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# Rate constants and products for the reaction of $HBr^+$ with HBr and DBr

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**Abstract**

The proton transfer channel for the reaction of $HBr^+$ with HBr is investigated in a state-specific manner by preparing the reagent ion in a selected internal state by resonance-enhanced ionization (REMPI) and monitoring the disappearance of this ion by laser-induced fluorescence (LIF). A rate constant for proton transfer of $(6.7 \pm 1.6) \times 10^{-10}$ $cm^3/s$ is found. The reaction of $HBr^+$ with HBr and DBr was also studied in a selected ion flow tube. The reactions were found to be quite complex producing charge transfer, proton transfer, and hydrogen transfer products. The rate constants are $(5.3 \pm 1.3) \times 10^{-10}$ $cm^3/s$ for the removal of $HBr^+$ by HBr and DBr neutrals. © 1997 Elsevier Science B.V.

## 1. Introduction

Previously, we have investigated the charge transfer reaction:

$$DBr^+\left(^2\Pi_i, v^+, J^+\right) + HBr \rightarrow HBr^+\left(^2\Pi_{i'}, v'^+, J'^+\right) + DBr \quad (1)$$

under thermal conditions in which the absolute state-to-state rate constants were measured [1]. This study found a propensity for resonant charge exchange. Although the charge transfer was studied in detail, it is only one of several channels possible. In this paper we extend this work by measuring the total reactivity in two ways. We have measured the proton transfer reaction of $HBr^+$ with HBr:

$$HBr^+\left(^2\Pi_{3/2}, v^+ = 0, J^+\right) + HBr \rightarrow H_2Br^+ + Br \quad (2)$$

using a spectroscopic technique similar to that used to study reaction (1). We refer to reaction (2) as proton transfer for convenience, although we cannot distinguish between proton transfer and hydrogen-atom abstraction. This work extends our previous spectroscopic work to the measurement of a thermal reaction rate for a case in which the reaction product is not directly observed. The disappearance of ground-state $HBr^+$ ion allows us to infer the rate constant for reaction (2).


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We have studied the kinetics of $HBr^+$ with HBr and DBr in a selected ion flow tube apparatus. The selected ion flow tube has the advantage that all products can be measured and for reaction (2) this means charge transfer, proton transfer and hydrogen transfer. By selecting only one isotope of the $HBr^+$ information on all three channels can be obtained:

$$H^{79}Br^+ + H^{79,81}Br \rightarrow H^{79}Br^+ (80), \quad \text{charge transfer not observable} \tag{3a}$$

$$\rightarrow H^{81}Br^+ (82), \quad \text{charge transfer} \tag{3b}$$

$$\rightarrow H_2{}^{79}Br^+ (81), \quad \text{proton transfer} \tag{3c}$$

$$\rightarrow H_2{}^{81}Br^+ (83), \quad \text{proton transfer} \tag{3d}$$

$$\rightarrow H_2{}^{79}Br^+ (81), \quad \text{hydrogen transfer.} \tag{3e}$$

We have also studied the reaction with DBr as the neutral:

$$H^{79}Br^+ + D^{79,81}Br \rightarrow D^{79}Br^+ (81), \quad \text{charge transfer} \tag{4a}$$

$$\rightarrow D^{81}Br^+ (83), \quad \text{charge transfer} \tag{4b}$$

$$\rightarrow HD^{79}Br^+ (82), \quad \text{proton transfer} \tag{4c}$$

$$\rightarrow HD^{81}Br^+ (84), \quad \text{proton transfer} \tag{4d}$$

$$\rightarrow HD^{79}Br^+ (82), \quad \text{deuterium transfer.} \tag{4e}$$

The advantage of studying spectroscopically ion–molecule reactions is the ability to know with confidence the individual internal states of the species taking part in the reaction. This letter shows that in some favorable cases a reaction can be studied even without direct observation of the product. Product information, however, cannot be extracted as easily as with conventionally mass spectrometric techniques and the two approaches together yield complementary data.

## 2. Experimental

The apparatus for the spectroscopic study has been described previously by Xie and Zare [1]. $HBr^+(^2\Pi_{3/2}, v^+ = 0)$ was prepared state selectively using (2 + 1) REMPI through the R(1) line of the f $^3\Delta_2$–$X\,^1\Sigma^+$ (0,0) band of HBr at 269.26 nm. The decay of the ion population was measured via LIF of the $A^2\Sigma$–$X\,^2\Pi_{3/2}$ (0,0) band of $HBr^+$. The isotopes of bromine cannot be distinguished in the LIF measurements owing to the small change in the reduced mass of the hydrogen. The rate of this decay should be equal to the rate of reaction (2) plus the rate with which the ion moves outside of the detection region. We refer to this latter rate as the rate of 'flyout'. Charge transfer and rotational energy transfer will not lead to a decay of the total $HBr^+(^2\Pi_{3/2}, v^+ = 0)$ population owing to the fact that the $HBr^+(^2\Pi_{1/2}, v^+ = 0)$ and $HBr^+(^2\Pi_{3/2}, v^+ = 1)$ states are energetically inaccessible. These processes will contribute to relaxation of the LIF spectra but will not reduce the integrated populations derived from the spectra. Thus by measuring the pressure dependence of the decay rate and using a model to correct for the flyout we are able to ascertain the absolute rate constant for reaction (2).

