ditional information about this competition.

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Gas-Phase Isotope-Exchange Reactions with Chloride Ion

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Gas-phase isotope-exchange reactions of $^{37}Cl^-$ have been studied in a selected ion flow tube at thermal energy. The S_N2 reaction of $^{37}Cl^-$ with methyl chloride is immeasurably slow at room temperature, indicating that the transition state is close to or projects above the energy of the reactants. In contrast, the corresponding displacement reactions with chlorotrimethylsilane and chlorodimethylphosphine are facile, indicating that reaction barriers are low and suggesting the possible formation of low-energy intermediates. Exchange with acetyl chloride occurs at a moderate rate while exchange with thionyl chloride occurs at the statistical limit; for sulfuryl chloride only chlorine atom abstraction is observed. Reaction of $^{37}Cl^-$ with molecular chlorine proceeds in half of the collisions, suggesting formation of Cl_3^- from end-on attack; the unique central atom is not exchangeable. Isotope exchange with hydrogen chloride and deuterium chloride occurs with ~50% efficiency, implicating reaction through a long-lived complex rather than by a direct mechanism.

Symmetrical exchange reactions, in which an atom or group within a molecule is replaced by an identical atom or group, have always played key roles in the elucidation of reaction mechanisms and in correlations of the effect of structure on reaction rates. Such exchange reactions also hold great potential for exploring the detailed dynamics of gas-phase ion-molecule processes. Due largely to the work of Brauman and co-workers,[1] most thermal energy gas-phase ion-molecule reactions are described by double-well potential energy surfaces, as shown in Figure 1. The ion and neutral molecule are attracted to one another to form an electrostatically bound complex [$^*X^- \cdot RX$]. Reaction then proceeds through a transition state [$^*X \cdots R \cdots X]^-$ in which the rate-determining chemical transformations occur. In the final step, a complex of the ion and neutral products is formed which then separates. In the symmetrical exchange process shown in Figure 1, the reaction is thermoneutral so that the reactants and products are at the same energy as are the reactant and product complexes. Such reactions are particularly important because they allow one to make inferences about intrinsic barriers to reactions, i.e., activation energies in the absence of an energetic driving force. The height of the intrinsic barrier is expected to be very sensitive to the structure of the transition state and thus to the detailed mechanism of the reaction. As shown in Figure 1, we can envision barriers that are sufficiently low so as to have no effect on the reaction rate, barriers so high that the reaction cannot proceed at thermal energy, and, most usefully for the study of reaction dynamics, barriers of intermediate height which retard but do not prevent the reaction. Thus, a study of the rates of these symmetrical ion-molecule processes allows us to probe the nature of their reaction barriers. These reactions are also of great importance in the widening application[2] of Marcus theory[3] to the prediction of reaction rates. In this theory the rate of an unsymmetrical reaction is estimated from the intrinsic barriers of the two symmetrical processes and the overall reaction thermochemistry. By combining intrinsic barriers, reaction enthalpies, and experimental ion-neutral complexation energies, one can define many of the features of the double-minimum potential energy surfaces that describe ion-molecule reactions.

In view of the importance of symmetrical reactions, there are surprisingly few such rate coefficients available in the field of gas-phase ion chemistry, especially at thermal energies. In this paper we report the rate coefficients, measured in a selected ion flow tube, of the gas-phase exchange reactions of $^{37}Cl^-$ with methyl and acetyl chloride, chlorotrimethylsilane, chlorodimethylphosphine, thionyl and sulfuryl chloride, chlorine, and hydrogen and deuterium chloride.

