

Rate constant measurements for the ion/molecule reactions of I^- , F^- , Br^- and $HFBr^-$ with Cl_2

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ABSTRACT

Measurements are reported of the two-body rate constants at room temperature for the ion/molecule reactions of the ions I^- , F^- , Br^- and $HFBr^-$ with Cl_2 . The measurements were made in a classical flow tube and the results are compared with the calculated Langevin rate constants and with existing data (for $F^- + Cl_2$).

Keywords: rate constant; ion/molecule reaction; flow tube; Langevin.

INTRODUCTION

Ion mass spectrometry, combined with active chemical ionization, seems to be a most promising technique for the detection of trace gases in the atmosphere [1]. This method relies upon the fact that some atmospheric trace gases react with ions produced by an ion source mounted in front of a balloon- or airplane-borne mass spectrometer and give rise to specific product ions. From the analysis of the relative abundances of precursor and product ions measured with the mass spectrometer, the concentrations of the reactive trace gases can be inferred. Recently remarkable results for the derivation of nitric acid vapour concentrations in the Arctic have been obtained using this approach [2]. It has been suggested [3,4] to use the active chemical ionization method to determine simultaneously HNO_3 and N_2O_5 mixing ratios in the stratosphere using the following reactions:

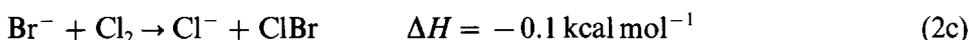
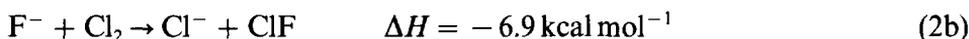
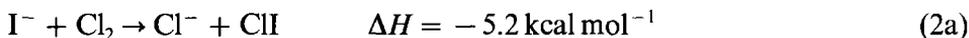


The idea is to develop an ion source producing alternately Cl^- and I^- ions and

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to mount it in front of a balloon-borne mass spectrometer. From the abundances of the NO_3^- ions and either the Cl^- or the I^- ions the mixing ratio of HNO_3 and N_2O_5 can be derived, since Cl^- reacts with both HNO_3 and N_2O_5 whereas I^- only reacts with N_2O_5 and the rate constants for the reactions 1 are known [5,6].

In order to investigate the experimental problems associated with the use of halogen negative ions in the active chemical ionization method, a flowing afterglow apparatus has been constructed in our laboratory. As a first exercise we decided to study the following two-body ion/molecule reactions:



(The reactions are listed in chronological order of our study and the enthalpy changes for reactions 2a–d have been calculated using the thermochemical data of the NIST database [7] and of the JANAF tables [8].)

We have chosen to use Cl_2 as the common reactant gas because it is the most obvious parent gas to produce Cl^- in an ion source without any parasite ions except possibly for Cl_2^- and Cl_3^- . It is interesting to measure the reaction of this parent gas with I^- , because, if in the use of an ion source producing alternately Cl^- and I^- , Cl_2 background gases remain present in the mode where I^- is produced, this reaction can perturb the measurement. Furthermore, it is possible that, owing to technical problems of producing I^- in a balloon-borne experiment, we will be led to use Br^- or F^- ions. Therefore, we decided to study also the reaction of these ions with Cl_2 , while the HFBr^- ion appeared in our spectra as an impurity.

EXPERIMENTAL

The flowing afterglow apparatus used here is of the classical design as described by Ferguson et al. [9]. A schematic view of the instrument is shown in Fig. 1. It consists of a flow tube and associated ion source coupled to a quadrupole mass spectrometer.

The ion source consists of a small chamber of about 100 cm^3 , separated from the flow tube by a small aperture, in which a thoriated iridium filament is glowing and kept at a negative potential ($\approx 100 \text{ V}$) with respect to ground.

Two gas inlet ports with MKS flowmeters are used to inject into the source both ion buffer and ion parent gas. Argon was used as ion buffer gas with a typical flow rate of a few hundred $\text{atm cm}^3 \text{ min}^{-1}$, resulting in medium pressures ($p \geq 5 \text{ Torr}$) in the ion source. Negative ions were produced by

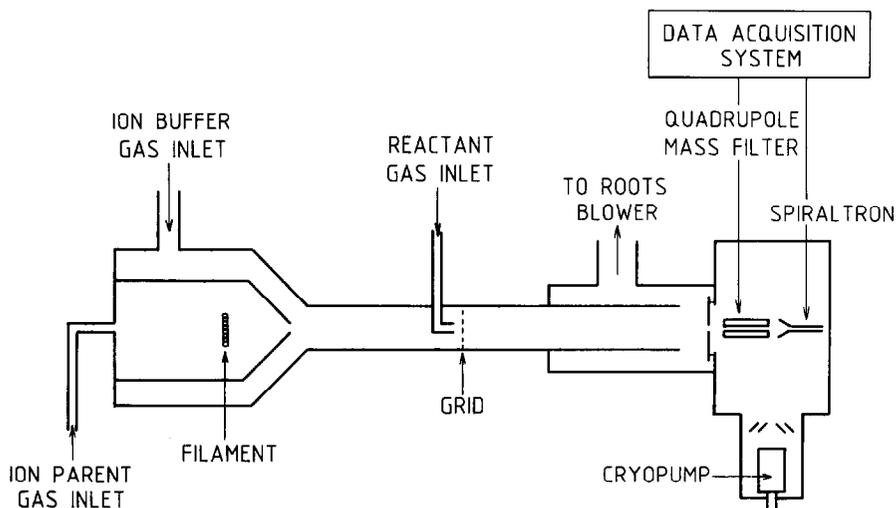


Fig. 1. Schematic view of the instrument.

