vibrational levels at the bottom of the potential WC], while the phenomena relating to radiative stabilization is for energies at, or above, the dissociation limit.
Acknowledgment

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References


Table 1. Evaluation of rate coefficients in the CH$_2$CHCN$^+$/CH$_2$CHCN and the CH$_2$CHCNI$^+$/CH$_2$CHCN reactions based on the model represented in reactions (3) through (6) (with the assumption that the branching ratio for association in the CH$_2$CHCN$^+$/CH$_2$CHCN system is ≥ 60%).

<table>
<thead>
<tr>
<th>Rate Coefficient</th>
<th>Units</th>
<th>CH$_2$CHCN$^+$/CH$_2$CHCN</th>
<th>CH$_2$CHCNI$^+$/CH$_2$CHCN</th>
</tr>
</thead>
<tbody>
<tr>
<td>$k_f$</td>
<td>cm$^3$ s$^{-1}$</td>
<td>2.9 x 10$^{-9}$</td>
<td>3.6 x 10$^{-9}$</td>
</tr>
<tr>
<td>$k_{-1}/\beta$</td>
<td>s$^{-1}$</td>
<td>9,000-300,000</td>
<td>850,000-460,000</td>
</tr>
<tr>
<td>$k_{1}/\beta$</td>
<td>s$^{-1}$</td>
<td>&lt; 10,000</td>
<td>&lt; 600</td>
</tr>
<tr>
<td>$k_{-2}/\beta$</td>
<td>s$^{-1}$</td>
<td>60,000-2,000,000</td>
<td>4,300-6,000</td>
</tr>
<tr>
<td>$\beta*\tau$</td>
<td>μs</td>
<td>14-0.44</td>
<td>1.2-2.1</td>
</tr>
<tr>
<td>$k_3$ (M = He)</td>
<td>cm$^6$ s$^{-1}$</td>
<td>(2-0.06) x 10$^{-24}$</td>
<td>1.5 x 10$^{-24}$</td>
</tr>
</tbody>
</table>
Table 2 A comparison of the reactions of \( \text{CH}_2\text{CHCN}^+ \) and \( \text{CH}_2\text{CHCNH}^+ \) with \( \text{CH}_2\text{CHCN} \) using ICR and SIFT techniques.

<table>
<thead>
<tr>
<th>Reactant ION</th>
<th>Branching Ratio</th>
<th>ICR Products</th>
<th>( k_{\text{ICR}} ) ( \text{(10}^{-9} \text{cm}^3 \text{s}^{-1}) )</th>
<th>Branching Ratio</th>
<th>SIFT Products</th>
<th>( k_{\text{SIFT}} ) ( \text{(10}^{-9} \text{cm}^3 \text{s}^{-1}) )</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \text{CH}_2\text{CHCN}^+ )</td>
<td>1.0</td>
<td>( \text{CH}_2\text{CHCNH}^+ + \text{C}_3\text{H}_2\text{N} )</td>
<td>2.5(^b)</td>
<td>( \leq 0.4 )</td>
<td>( \text{CH}_2\text{CHCNH}^+ + \text{C}_3\text{H}_2\text{N} )</td>
<td>2.8</td>
</tr>
<tr>
<td>( \text{CH}_2\text{CHCNH}^+ )</td>
<td>1.0</td>
<td>( (\text{CH}_2\text{CHCN})_2\text{H}^+ )</td>
<td>0.092(^c)</td>
<td>1.0</td>
<td>( (\text{CH}_2\text{CHCN})_2\text{H}^+ )</td>
<td>( \geq 1.3)^d</td>
</tr>
</tbody>
</table>

\(^a\) Flow tube pressure = 0.30 Torr of helium.

\(^b\) At pressure \( P \leq 3 \times 10^4 \) Torr.

\(^c\) At a pressure of \( \text{CH}_2\text{CHCN} \) of 3.0x 10^-4 Torr. The rate coefficient is pressure dependent, \( k_3 = 1.2 \times 10^{-23} \text{ cm}^6 \text{ s}^{-1} \) (\( M = \text{CH}_2\text{CHCN} \)).

\(^d\) See text.
Figure Captions

Figure 1. The position of crossover between second and third order kinetics for the system Cl\_2ClCN\^+/Cl\_2ClICN. The effective bimolecular reaction rate coefficient is plotted against the pressure of Cl\_2ClICN (solid line) and helium (dashed line) as bath gases. The helium data (shown as hollow circles for termolecular kinetics and solid circles for bimolecular kinetics) represent the sum of both channels that were found in the SIFT.

Figure 2. The variation in the apparent bimolecular rate coefficient for the system Cl\_2ClICN\^+ + Cl\_2ClICN shown as a function of pressure for the two bath gases Cl\_2ClICN (solid line) and helium (dashed line).
Figure 1.