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The S_N2 Identity Exchange Reaction $^{37}Cl^- + {}^{35}ClCH_2CN \rightarrow {}^{35}Cl^- + {}^{37}ClCH_2CN$: Kinetic Energy and Temperature Dependence

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The detailed dynamics of S_N2 reactions are not fully understood. Although various statistical reaction rate theories, including Rice–Ramsperger–Kassel–Marcus (RRKM) theory, have been used to model the experimental kinetics and predict energies of activation for these reactions,[1-8] recent experimental and theoretical results suggest that certain S_N2 reactions behave "nonstatistically".[9-17] These results raise important concerns regarding the use of statistical theories to model S_N2 reaction kinetics.

Viggiano and co-workers[18-20] recently developed a technique to measure directly both the relative kinetic energy dependence and the overall temperature dependence for ion–molecule reactions in the gas phase. A previous paper[20] reported the energy dependence for the S_N2 reaction, eq 1:

$$Cl^- + CH_3Br \rightarrow CH_3Cl + Br^- \qquad (1)$$

For eq 1, (a) the overall reaction rate exhibits a negative temperature dependence, (b) the reaction rate exhibits a negative dependence on kinetic energy which accounts for the overall temperature dependence, and (c) the dependence of the reaction rate on kinetic energy is significantly greater than the dependence of the classical capture rate on kinetic energy. Thus, the overall reaction rate does not depend on the internal temperature of the reacting neutral. The kinetic energy and internal energy of the reactants do not interconvert, and therefore the behavior of the reaction in eq 1 is said to be nonstatistical.

Here, we report the overall temperature dependence and relative kinetic energy dependence for eq 2:

$$^{37}Cl^- + {}^{35}ClCH_2CN \rightarrow {}^{35}Cl^- + {}^{37}ClCH_2CN \qquad (2)$$

The reaction rate for this system exhibits both a strong negative temperature dependence between 303 and 553 K and a negative dependence on relative kinetic energy (Figure 1). Unlike eq 1, however, the kinetic energy dependence of eq 2 accounts for only a small part of the overall energy dependence of the reaction rate. Thus, the reaction rate for eq 2 must strongly depend on the *internal* energy of the neutral, in contrast to previous work on the system in eq 1.

Recently, a detailed experimental and *ab initio* quantum study of the reaction surface for eq 2 was presented by Wladkowski *et al.*,[7] in which the system was modeled with μVTS-RRKM theory using the *ab initio* results (geometries and vibrational frequencies). The theory gave excellent agreement with the experimentally observed rate constant measured initially by DePuy, Bierbaum, and co-workers[21] as 3.2×10^{-10} cm^3 s^{-1} and later measured by Wladkowski *et al.*[7] as 3.3×10^{-10} cm^3 s^{-1} at 350 K in an ICR. In this paper, we expand on the previous study with an experimental and theoretical study of the overall temperature dependence and relative kinetic energy dependence of the reaction rate. We model both the relative kinetic energy dependence and the temperature dependence using RRKM theory.[22-24] Reasonable agreement between experiment and theory is found in both cases.

Experimental measurements were obtained in a variable temperature–selected ion flow drift tube instrument and are essentially identical to those routinely performed in our laboratory.[18,19,25] $^{37}Cl^-$ is injected into a helium buffer and reacts downstream with a mixture of He and a natural isotopic abundance of $ClCH_2CN$. The low vapor pressure limits the maximum amount of $ClCH_2CN$ that could be added and therefore the maximum energy at which the reaction could be studied, since at high energy the residence time and therefore the time available for reaction decreases in a drift tube. For simplicity, the experiments were done under low depletion[26] (factor of 2 or less) conditions to avoid back reaction and have been corrected for the natural abundance of ^{37}Cl.

The overall rate constant for the reaction may be expressed as:

$$k_{obs}(T) = k_{cap}(T)\Phi(T) \qquad (3)$$

where k_{cap} is the bimolecular capture rate constant and $\Phi(T)$ is the reaction efficiency and is a function of various unimolecular steps. The capture rate constant can be calculated in a number of different ways. In this case we use classical trajectory calculations which allow for a determination of the capture rate as a function of relative kinetic energy.[27,28] For purposes of the efficiency calculations, we assume that the complexes, once

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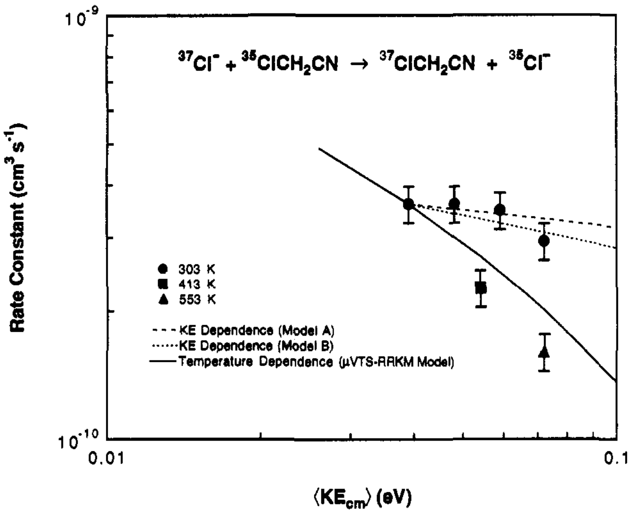