dissociative attachment on ion parent source gases. For the production of I^- , CF_3I was used, whereas CF_4 was chosen for F^- and CH_2Br_2 or $CHBr_3$ for Br^- . Small quantities ($< 1 \text{ atm cm}^3 \text{ min}^{-1}$) or sometimes not even measurable traces were mixed with the ion parent gas. A contamination of the source quickly occurred during the use of CF_3I leading to the simultaneous production of I^- when we produced Br^- or F^- afterwards. Fortunately no undesired interference was observed and the reaction of I^- with Cl_2 was even used as a consistency check when measuring other reactions.

It should also be mentioned that some of the trace gases (especially CF_4) strongly perturbed the functioning of the ion source, probably via the dissociative attachment itself. This led us to apply different working modes (low or high thermo-emission current for instance) with a delicate tuning of all the source parameters. Once the working point was found, it was however possible to maintain the ion source within reasonable stability conditions (a typical value of which being 20% over 1 h).

The negative ions produced flowed into the flow tube through a 2 mm hole. An electrostatic lens system was added between the filament and the hole but it turned out to be rather inefficient and the ion transport efficiency to the flow tube was mainly governed by the pressure gradient between ion source and flow tube.

At the entrance of the flow tube the ion carrier gas dragging the ions along merges with the main carrier gas entering the flow tube around the conically shaped canalisation surrounding the source. Typical values for the main carrier gas flow (argon) were $2000 \text{ atm cm}^3 \text{ min}^{-1}$. The flow tube itself is of stainless-steel and has a diameter of 4 cm and a total length of about 60 cm.

The gas flow in it is maintained by a $250\text{ m}^3\text{ h}^{-1}$ roots blower backed by a $60\text{ m}^3\text{ h}^{-1}$ mechanical rotary pump resulting in an effective pumping speed of about 30 l s^{-1} at 0.75 Torr.

The reactant gas inlet port is located 20 cm downstream from the ion source. At this location the flow crosses a grid, which can be biased to chop the ion flow and produce bursts of ions. This allows the measurement of the time of flight by applying to the grid a square wave (+5 V amplitude, 1 ms duration) superimposed on a -5 V offset. The arrival of the burst is detected by scanning the gate delay (gate width $\approx 10^{-4}\text{ s}$) of the counter which is triggered by the pulse generator producing the square wave signal applied on the grid.

The reactant gas was obtained from a commercial supplier (Air Products) and consists of a mixture of Ar and Cl_2 with a volume mixing ratio of 1000 ppm (within 5% accuracy). Such a low concentration of Cl_2 was imposed by the quite high rate constants of the studied reactions and the limited pumping speed of our roots blower. It also allowed us to work within the whole range of a $100\text{ atm cm}^3\text{ min}^{-1}$ MKS flowmeter with a good precision. The reaction length itself is about 40 cm.

At the other extremity of the flow tube the ions are sampled into the mass spectrometer through a 0.3 mm orifice drilled in a stainless-steel draw-in plate. The latter is electrically insulated, allowing the application of a bias potential and permitting the measurement of the total ion current on the draw-in plate by means of a floating electrometer.

The mass spectrometer chamber is pumped by a Leybold–Heraeus RG210 cryopump with a pumping speed of about 1500 l s^{-1} , capable of maintaining the pressure in the 10^{-5} Torr range while the pressure in the flow tube is of the order of 0.5–2 Torr. The mass spectrometer itself is a quadrupole filter (with an r.f. power supply and control unit from Extrel Inc.) followed by a Spiraltron electron multiplier. The signal is recorded in a pulse counting mode by means of a SR400 Stanford Research counter at the output of the Spiraltron preamplifier.

The interface with the experimenter is achieved by a Hewlett-Packard HP9000/345 workstation running under Unix (HP-UX Basic) and communicating with the experiment through an IEEE488 bus.