Experimental Section

The rate coefficients were measured at room temperature in a selected ion flow tube (SIFT) which has been previously described.[4] The $^{37}Cl^-$ ions were formed in a low-pressure electron impact source from carbon tetrachloride, separated from the neutral precursor and other ions in a quadrupole mass filter, and injected into a flowing afterglow in which helium at 0.4 Torr was used as the buffer gas. Methyl chloride (Matheson, 99.5%), chlorine (Matheson High Purity grade, 99.5%), hydrogen chloride (Matheson Technical grade, 99.0% minimum), and deuterium chloride (MSD Isotopes, 99% minimum D) were used without further purification. Chlorotrimethylsilane (Aldrich, 98%) was distilled before use. Chlorodimethylphosphine (Strem Chemical) was distilled onto pure 1,10-phenanthroline to absorb any HCl and then distilled directly into the flow tube. Reaction with H_3O^+ showed 97% $[M + 1]^+$ of the chlorodimethylphosphine and 3% $[M + 1]^+$ of dichloromethylphosphine. Thionyl chloride (Aldrich

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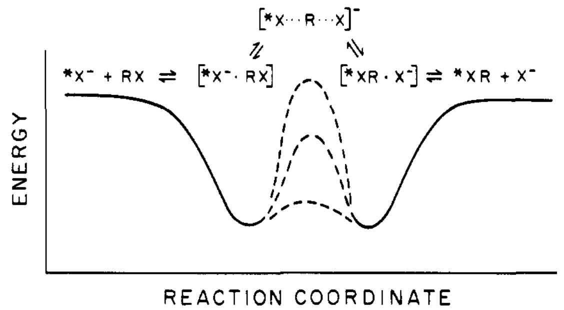

Figure 1. Double-minimum potential energy surface for symmetrical exchange reactions. The dashed lines indicate three possible intrinsic barriers.

Gold Label, 99+%) was transferred to the reagent flask under argon. Sulfuryl chloride (Aldrich, 97%) was doubly distilled and transferred to the reagent flask under argon. Flow rates of the neutral reactants were determined by measuring the pressure increase with time in a calibrated volume.

The rate coefficients were determined by varying the reaction distance for a constant neutral reactant flow and monitoring both the $^{37}Cl^-$ and $^{35}Cl^-$ ion intensities at each distance. The intensities were normalized to correct for changes in diffusion and to allow the analysis below to be applicable.

We wish to determine the rate coefficient for the exchange reaction

$$^{37}Cl^- + R^{35}Cl \xrightarrow{k} {}^{35}Cl^- + R^{37}Cl \tag{1}$$

However, a natural abundance isotopic mixture of the neutral reactant was used in this study. Therefore, approximately one-quarter of the neutral reactants contain chlorine-37 and the back-reaction forming $^{37}Cl^-$ is important.

$$^{35}Cl^- + R^{37}Cl \xrightarrow{nk} {}^{37}Cl^- + R^{35}Cl \tag{2}$$

We assume that reactions 1 and 2 represent the only sources and sinks for $^{37}Cl^-$ and $^{35}Cl^-$ and the efficiencies of these reactions are identical; n is the ratio of collision rate coefficients for reaction 2 to reaction 1 arising from differences in the reduced mass of the reactants. We can express the change in concentration of each of these ions with time:

$$\frac{d[^{37}Cl^-]}{dt} = -0.758k[^{37}Cl^-][RCl] + 0.242nk[^{35}Cl^-][RCl] \tag{3}$$

$$\frac{d[^{35}Cl^-]}{dt} = \frac{-d[^{37}Cl^-]}{dt} \tag{4}$$

where the factors 0.758 and 0.242 are the fraction of natural abundance of the appropriate isotope. From the equations we solve for the concentration of $^{37}Cl^-$ at all times. If we apply the boundary condition that at $t = \infty$ the ratio $[^{35}Cl^-]/[^{37}Cl^-] = 0.758/0.242n$, we find

$$\ln \{(a + b)[^{37}Cl^-] - b([^{37}Cl^-]_{t=0} + [^{35}Cl^-]_{t=0})\} = -(a + b) \times [RCl](\text{rcn distance})k/\alpha\bar{v} + \ln (a[^{37}Cl^-]_{t=0} - b[^{35}Cl^-]_{t=0}) \tag{5}$$

where $\alpha\bar{v}$ is the average ion velocity, $a = 0.758$, and $b = 0.242n$.

