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A SELECTED ION FLOW TUBE STUDY OF THE REACTIONS OF THE GASEOUS ION HCl^+ AT 295 K

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Reactions of the gaseous ion HCl^+ in its ground state were studied at 295 ± 5 K using a selected ion flow tube Reaction rate coefficients and product ion branching ratios were determined for the reactants H_2, Xe, NO, O_2, CO, CO_2, N_2O, H_2S, COS, SO_2, NH_3 and CH_4. The reaction channels observed were proton or electron transfer, or both, except for H_2 where H-atom transfer was observed.

1. Introduction

The thermal energy reactions of the gaseous ion HCl^+ have previously only been studied with the neutral reactant H_2, i e.

$$HCl^+ + H_2 \rightarrow H_2Cl^+ + H. \quad (1)$$

This reaction has been investigated in a flowing afterglow (FAG) apparatus at a temperature of ≈300 K [1], and more recently has been the subject of an investigation over the temperature range 150–400 K in an ion cyclotron resonance (ICR) experiment [2] and over the range 80–470 K in a selected ion flow tube (SIFT) experiment [3]. The reaction

$$HCl^+ + Xe \rightarrow Xe^+ + HCl \quad (2a)$$

has been studied by a merging beams (MB) technique [4] in the relative energy range 0.01–870 eV; however, in such an experiment the internal and translational energy distributions of the reactants are not thermal.

The present work concerns the reactions of HCl^+ with a range of neutral reactants studied using the SIFT technique in which the reactants do possess a thermal distribution of translational and rotational energy (see comments below on vibrational energy). The reaction zone temperature in these experiments was 295 ± 5 K.

The sequential reactions of Cl^+ and HCl^+ with H_2 are part of the reaction scheme leading to the production of HCl in interstellar clouds [5], the present results for reaction (1) tend to exceed those obtained in the previous FAG and ICR studies possibly because, in the latter case, the ions are suprathermal. Although H_2 is the dominant neutral species in these clouds, CO and N_2 also exist in concentrations of 0.01% and 0.001%, respectively [6]. The reactions of HCl^+ with these two gases are studied in the present work.

The reaction of HCl^+ with Xe is important in XeCl excimer laser systems using HCl as the chlorine donor, and the present work includes a study of this reaction. In addition to the electron transfer observed in the MB experiment [4], we have observed the proton transfer channel

$$HCl^+ + Xe \rightarrow XeH^+ + Cl \quad (2b)$$

to be significant.

2. Apparatus and experimental

The SIFT used in the present experiments is similar to that described in a previous publication [7,8]. However, the present apparatus was designed for versatility, and in particular will allow the rapid installation of more specialised ion sources The primary ions were generated in an electron impact ion source containing either CH_3Cl or HCl. The ionising electron

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Table 1
Reactions of HCl^+ at 295 K

Reaction	Branching ratio (%)	Rate coefficient (10^{-10} cm^3 s^{-1})	
		experimental (± 20%)	gas kinetic [9,10]
$HCl^+ + H_2 \rightarrow H_2Cl^+ + H$	100	8.9	15.3
$HCl^+ + Xe \rightarrow Xe^+ + HCl$	80 ± 10	6.3	8.2
$\rightarrow XeH^+ + Cl$	20 ± 10		
$HCl^+ + NO \rightarrow NO^+ + HCl$	63 ± 5	6.4	8.1
$\rightarrow NOH^+ + Cl$	37 ± 5		
$HCl^+ + O_2 \rightarrow O_2^+ + HCl$	100	6.9	7.1
$HCl^+ + CO \rightarrow COH^+ + Cl$	100	7.1	8.6
$HCl^+ + CO_2 \rightarrow CO_2H^+ + HCl$	100	9.3	8.4
$HCl^+ + N_2O \rightarrow N_2OH^+ + Cl$	100	10.1	10.4
$HCl^+ + H_2S \rightarrow H_2S^+ + HCl$	75 ± 10	13.2	16.3
$\rightarrow H_3S^+ + Cl$	25 ± 10		
$HCl^+ + COS \rightarrow COS^+ + HCl$	72 ± 5	13.6	16.2
$\rightarrow COSH^+ + Cl$	28 ± 5		
$HCl^+ + SO_2 \rightarrow SO_2^+ + HCl$	40 ± 5	19.0	20.3
$\rightarrow SO_2H^+ + Cl$	60 ± 5		
$HCl^+ + NH_3 \rightarrow NH_3^+ + HCl$	35 ± 10	20.4	20.4
$\rightarrow NH_4^+ + Cl$	65 ± 10		
$HCl^+ + CH_4 \rightarrow CH_4^+ + HCl$	30 ± 5	12.2	11.2
$\rightarrow CH_5^+ + Cl$	70 ± 5		
$HCl^+(v > 0) + N_2 \rightarrow N_2H^+ + Cl$	100	9 ± 3	7.8

energy was normally 40 eV, but was varied between 40 and 120 eV in experiments to investigate the possible presence of excited HCl^+. No effect of electron energy on the results presented was observed within experimental error.

