COMPARISON OF NUMERICAL CAPTURE CROSS SECTIONS WITH EXPERIMENTAL REACTION CROSS SECTIONS FOR NH$_3^+$ + NH$_3$

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ABSTRACT

Numerically calculated capture cross sections $\sigma_c$ are compared with Ryan's experimental reaction cross sections for NH$_3^+$ + NH$_3$, NH$_4^+$ + NH$_2$. The numerical reaction cross section $\sigma_R = 0.6 \sigma_c$ is obtained assuming that vibrationally excited NH$_3^+$ do not react. Theory and experiment agree satisfactorily from thermal energy to nearly 1 eV although their slopes are slightly different and both steeper than Langevin.

INTRODUCTION

Experimental cross sections have been reported by Ryan$^1$ for the NH$_3$-parent ion reaction at low ion energies where:

\[ \text{NH}_3^+ + \text{NH}_3 \rightarrow \text{NH}_4^+ + \text{NH}_2 \]

The purpose of this note is to compare the numerically calculated capture cross sections with Ryan's experimental results. These numerical capture cross sections for ion-dipole collisions have been obtained by solving many randomly generated trajectories,$^2,^3$ These capture cross sections should set upper limits to reaction cross sections in the region where rotational quantum numbers are large so
that classical approximations are valid. Chupka has shown that
NH$_3^{+}$ in higher vibrational states react less efficiently to produce
NH$_4^{+}$. Ryan reports that the vibrational distribution of NH$_3^{+}$ species
in his experiment is such that the observed reaction cross section
should be only 60% of the capture cross section,\(^5\) (assuming that the
reaction efficiency for unexcited ions is unity). In the region of
ion energy from thermal to one eV the permanent dipole plays a
dominant role in determining the capture cross section.\(^2,3\) Thus,
one should not expect the Langevin formula to predict accurate values
or slope for the capture cross section.

**EXPERIMENTAL REACTION CROSS SECTIONS**

In Ryan's studies\(^1\) an applied repeller voltage sets an upper limit
to the ion energy at the exit. At exit energies \(E_m\) somewhat greater
than thermal (0.3 to 4 eV) the reaction cross section is obtained
from the measured rate coefficient \(k\) by the relation \(\sigma = k/(v)\)
where \(\langle v \rangle = (2\epsilon_1/(m_r)^1/2)\); \(\epsilon_1\) is the average ion energy = \(E_m/4\) and
\(m_r\) is the reduced mass. Because of the uncertainties about the ion
energy distribution in the thermal region\(^6\) the experimental cross sec-
tion for thermal energy is herein obtained both from the Maxwell
averaged results and by extrapolation of the higher energy results to
the thermal region.

**MONOENERGETIC NUMERICAL CROSS SECTIONS**

The numerical capture cross sections \(\sigma_c\) are obtained from the
capture ratio \(C_R\) which is the fraction of collisions in which the
ion and molecule approach within a specified separation (2 Å was used for all calculations in this paper). The capture ratios for \( \text{NH}_3^+ + \text{NH}_3 \) are plotted against the square of the impact parameter in Fig. 1 for 3 different ion velocities. Fifty trajectories were calculated for each point. The higher ion velocities correspond to ion energies of 0.2 and 0.8 eV; the lower velocity corresponds to relative thermal energy. These \( C_R \) values are obtained for the same random number sets; it has been shown that the variation of cross sections with random number sets is within 20%. The simple step function behavior which would be expected for Langevin capture collisions with \( \text{NH}_3 \) is shown for comparison at \( b = b_L \). The corresponding monoenergetic cross section \( \sigma_c \) is simply \( \pi \) times the area under the curve of \( C_R \) against \( b^2 \). This cross section is plotted against relative translational energy \( \epsilon \) in Fig. 2. The experimental cross section \( \sigma_{\text{exp}} \) and Langevin cross section \( \sigma_c \) (using \( \text{NH}_3 \) polarizability = 2.26 Å\(^3\)) are plotted for comparison.