The rate coefficient for reaction 1 is evaluated from the slope of the least-squares line fit of $\ln \{(a + b)[^{37}Cl^-] - b([^{37}Cl^-]_{t=0} + [^{35}Cl^-]_{t=0})\}$ versus reaction distance:

$$k = \frac{-(\text{slope})\alpha\bar{v}}{(a + b)[RCl]} \tag{6}$$

Evaluation of the rate coefficient for the exchange reactions with neutral reactants containing two chlorine atoms (Cl_2 and $SOCl_2$) is more complicated because four reactions must be considered. For Cl_2, for example, there are the following possibilities:

$$^{37}Cl^- + {}^{35}Cl_2 \xrightarrow{k} {}^{35}Cl^- + {}^{37}Cl^{35}Cl \tag{7}$$

$$^{37}Cl^- + {}^{37}Cl^{35}Cl \xrightarrow{pk/2} {}^{35}Cl^- + {}^{37}Cl_2 \tag{8}$$

$$^{35}Cl^- + {}^{37}Cl_2 \xrightarrow{qk} {}^{37}Cl^- + {}^{37}Cl^{35}Cl \tag{9}$$

$$^{35}Cl^- + {}^{37}Cl^{35}Cl \xrightarrow{rk/2} {}^{37}Cl^- + {}^{35}Cl_2 \tag{10}$$

where p, q, and r account for slight differences in the collision rates of these processes due to the differences in masses of the reactants. The expressions for calculating the rate coefficient for the Cl_2 and $SOCl_2$ exchange reactions differ only in the values of a and b in eq 5 and 6. For the Cl_2 reaction, $a = (0.758)^2 + p(0.758)(0.242)$ and $b = (0.242)^2q + r(0.758)(0.242)$. For $SOCl_2$ the expressions for a and b are identical except that the values of p, q, and r refer to the relative collision rates of the reactions corresponding to eq 7–10 for $SOCl_2$.

The reported rate coefficients are an average of several determinations, as noted in the table. For the reaction of $^{37}Cl^-$ with CH_3Cl no $^{35}Cl^-$ was observed even at very high CH_3Cl flows. The rate coefficient given is thus the upper limit for this reaction.

Results and Discussion

The rate coefficients that we measured in this study are given in Table I. Also given are the *reaction efficiencies*, the reaction rate coefficient divided by the calculated collision rate coefficient. In the gas phase an ion and a neutral molecule are attracted to one another by ion–dipole and ion–induced dipole forces which depend upon the mass of the reactants and the dipole moment and polarizability of the neutral reagent.[5] Therefore, the collision rates vary as the structure of the reactants vary; it is more meaningful to compare the fractions of collisions that lead to reaction, i.e., the reaction efficiencies, rather than the rate coefficients themselves. Table I includes reaction efficiencies calculated both by the average dipole orientation theory[5] and by variational rate theory.[6]

We began our investigation by remeasuring in the SIFT two important rate coefficients which had been measured in an ion cyclotron resonance spectrometer, namely, those of $^{37}Cl^-$ with acetyl chloride[1c] and methyl chloride.[1a] Occasionally, rate coefficients in the thermally equilibrated regime of a flowing afterglow or SIFT differ from those measured at low pressure in an ICR cell.[7] Indeed, for the first of these reactions (eq 11) our