In all reactions He was used as the carrier gas with a pressure in the flow tube of ≈0.5 Torr. Reaction rate coefficients given in table 1 were determined from experimental data by plotting the logarithm of the ion count rates against corresponding neutral reactant flow rates [7]. For some of the reported reactions, the branching ratio of product ions was determined by plotting product ion count rates as a percentage of the total product ion intensity against the corresponding neutral reactant flow rate. In cases where product ions undergo further reaction with the neutral reactant, the rate equations specified by the kinetic scheme of those reactions were solved and a best fit to the experimental data was then obtained as a function of the branching ratio. It is believed that the reaction rate coefficients presented in table 1 refer to ground electronic state reactions. This conclusion was supported by the observation of linear semi-logarithmic data over two orders of magnitude for all the reported reactions except for reaction with N_2 which is discussed below.

In addition except in the case of N_2 reactant (see below) no reaction channels endoergic for ground-state reactants were observed, the first electronically excited state of HCl^+ lying 3.55 eV above the ground state.

3. Results and discussion

The reaction rate coefficients and product channel branching ratios determined here are shown in table 1. The classical model gas kinetic rate coefficients calculated using the Langevin [9] or average dipole orientation (AADO) [10] models, for non-polar and polar reactant molecules respectively, are shown for comparison.

For all reactions, with the exception of that with H_2, electron or proton transfer was observed. In cases where both were known to be energetically possible, then both these processes were observed. In the case of H_2, electron and proton transfer are endoergic and reaction was by H atom transfer [reaction (1)].

3.1. Reactant internal energy states – the reaction $HCl^{+*} + N_2$

As already mentioned, it is believed that the data presented here refer to ground electronic states of the reactants. However, the reaction of HCl^+ with N_2 indicates the presence of a reactive (HCl^{+*}) and a non-reactive component of HCl^+. It is most likely that the reactive component consists of $HCl^+(v > 0)$, the transfer of a proton from these states being exoergic (see below) whereas proton transfer from $HCl^+(v = 0)$ is endoergic. The increase in intensity of product N_2H^+ with increasing N_2 flow rate, to a constant value shows that ≈3% of the HCl^+ reacts to give N_2H^+ when the HCl^+ was generated using either HCl or CH_3Cl in the ion source. This figure represents a lower limit of the amount of HCl^{+*} entering the flow tube as quenching of HCl^{+*} could occur.

The rate constant for the reaction

$$HCl^{+*} + N_2 \rightarrow N_2H^+ + Cl,$$
$$\rightarrow HCl^+ + N_2 \qquad (3)$$

could not be estimated from the slight decay of the HCl^+ but was calculated from the product N_2H^+ rise to be 9×10^{-10} cm^3 s^{-1} ± 30% which is to be compared with the Langevin rate constant of 7.8×10^{-10} cm^3 s^{-1}.

The proton affinity of Cl can be calculated to be 5 29 ± 0.01 eV [11,12]. The proton affinity of N_2 is given by Bohme et al. [13] as 5.09 ± 0.03 eV and the endoergicity of the reaction

$$HCl^+ + N_2 \rightarrow N_2H^+ + Cl \qquad (4)$$

is therefore 0.20 ± 0.4 eV for ground-state species. As the $v = 1$ level of HCl^+ lies 0.32 eV above the $v = 0$ level, the proton transfer for $HCl^+(v = 1)$ is exoergic.

The primary ion decay plots for all neutral reactants other than N_2 correctly give the rate constant for the $HCl^+(v = 0)$ but the possibility exists that for reactions in which more than one product was observed, the branching ratio could differ for $HCl^+(v = 0)$ and $HCl^+(v > 0)$. In order to investigate the effect of $HCl^+(v > 0)$ on the observed branching ratios experiments were carried out in which N_2 was introduced to the flow tube with the buffer gas in sufficient quantity that the HCl^{+*} was removed before the reactant gas entry port, leaving 3% N_2H^+ and 97% $HCl^+(v = 0)$ as the only reactant ions. The branching ratios obtained in this case were within experimental error the same as those obtained without the introduction of N_2 with the buffer gas. We therefore conclude that the branching ratios given in table 1 refer to $HCl^+(v = 0)$.