The experiment was performed in a flowing gas cell in which HBr (from source) used without further purification maintains a specific pressure chosen between 3 and 100 mTorr. For a given set of spectra the pressure was held constant. Spectra were taken at several time delays from 10 to 800 ns between the REMPI laser and the LIF probe at a given pressure. The LIF signal is normalized with respect to the power of the LIF laser and number of reagent ions formed by REMPI. The pressure was then changed and a new series of spectra acquired.

The selected ion flow tube has been described in detail previously and only details pertinent to the present experiments are presented here [2]. $HBr^+$ was made in a high-pressure electron impact ion source. Only the $H^{79}Br^+$ isotope was injected into the flow tube. The kinetics and branching ratios were taken in the normal fashion and will not be discussed further. We estimate the error limits to be $\pm 25\%$ for the rate constants and 5% for the branching percentages. We checked for excited states of $HBr^+$ through the reactions of $HBr^+$ with $CH_4$ and $CF_4$ [3]. The maximum amount of excited states (sum of spin and vibrational excitation) was determined to be 20%. The decay curves for both reactions were linear so the presence of excited states did not affect the rate constant measurements. The product branching ratios are for the mixture of states.

## 3. Results and discussion

Fig. 1 shows LIF spectra at different time delays and the decay of the signal with time. The relative populations were derived from each spectra using appropriate linestrength formulas [4] and were summed together to obtain a total population for each time delay. The natural logarithm of the populations was plotted versus time delay and fit to a straight line. A rate constant $k_{meas}$ for a given pressure was derived from the slope.

We account for flyout by measuring the pressure dependence of this rate constant. Let $k_1$ be the rate constant of the reaction and let $k_2$ be the rate of flyout. The rate of decay of the $HBr^+$ can be expressed as:

$$-\frac{d[HBr^+]}{dt} = k_1[HBr^+][HBr] + k_2[HBr^+]/[HBr], \quad (5)$$

with the assumption that the rate of flyout varies inversely with pressure. The mean free path varies inversely with pressure and flyout is assumed to be proportional to the mean free path. The rate of flyout should depend on the number of ions present, whereas the rate of bimolecular reaction depends on both the number of ions present and the number density of the neutral. Integrating Eq. 3 over a time interval $\Delta t$ yields:

$$-\frac{\ln[HBr^+]}{\Delta t} = k_1[HBr] + k_2/[HBr]. \quad (6)$$

The expression on the left-hand side will have the correct units for a pseudo first-order rate constant if the entire equation is divided by [HBr]. We define $k_{meas} = -\ln[HBr^+]/([HBr]\Delta t)$ and write

$$k_{meas} = k_1 + k_2/[HBr]^2. \quad (7)$$

Fig. 2 shows $k_{meas}$ plotted against $[HBr]^{-2}$ where [HBr] is expressed as a number density derived from the pressure assuming the ideal gas law at 300 K. The $y$-intercept yields a value for $k_1$ of $(6.7 \pm 1.6) \times 10^{-10}$ $cm^3/s$, where the error is reported as two standard deviations of the intercept from the weighted fit.

For both reactions (3) and (4), the selected ion flow tube values of the rate constant are $(5.3 \pm 1.3) \times 10^{-10}$ $cm^3/s$. Table 1 shows the branching fractions for the various channels for both reactions. Two columns for each reaction are shown. The first gives the experimental branching. For some masses some of the reactivity is either hidden (symmetric charge exchange) or the sum of two competing processes. The second column is an estimation of the branching for each channel as discussed below.

The charge transfer channel with DBr has a dependence on the isotope, with the $H^{79}Br^+$ isotope being favored. If the reaction proceeded by long-range charge transfer one would expect equal formation of masses 81 and 83. The fact that mass 81 is favored is indicative that at least some of the reaction proceeds through a long-lived complex with scrambling of the H and D. The preference for the mass 79 isotope then comes from the fact that in half the reactions there are two $^{79}Br$ isotopes and the other half has one $^{79}Br$ and one $^{81}Br$. If all the reaction proceeded through a long-lived complex with complete isotopic scrambling, then we would expect a ratio of 3 for $D^{79}Br^+$ to $D^{81}Br^+$. The fact that the ratio is less than 2 indicates that either some of the reaction is direct or that incomplete scrambling is occurring. A further implication is that a significant fraction of the complex forming channel must revert to primaries. The fraction of the complex

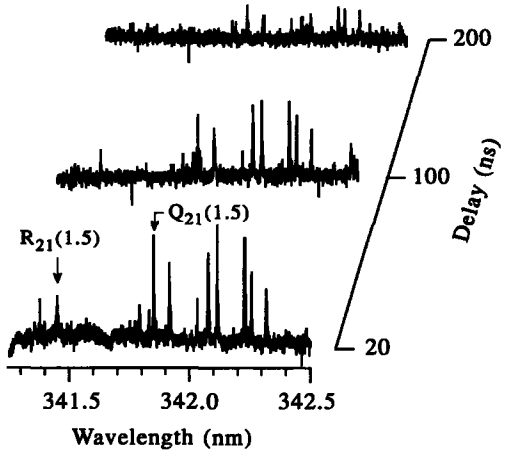


Fig. 1. LIF spectrum of the $A^2\Sigma - X^2\Pi_{3/2}$ (0,0) band of $HBr^+$ and its decay with time after initial formation of $HBr^+$ $^2\Pi_{3/2}$, $v = 0$.