$$^{37}Cl^- + CH_3CO^{35}Cl \rightarrow {}^{35}Cl^- + CH_3CO^{37}Cl \tag{11}$$

$$^{37}Cl^- + CH_3{}^{35}Cl \rightarrow {}^{35}Cl^- + CH_3{}^{37}Cl \tag{12}$$

value (2.0×10^{-10} cm^3 s^{-1}, efficiency = 0.09 using ADO theory and 0.06 using variational theory) is larger than that reported earlier (1.2×10^{-10} cm^3 s^{-1}); the agreement is reasonable considering the differences in conditions in the two techniques. We found, however, that methyl chloride is totally unreactive with $^{37}Cl^-$ in the SIFT and that no $^{35}Cl^-$ is formed even at high flow rates of methyl chloride; we place an upper limit of 2×10^{-13} cm^3 s^{-1} on the rate coefficient for this exchange reaction (eq 12). Since we carried out this work, the initial report of a slow but measurable rate for this important reaction in the ICR has been withdrawn.[2d] The fact that no reaction occurs at room temperature suggests that the central S_N2 barrier is close to or projects above the energy of the reactants; existing data on other systems[2d] combined with Marcus theory predict a barrier for reaction 12 that lies 1–2 kcal mol^{-1} above the energy of the reactants. A direct experimental measurement of this barrier height would also be valuable because recent advances in computational techniques and facilities have allowed high-level calculations of the potential energy surfaces involved in the S_N2 reaction in the gas and liquid phase. In particular, the thermoneutral exchange of Cl^- with CH_3Cl has been the subject of many papers.[8] We are currently studying

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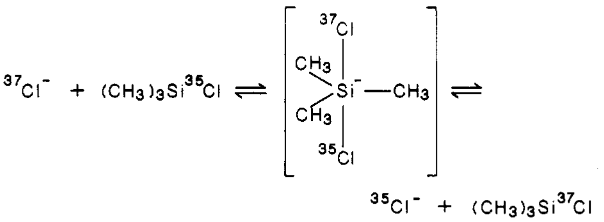
TABLE I: Rate Coefficients and Efficiencies for Exchange Reactions of $^{37}Cl^-$

neutral reactant	k_{expt},[a] 10^{-9} cm^3 s^{-1}	N[b]	reaction efficiency[c]	reaction efficiency[d]
$CH_3{}^{35}Cl$	<0.0002	3	<0.0001	<0.0001
$CH_3CO^{35}Cl$	0.20 (±0.02)	3	0.09	0.06
$(CH_3)_3Si^{35}Cl$	0.45 (±0.08)[e]	12	0.24	0.20
$(CH_3)_2P^{35}Cl$	1.1 (±0.1)	4		
$SO^{35}Cl_2$	1.2 (±0.1)	3	0.70	0.57
$^{35}Cl_2$	0.53 (±0.08)	5	0.52	0.52
$H^{35}Cl$	0.71 (±0.03)	5	0.53	0.42
$D^{35}Cl$	0.74 (±0.05)	5	0.56	0.44

[a] Number in parentheses is standard deviation of average experimental rate coefficient. The absolute error in the rate coefficients is estimated to be ±25%. [b] Number of determinations. [c] Reaction efficiency = k_{expt}/k_{ADO} where k_{ADO} is calculated by the method of ref 5. [d] Reaction efficiency = k_{expt}/k_{var} where k_{var} is calculated by the method of ref 6. [e] From ref 9. This rate coefficient represents the exchange channel only; association also occurs.

this reaction as a function of ion kinetic energy in an attempt to determine the intrinsic barrier height. A study of the temperature dependence of this reaction would also be of great importance.