3.2 *Proton affinity data*

Sufficient thermochemical data are not available to determine whether proton transfer from HCl^+ to NO and SO_2 would be exoergic, although table 1 shows these reactions to be fast. It is well known that the rate coefficient for proton transfer falls off very rapidly with the onset of reaction endoergicity (see, for example ref. [14]) which suggests that PA(NO) and $PA(SO_2) \gtrsim PA(Cl) = 477$ kJ mol^{-1} [15].

3.3. *$HCl^+ + H_2$*

Rate coefficients for reaction (1) (k_1) of 5.5 and 4.9×10^{-10} cm^3 s^{-1} have been obtained at 300 K by drift cell and trapped cell ICR respectively [2], and a negative temperature dependence, $k_1 \propto T^{-0 6}$, was found using the drift cell ICR over the temperature range 150–400 K. The previous FAG result [1] was $k_1 = (5 2 \pm 1.6) \times 10^{-10}$ cm^3 s^{-1} at 300 K. It may be seen from table 1 that the present result tends to exceed these values, and is slightly outside the combined estimates of experimental error. The rate coefficient of $(1.3 \pm 0.4) \times 10^{-9}$ cm^3 s^{-1} obtained in a previous SIFT experiment [3] is substantially higher than the present value but lies within the combined estimates of experimental error. In contrast with the drift cell ICR result [2] the SIFT experiment showed no temperature dependence for reaction (1) over the temperature range 80–470 K.

To increase confidence in the present result, and to discount the possibility that some particular experimental problem may attend the use of hydrogen as a neutral reactant, further calibration experiments were carried out. These experiments included an absolute calibration of the neutral reactant metering system using hydrogen as the calibrating gas, and the redetermination of rate coefficients for the reaction of other ions with H_2, comparison being made with results from other flow reactors [16]. No anomalies were found.

In section 1, the relevance of reaction (1) to a reaction scheme [5] for the production of HCl in interstellar clouds was mentioned. A higher value for k_1 would not significantly change the HCl concentration predicted by this scheme, but would reduce the concentration of the intermediate species HCl^+.

3.4. *$HCl^+ + Xe$*

An absolute cross section for reaction (2a) has been measured in a MB experiment [4], and it is possible to make an approximate comparison of this result with the present result. A velocity-dependent reaction cross section, $\sigma(v)$, is related to a rate coefficient, k, for a velocity distribution, $f(v)$, by

$$k = \int \sigma(v) f(v)\, v \, dv. \qquad (5)$$

The rate coefficient presented here is measured for a Maxwell–Boltzmann velocity distribution at 295 K so that the MB (merging beams) cross section may be approximately converted using

$$k_{2a}(\mathrm{MB}) = \nu' \sigma(\nu'), \qquad (6)$$

where ν' is the mean relative velocity for the HCl^+/Xe collision pair in a Maxwell–Boltzmann distribution at 295 K. ν' corresponds to a collision energy of 38 meV for which the MB reaction cross section is 7.15×10^{-15} cm^2. From eq. (6), $k_{2a}(\mathrm{MB}) = 3.6 \times 10^{-10}$ cm^3 s^{-1}. The present result for the total rate coefficient of reaction (2), $k_2(\mathrm{SIFT}) = (6.6 \pm 1.3) \times 10^{-10}$ cm^3 s^{-1}, together with the measured branching ratio (and associated experimental error) for reaction (2a) gives $k_{2a}(\mathrm{SIFT}) = (5.4 \pm 1.7) \times 10^{-10}$ cm^3 s^{-1}. When comparing the MB and SIFT results it should be noted that the authors of ref. [4] believed their HCl^+ reactant ions to be vibrationally excited, and inferred that a larger cross section would be obtained for ground-state HCl^+.

A typical XeCl gas laser mixture would comprise some tens of Torr of Xe and a few Torr of HCl in ≈2 atm of Ar or He buffer gas. This mixture is excited by high-energy electrons which will produce mainly positive buffer gas ions and secondary electrons. HCl^+ is produced by charge transfer from these positive ions, and the present work shows that it will be rapidly lost by reaction (2) (with a time constant of a few ns) to produce Xe^+ and XeH^+. The presence of XeH^+ in the XeCl laser has not been discussed previously but may possibly contribute to the formation of the XeCl excimer

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