**COMPARISON OF RESULTS**

The numerical capture cross section \( \sigma_c \) has a slope \( \epsilon^{-0.69} \) whereas the experimental cross section has a steeper slope \( \epsilon^{-0.78} \). Ryan obtained a reaction rate coefficient of \( 18.1 \times 10^{-10} \) cm\(^3\) sec\(^{-1}\) at 350 K which corresponds to a cross section \( \sigma_{\text{exp}} = 181 \) Å\(^2\) \( (1.81 \times 10^{-14} \) cm\(^2\)\) for an average velocity of \( (8kT/m)_{1/2} = 9.5 \times 10^4 \) cm sec\(^{-1}\) \( (\epsilon = 0.030 \) eV\). This \( \sigma_{\text{exp}} \) value is only slightly lower than the extrapolated value of 185 Å\(^2\). A theoretical value of the thermal collision coefficient \( \left( \sigma_c v \right) \) can be obtained by integrating the mono-
energetic $\sigma_c$ over a Maxwellian distribution at $T = 350$ K. The expression for the capture collision coefficient is

$$ (\sigma_c v) \approx 10^{-8} \int_0^\infty (\sigma_o)^{n'} c^n e^{-e/kT} \, de $$

(1)

where $(\sigma_o)^{n'} = 33 \frac{A^2}{(eV)^{n'}}$

$n = 1 - n'$ and $n'$ describes the power dependence of the numerical cross section, i.e., $\sigma = (\sigma_o)^{n'} e^{-n'}$. The $n'$ is 0.69 for $\sigma_c$ and 0.78 for $\sigma_{\text{exp}}$. The integral of Eq. (1) is

$$ (\sigma_c v) \approx 10^{-8} (kT)^{1.3} (\sigma_o)^{n'} \Gamma(1.3) = 3.3 \times 10^{-9} \text{ cm}^3 \text{ sec}^{-1} \quad (2) $$

where $\Gamma(1.3)$ is the gamma function and $kT = e = 0.030$ eV. For thermal velocity, $\langle v \rangle = 9.5 \times 10^4 \text{ cm sec}^{-1}$, this corresponds to a cross section $\sigma_c \approx 347 \frac{A^2}{cm^2}$ or a theoretical reaction cross section of $208 \frac{A^2}{cm^2}$ (using $\sigma_R = 0.6 \sigma_c$). This latter value is about 13% larger than the extrapolated experimental cross section which is satisfactory agreement.

The experimental reaction cross section of Fig. 2 is 0.45 to 0.50 of the numerical values over the range of relative energy shown. The ion-dipole interaction is the chief potential term over this range. This cross section ratio is in satisfactory agreement with the reaction efficiency factor of 0.6, although the slope of $\sigma_{\text{exp}}$ is a little steeper than for $\sigma_c$. 
CONCLUDING REMARKS

The numerically calculated capture cross sections for NH$_3^+$ on NH$_3$ are in good agreement with experimental values in the low energy region from thermal to several eV if a constant reaction efficiency is used. The dependence of the cross section on relative translational (or ion) energy is also in satisfactory agreement with the experimentally observed $\epsilon^{-0.78}$. Fortuitous agreement between Langevin theory and experiment suggests that the reaction efficiency masks the role which the permanent dipole plays in the capture mechanism. Better agreement could be obtained if the reaction efficiency were known as a function of relative energy. Earlier experiments suggested that the $\sigma_{\text{exp}}$ values were Langevin-like.\textsuperscript{7} Although the dipole term determines the capture cross section the absolute value of this cross section is considerably less than the maximum capture cross section and coincidentally near the Langevin capture cross section. This behavior has been discussed for other polar targets in mass spectrometry.\textsuperscript{2,3}
Figure 1. - Variation of capture ratio with impact parameter for NH$_3^+$ + NH$_3$ capture collision at 3 ion velocities. Target rotators are chosen from a heat bath at 350 K.

Figure 2. - Variation of numerical, experimental and Langevin capture cross sections with relative (ion-molecule) translational energy for NH$_3^+$ + NH$_3$ capture and reactive collisions.
REFERENCES