Chloride ion reacts inefficiently with acetyl chloride and extremely slowly, if at all, with methyl chloride. It is interesting to compare these reactions with analogous ones among second-row elements, where pentacoordinate intermediates are possible. The first such example (eq 13) is that of $^{37}Cl^-$ reacting with chlorotrimethylsilane, which we reported earlier[9] occurs with a rate coefficient of 4.5×10^{-10} cm^3 s^{-1}, corresponding to a reaction efficiency of 0.24, using ADO theory and 0.20 using variational theory. Moreover, we found that substitution reactions of chlorotrimethylsilane with other nucleophiles occur upon every collision when the reaction is exothermic; this is in contrast to reactions of methyl chloride which show decreasing reactivity with decreasing exothermicity.[9] These observations suggest that the silicon reactions may proceed through low-energy pentacoordinate intermediates of the type shown in eq 13 rather than through high-energy transition states typical of carbon reactions.[9] To determine whether phosphorus halides behave similarly, we examined the exchange reaction of chlorodimethylphosphine with $^{37}Cl^-$. The experimental rate coefficient of $k = 1.1 \times 10^{-9}$ cm^3 s^{-1} is considerably larger than that for chlorotrimethylsilane. Neither the dipole moment nor the polarizability of chlorodimethylphosphine is known, so that it is difficult to estimate the collision rate coefficient for this reaction. However, rough estimates of this value suggest that the exchange rate coefficient corresponds to the maximum reaction efficiency of one-half. In any event, chloride exchange on a P–Cl bond is even more facile than that for either a Si–Cl or a C–Cl bond. A symmetrical or rapidly equilibrating pentacoordinate complex again seems a likely intermediate in this reaction (eq 14).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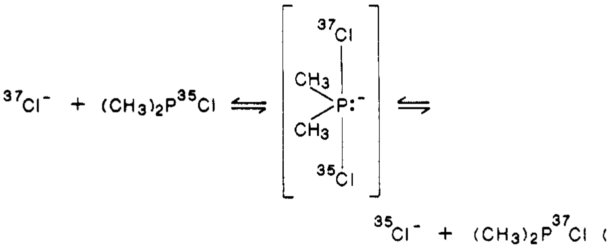
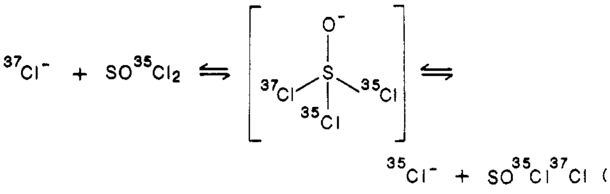

(14)

In order to compare first- and second-row acid chlorides, we examined exchange reactions of chloride ion with thionyl and sulfuryl chloride. For the first of these reactants the exchange rate coefficient is $k = 1.2 \times 10^{-9}$ cm^3 s^{-1}, corresponding to a reaction efficiency of 0.70 using ADO theory and 0.57 using variational theory. This is close to the statistical efficiency of 0.67 expected if the three chlorine atoms become equivalent in a long-lived adduct (eq 15). However, a reaction efficiency of 0.67 would also be observed if the reaction proceeds through a transition state in which only two chlorines are equivalent (eq 16). If the complex is long-lived and chloride displacement is rapid compared to dissociation of the complex, complete equilibration of the isotopes will be observed. Regardless of the exact mechanism of exchange, it is clear that rapid, statistical isotope exchange occurs for second-row acid chlorides, in contrast to the relatively slow exchange observed for the corresponding first-row compounds.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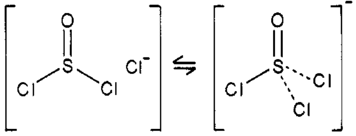
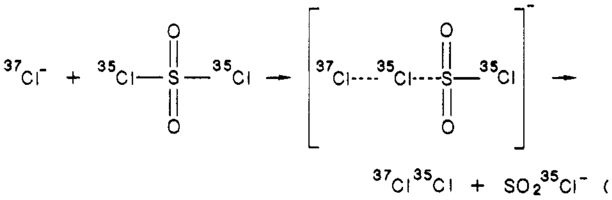

(16)

Reaction of sulfuryl chloride (SO_2Cl_2) with chloride ion forms SO_2Cl^-.[10] A likely mechanism for this reaction is direct displacement by chloride ion on one of the chlorine atoms. However, a study with isotopically labeled chloride ion would reveal if equilibration of the chlorines, resulting from attack on sulfur, occurs faster than or in competition with this reaction. We found, in fact, that reaction occurs rapidly but *no isotope exchange occurs*. Thus, direct attack on chlorine is more efficient than attack on sulfur (eq 17).


(17)

We next examined exchange with Cl_2. The rate coefficient for exchange of $^{37}Cl^-$ with molecular chlorine is 5.3×10^{-10} cm^3 s^{-1}, corresponding to about 50% of the collision rate coefficient. This result is best accommodated if the reaction occurs through a long-lived Cl_3^- intermediate which can dissociate either to reactant $^{37}Cl^-$ or to product $^{35}Cl^-$ ions.

$$^{37}Cl^- + {}^{35}Cl\text{–}{}^{35}Cl \rightarrow [{}^{37}Cl\text{–}{}^{35}Cl\text{–}{}^{35}Cl]^- \rightarrow {}^{37}Cl\text{–}{}^{35}Cl + {}^{35}Cl^- \quad (18)$$