Figure 1. Rate constants for eq 2 plotted as a function of average center-of-mass kinetic energy at three different temperatures. Circles, squares, and triangles represent experimental measurements at 303, 413, and 553 K, respectively. Error bars represent a 20% relative error displayed as ±10%.

formed, are long-lived and behave statistically at these low (0.01-0.1 eV) relative kinetic energies.[29] The unimolecular efficiency, $\Phi(T)$, for reaction of these complexes is calculated using μVTS-RRKM theory.[7] All of the molecular parameters of $ClCH_2CN$ used here, including the geometries, vibrational frequencies, polarizability, and dipole moment, are the same as those used previously.[7]

The overall reaction rate is calculated in a straightforward manner for each temperature using a thermal distribution of reacting species[7] and is displayed in Figure 1. Additionally, the kinetic energy dependence of the capture rate at 303 K is given by model A, which assumes that none of the excess energy present in relative translation will be converted to internal energy of the system. In this case, the unimolecular efficiency term is fixed at Φ(303 K). Model B assumes that the excess kinetic energy is fully interconverted with internal energy upon collision and is distributed statistically throughout the system. The system is at a higher effective internal temperature T after the collision event, and Φ(T) decreases as does $k_{cap}(T)$, giving a slightly greater negative energy dependence than model A.

Figure 1 shows the experimental kinetic data both as a function of overall temperature (303, 413, 553 K) and as a function of relative kinetic energy (0.04–0.07 eV) at a constant internal temperature of 303 K. For convenience, the data are plotted as a function of ion–neutral average center-of-mass kinetic energy, $\langle KE_{cm} \rangle$, which is only a component of the total energy of the system. Also given in Figure 1 are the rates calculated using the various models described above.

As seen in Figure 1, the reaction rate constants exhibit a negative temperature dependence, approximately $T^{-1.35}$ (or $\langle KE_{cm} \rangle^{-1.35}$), but increasing the relative kinetic energy of the reactants over a range 0.04-0.07 eV (keeping the internal temperature fixed at 303 K) has only a very slight effect on the overall rate. Therefore, at a constant $\langle KE_{cm} \rangle$, the system with an internal temperature of 553 K has a rate constant that is almost a factor of 2 smaller than the rate constant for the system with an internal temperature of 303 K. This shows unambiguously that excitation of the internal modes of $ClCH_2CN$ has a dramatic effect on the overall rate, as expected from the statistical reaction rate model. These observations are distinctly different from those observed previously for the reaction in eq 1, in which excitation of the internal modes of CH_3Br appears to have little or no effect on the reaction rate over a temperature range of 207–564 K.

The solid line in Figure 1 represents the calculated rate constant as a function of overall temperature, based on our RRKM model, using capture rates obtained from the classical trajectory calculations.[30] The barrier height was chosen to reproduce the experimental rate at 303 K and was found to be 6.9 kcal mol^{-1} below separated reactants, in good agreement with our previous estimate. Although the calculated temperature dependence of $T^{-0.96}$ is less than that found experimentally, the agreement is good given the details of the calculations. The largest contribution to the temperature dependence comes from the low-frequency vibrational modes at the S_N2 transition state. By varying these frequencies and the activation energy over a modest range (15%), the observed temperature dependence can be reproduced exactly.

The effect of additional kinetic energy on the reaction rate (dashed lines) has also been modeled. The effects of energy interconversion (model B) are not, however, distinguishable from the kinetic energy dependence of the capture rate (model A) in the modest range of kinetic energies which are experimentally accessible.

In conclusion, the apparent agreement found here between the experimental results and the RRKM model is important since previous results for eq 1 demonstrate nonstatistical behavior. Equation 1 is slower at higher energy, and it is solely the kinetic energy which is important; internal energy has no effect on the kinetics. The behavior is unquestionably nonstatistical. Equation 2 is also slower at higher energy, but here the internal energy is clearly important; the effect, if any, of kinetic energy on the rate is very small in the range of these experiments. The reaction appears to be statistical inasmuch as the rate constants can be predicted by RRKM theory.

The dependence of the reaction rate on internal energy is a consequence of the relative heights of the entrance channel and the barrier to reaction. As the reaction barrier becomes higher than the entrance channel, the energy dependence changes from negative to positive. In eq 1, the difference between entrance channel and barrier is very small, and we expect relatively little energy dependence, even if the reaction is statistical. As kinetic energy increases, however, dissociation of the complex back toward reactants instead of across the barrier to products is enhanced, and we can see that the energy is not fully exchanged between partners in the reactive collision.

In contrast, in eq 2, there is a substantial difference between the entrance channel and the barrier, giving rise to a strong internal energy dependence of the rate. Energy exchange becomes more efficient with increasing complex lifetime,[31] and we know that the complex of Cl^- with $ClCH_2CN$ is longer lived (approximately 10^{-8} s) than the complex of Cl^- with CH_3Br, since a small percentage of eq 2 gives an association product, whereas no association was observed for eq 1. The long complex lifetime of eq 2 is a result of its large complexation energy, measured[7] as 19.6 kcal mol^{-1} which is roughly twice that of eq 1.[4] Although V–V and T–V energy exchange is often inefficient for systems of this size, the long complex lifetime of eq 2 suggests that the reaction may approach statistical energy exchange.[31] The contribution of the change in kinetic energy to the change in total energy is small over the range of these experiments, however, so that a lack of energy exchange would not be revealed. In any event, RRKM-μVTS theory accurately predicts the rate constant for this reaction across a temperature range of 303–553 K.

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