Table 1
Branching fractions for the reactions of $H^{79}Br^+$ with HBr and DBr

| Process | Masses (HBr) | % observed (HBr) | derived % (HBr [e]) | Masses (DBr) | % observed (DBr) | derived % (DBr [e]) |
|---|---|---|---|---|---|---|
| charge transfer | 80 | n/o | 25 [b] | 80 | n/a | 9 |
| | 82 | 28 | 21 | 81 | 28 | 25 |
| | | | | 83 | 18 | 16 |
| proton transfer | 83 | 22 | 16 | 84 | 15 | 14 |
| | 81 | 50 includes HT | 16 [c] | 82 | 38 includes DT | 14 [d] |
| H/D T [a] | 81 | see above | 21 [c] | 82 | see above | 21 [d] |

The $H^{79}Br^+$ in this study was > 80% in the ground vibrational and spin state, the remainder in an undetermined mixture of excited states.
[a] Hydrogen or deuterium transfer.
[b] See text for derivation.
[c] Assumes proton transfer channel is the same as for mass 83.
[d] Assumes proton transfer channel is the same as for mass 84.
[e] All numbers are adjusted for estimated hidden 'charge transfer' and include roundoff error.

reforming the primary can be estimated as follows. The experimental ratio of $D^{79}Br^+$ to $D^{81}Br^+$ product is 1.55. For a direct process this ratio should be 1 and for complex forming process this should be 3. Simple algebraic manipulation then finds that 28% of the reaction proceeds through a complex and that 9% of the reaction should reform $H^{79}Br^+$, with the other channels being smaller. Similar arguments for reaction (3) indicate that 25% of the reaction reforms $H^{79}Br^+$. The total rate constants including these hidden channels then become $6.9 \times 10^{-10}$ $cm^3/s$ and $5.8 \times 10^{-10}$ $cm^3/s$ for the HBr and DBr reactions, respectively.

In each reaction, one of the two proton transfer products has the same mass as the hydrogen/deuterium transfer channel. In order to calculate the product distribution for each channel we assume that the proton transfer fraction of the mixed product is the same as the proton transfer channel in the unambiguous channel, the remainder arising from hydrogen/deuterium transfer. With these considerations, the HBr/DBr reactions produce about equal amounts of the various products, namely, 46/50%, 32/28%, and 21/21% for charge transfer, proton transfer, and hydrogen/deuterium transfer respectively.

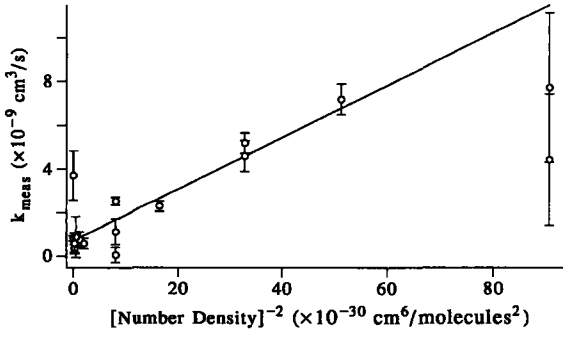


Fig. 2. The measured decay rate constant plotted vs. the inverse square of the number density. The $y$-intercept yields the pressure-independent rate constant for the proton transfer rate for the reaction of $HBr^+$ ($^2\Pi_{3/2}$, $v = 0$) + HBr.

The spectroscopic method for determining the rate constant refers to only the proton and hydrogen transfer channels. The corresponding selected ion flow tube rate constant for these channels is $(3.8 \pm 1.1) \times 10^{-10}$ $cm^3/s$. This rate constant is lower than the value of $(6.7 \pm 1.6) \times 10^{-10}$ $cm^3/s$, but the disagreement is only slightly outside the error limits of the combined measurements. We cannot offer an explanation for the disagreement, if present.

The present results show that reactions (3) and (4) are quite complex producing every conceivable product. While the charge transfer reactions has been probed in detail previously [1], the dynamics of the other channels have not. The complexity of the reaction makes this an interesting candidate for such detailed studies.

This work also shows that spectroscopic methods can be used to study ion–molecule reaction rates even in some cases where the product of reaction is

not directly observed. It has the advantage of being a truly state-selective study. This work could, in principle, be extended to study the rates of proton-transfer for the two fine-structure components for both $v = 0$ and $v = 1$ of the $HBr^+$ ion by correcting the decay rate of the higher-energy ions for charge-transfer and quenching rates to the energetically accessible states of the ion.

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