A long-lived complex in which multiple displacements occur or in which a symmetrical triangular transition state is accessed is less likely; this would give rise to complete equilibration of the three chlorine atoms and a reaction efficiency of 0.67. The ion Cl_3^- is stable and has been observed in the gas phase,[11,12] and the

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reaction of $^{37}Cl^-$ with Cl_2 has been studied at higher energies in the gas phase[13] where the only ionic product was found to be Cl_2^-. The isotopic distribution observed within this Cl_2^- is consistent with the formation of a linear Cl_3^- intermediate.

Finally, we have investigated chloride ion exchange upon reaction of $^{37}Cl^-$ with $H^{35}Cl$ and $D^{35}Cl$. We hoped to shed light on two questions. First, does reaction proceed directly, without complex formation, or is there a relatively long-lived reaction complex as an intermediate? Second, is tunneling important in these simple proton-transfer reactions? These experimental studies were inspired by the theoretical studies of Ali, Chapman, and Hynes.[14]

The wealth of data obtained on ion–molecule reactions over the past 20 years is best accommodated by the idea that most thermal energy reactions proceed through long-lived complexes. However, certain reactions appear to occur directly; that is, they occur without formation of a long-lived complex despite the long-range attractive potential which distinguishes an ion–molecule reaction from a reaction between two neutrals. In particular, Leone, Bierbaum, and co-workers[15] have studied a number of exothermic reactions between halide ions and hydrogen halides (Cl^- + HBr, F^- + HBr, etc.) and found that the vibrational distributions in the neutral products are very similar to those observed in the analogous neutral–neutral reactions. This led them to conclude that the presence of the attractive well in the ionic reactions has little or no effect on the energy disposal in the products; these ionic reactions do not proceed through a long-lived complex in which energy is randomized, but rather proceed directly.

All of the reactions studied by these workers were highly exothermic and proceed at approximately the collision rate. We were interested in determining whether the thermoneutral reaction

$$^{37}Cl^- + H^{35}Cl \rightarrow {}^{35}Cl^- + H^{37}Cl \qquad (19)$$

proceeds directly. The consequence of direct reaction is that the exchange rate coefficient can assume any value from 0 to k_c, the collision rate coefficient. For this reaction no significant barrier to formation of the complex is expected. Therefore, if a long-lived complex is formed, the efficiency of the reaction is predicted to approach the statistical value of 50% k_c.

The second question we hoped to address is whether tunneling is important in this reaction. The lowest energy reaction path for the Cl^-/HCl collinear reaction may be represented by a double-well potential energy surface; the minima correspond to ion–dipole complexes of the reactants and products, and the maximum represents the transition state in which the proton is symmetrically placed between the chloride ions. Experimentally, the wells have been found to lie ~23 kcal mol^{-1} below the energy of the reactants[16] and the central barrier has been estimated theoretically to lie only 1 kcal mol^{-1} above the bottom of the wells.[17] The low barrier height suggests that tunneling should be unimportant for Cl^- + HCl reactions that proceed by this pathway.

However, Hynes and co-workers[14] have explored the possibility of tunneling in this system at large chlorine–chlorine separations where the barrier for proton transfer is substantial. For the corresponding neutral–neutral process of Cl + HCl, Truhlar and co-workers[18] have found theoretically that such tunneling is very important.

In order to determine whether a significant fraction of the $^{37}Cl^-/H^{35}Cl$ exchange reaction proceeds by tunneling and to shed more light on the question of direct reaction versus complex formation, we measured the rate coefficients for reactions 19 and 20. In general, if tunneling is important, we expect the efficiency of the HCl reaction to be greater than that of the DCl reaction, i.e., $k_H/k_D > 1$.

$$^{37}Cl^- + D^{35}Cl \rightarrow {}^{35}Cl^- + D^{37}Cl \qquad (20)$$

We found that the rate coefficient for the $^{37}Cl^-/H^{35}Cl$ reaction is 7.1 (±0.3) × 10^{-10} cm^3 s^{-1} and for the $^{37}Cl^-/D^{35}Cl$ reaction is 7.4 (±0.5) × 10^{-10} cm^3 s^{-1}. These correspond to reaction efficiencies of 53 and 56%, respectively, using ADO theory, and to reaction efficiencies of 42 and 44%, respectively, using variational theory. It is clear, therefore, that these reactions are proceeding with comparable efficiency at or near the statistically predicted limit of 50%. The reaction may be direct, since the efficiency of a direct process may assume any value between 0 and k_c. However, it is unlikely that these reactions will have the same efficiency if the processes occur directly. We favor, therefore, the conclusion that the reaction is proceeding through a long-lived complex. As discussed above, complex formation is not important in the exothermic halide/hydrogen–halide systems previously investigated.[15] We propose that the lack of an energetic driving force in the Cl^-/HCl system promotes formation of a long-lived complex.

If the system proceeds through a long-lived complex, our data give us little information on the tunneling process in this reaction. We can only conclude that if tunneling occurs, it must be facile on time scales corresponding to the complex lifetime. However, the quantum calculations of Ali et al.[14] predict that tunneling is not important in this reaction; the attractive potential results in rapid passage of the reactants through the "tunneling region" resulting in a small probability for tunneling.

The calculations of Ali et al.[14] also indicate that the collinear reaction of Cl^-/HCl proceeds directly (i.e., is vibrationally adiabatic), with a reaction probability of ~80%. Resolution between their results and our statistical efficiency indicating complex formation lies in the fact that the collinear collisions make up only a small fraction of the total collisions. Apparently, the noncollinear collisions principally proceed through a long-lived complex.

Conclusion

In conclusion, the isotope-exchange reactions of a series of chlorine-containing compounds reveal diverse behavior. The S_N2 reaction of $^{37}Cl^-$ with methyl chloride does not proceed at a measurable rate at room temperature, suggesting that the transition-state barrier is close to or protrudes above the energy of the reactants. In contrast, chloride exchange on the second-row analogues, chlorotrimethylsilane and chlorodimethylphosphine, proceeds at least 2000 times faster; this indicates that barriers are low and suggests the possible formation of low-energy pentacoordinate intermediates in these latter reactions.

Chloride ion exchange with thionyl chloride occurs at the statistical limit in contrast to the moderately slow exchange observed for acetyl chloride. Once again, the barrier to exchange for second-row compounds appears to be lower than for the first-row analogues. Reaction of $^{37}Cl^-$ with sulfuryl chloride occurs only by chlorine atom abstraction with no isotope exchange, indicating that direct attack on chlorine is more facile than attack on sulfur.

The exchange reaction with molecular chlorine proceeds in half of the collisions, indicating that only two chlorine atoms become equivalent. This observation suggests that a bound Cl_3^- intermediate is formed from end-on attack.

Finally, the exchange reactions of $^{37}Cl^-$ with $H^{35}Cl$ and $D^{35}Cl$ are facile, indicating that barriers to proton transfer are low. The reaction efficiency of ~50% suggests that these thermoneutral reactions proceed through a long-lived complex rather than directly as has been proposed for exothermic halide/hydrogen–halide systems.

Acknowledgment. This paper is dedicated to Professor Frederick Kaufman, a devoted teacher, stimulating colleague, and dear

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Registry No. $^{37}Cl^-$, 42150-36-7; $CH_3{}^{35}Cl$, 74-87-3; $CH_3CO^{35}Cl$, 75-36-5; $(CH_3)_3Si^{35}Cl$, 75-77-4; $(CH_3)_2P^{35}Cl$, 811-62-1; $^{35}Cl_2$, 7782-50-5; $H_3{}^5Cl$, 7647-01-0; $D^{35}Cl$, 7698-05-7; SO_2Cl_2, 7791-25-5; D_2, 7782-39-0.

Electron Dissociative Attachment to NF_2 Radicals

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Measurements of discharge current in an electron beam sustained-discharge device have been used to determine the dissociative attachment rate constant of electrons to NF_2 radicals. This was done by measuring the relative rate of electron attachment to NF_2 compared to dilute molecular chlorine in a nitrogen buffer in separate experiments in the same device. A comparison of the steady-state current measured for these two different mixtures at identical total pressures and applied electric fields provides a relative measurement for the rate of disappearance of electrons. Since the attachment rate constant with molecular chlorine is well-known, rate constants for the fluoride radical could be determined. Values near 1.5×10^{-9} cm^3/s for average electron energies near 1 eV were obtained.

Introduction

Interest in attachment processes, particularly for the halogen molecules, has been most closely coupled to the interest in the corresponding rare-gas halide lasers, so-called excimer lasers. These lasers typically are operated in an electron beam[1] or a discharge pumped geometry.[2] Investigations into the fundamental kinetics of these laser systems suggest that one of the routes for forming the upper laser level is via ion–ion combination reactions of positive rare-gas ions with negative halogen ions.[3] These halogen anions are formed principally by dissociative attachment of electrons to the halogen fuel present in the laser mix, e.g., F_2 for KrF, NF_3 for XeF, and HCl for XeCl lasers, etc. Knowledge of the rate constants for these processes is fundamental for modeling the kinetics of this important class of lasers.

Beside providing the negative ion source for the upper laser level reaction formation channel, the halogen fuel also helps stabilize the discharge by clamping the electron number density buildup in the gas. This permits more efficient operation of the discharge and reduces the quenching of the upper laser level by electrons, which is a dominant quenching process in typical laser devices.[4,5]

In electron beam pumped devices, these secondary electrons arise as a result of high-energy electron beam collisions with the high-pressure rare gases present, viz.

$$e_p + Ne \rightarrow Ne^+ + e_p' + e_s$$

where e_p represents the primary electrons, and e_s the secondary electrons. Low-energy electrons are also produced with discharge pumping by source electrons being accelerated in the discharge circuit to energies that eventually produce secondary ionization. Regardless, the secondary electrons thus formed subsequently undergo a variety of energy-transfer collisions and attain average energies near 1 eV under typical laser operating conditions. The values for electron energy were obtained from utilization of a Boltzmann code,[6] which contains cross sections from swarm data for electron impact processes in N_2 as a function of applied electric field.

These electrons can undergo dissociative attachment reactions with halogen fuels to produce negative ions and radicals, e.g., xenon fluoride lasers operate with neon, xenon, and nitrogen trifluoride mixtures, so for these lasers the dominate process is electron attachment to the nitrogen trifluoride fuel:

$$e_s + NF_3 \rightarrow F^- + NF_2$$

It has also been observed[7] in XeF lasers that there is a gradual buildup of N_2 as a result of gas-phase reactions initiated with the electron beam firing. For multiple pulses on the same mix, eventually this buildup of nitrogen can prevent the laser from operating.[8] This arises as a result of absorption processes attributed to the nitrogen that reduce the gain-to-loss ratio in the laser cavity to an unfavorable value.

One proposed reaction sequence[7] that could produce nitrogen in such mixtures is electron attachment to the nitrogen difluoride radicals:

$$e_s + NF_2 \rightarrow NF + F^-$$

followed by

$$NF + NF \rightarrow N_2 + 2F$$

Ideally, one would like to obtain the elementary, state-selected, rate constants for electron attachment to NF_2 radicals in a variety of excited states (vibration, electronic, etc.) and then monitor the fate of the products, but this kind of detailed kinetic information is not available.

Procedure

To obtain some information, we have performed electron dissociative attachment experiments on equilibrium mixtures of dilute tetrafluorohydrazine in nitrogen at total pressures of 1 amagat heated to near 500 K, where thermodynamics indicate that the dominate species (>99%) are NF_2 radicals.[9]

To provide a well characterized source of electrons near the 1-eV energy regime, we used nitrogen as a buffer gas, since the behavior of electrons in nitrogen at total pressures near 1 atm is well-known. With the concentration of halogen small (≈1%) and the total pressure constant, the assumption that the electron energy distribution is determined by the nitrogen alone is reasonable.

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