RESULTS AND DISCUSSION

The rate coefficient for the different ion/molecule reactions studied has been derived by measuring the ion count rate at a given ion mass versus the reaction gas flow. The axial concentration of the parent ions, X^- , obeys the

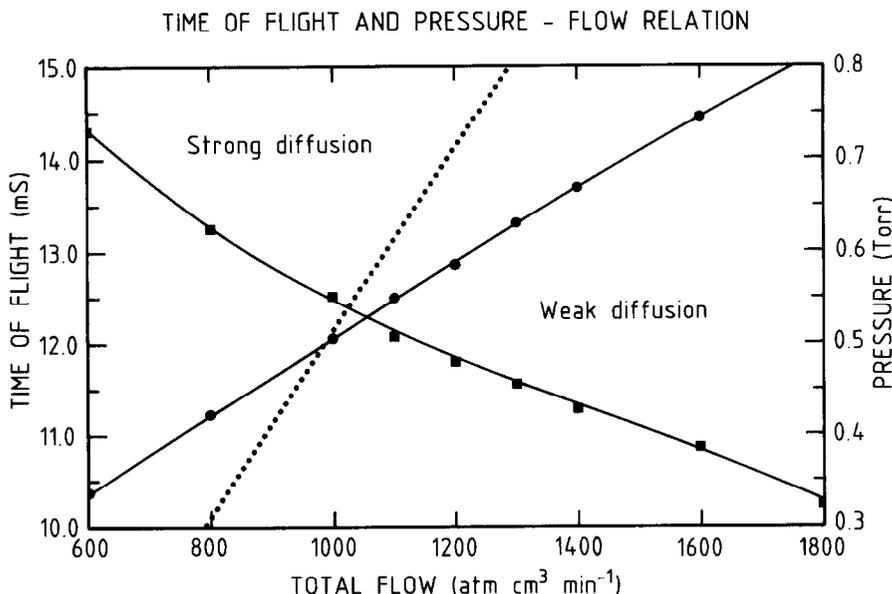


Fig. 2. Time of flight (■, left-hand scale) and pressure (●, right-hand scale) versus total flow relations. The dotted line is determined by relation 5 and corresponds to an $\exp(-1)$ attenuation by diffusion.

following equation:

$$\ln \frac{[X^-]}{[X_i^-]} = - \left(\frac{1}{\tau} + k[Cl_2] \right) t \quad (3)$$

Here τ is the characteristic diffusion time, $[X_i^-]$ is the initial ion concentration, k is the reaction rate coefficient, $[Cl_2]$ is the chlorine number density and t is the residence time of the ions from the reactant gas inlet to the mass spectrometer inlet. The chlorine number density is inferred from the flows and the pressure in the flow tube and X^- and X_i^- are measured. A separate measurement of the residence time or time of flight is performed with the method described in the Experimental section.

Figure 2 represents the results of the time of flight measurement together with the relation giving the pressure in the tube versus the total gas flow. We measured the time of flight of I^- ions for a total gas flow ranging from 600 to 2000 $\text{atm cm}^3 \text{ min}^{-1}$. Considering the coefficient of ambipolar diffusion of I^- and Ar^+ ions in Ar [10]:

$$D = (D^+K^- + D^-K^+) / (K^+ + K^-) \quad (4)$$

where D^+ , D^- , K^+ and K^- respectively stand for the normal diffusion coefficients and mobilities of positive and negative ions, we obtain the charac-

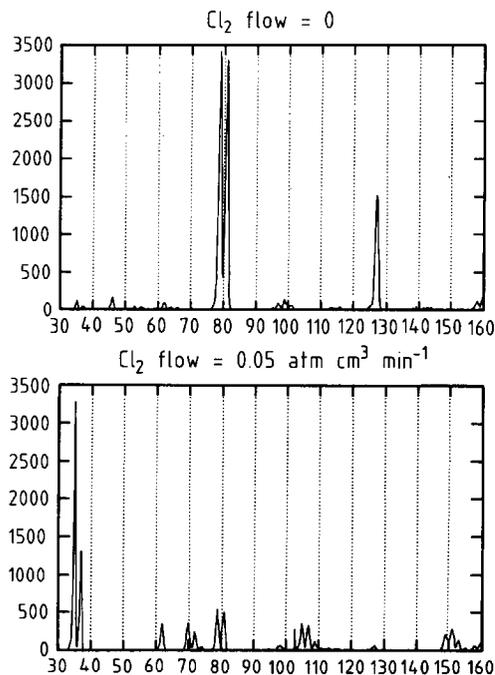


Fig. 3. Typical mass spectra obtained during the study of reaction 2c. Main peaks in the upper spectrum (without reactant gas) are mass 46(NO_2^-), 79–81(Br^-), 99–101(HFBr^-) and 127(I^-). When Cl_2 is added ($0.05 \text{ atm cm}^3 \text{ min}^{-1}$, lower spectrum), Br^- and I^- signals strongly decrease while mass 35–37(Cl^-) appear as the product ion.

teristic time of diffusion:

$$\tau = \frac{r_0^2}{\gamma^2 D} \approx 0.024 \times p \quad (5)$$

where r_0 is the radius of the flow tube in cm (here 2 cm), p is the pressure (in Torr) and τ is expressed in seconds.

If we assume from Ferguson et al. [9] the first diffusion mode of a parabolic flow ($\gamma^2 = 3.66$), we can conclude from eqn. 5 that for flows below $1000 \text{ atm cm}^3 \text{ min}^{-1}$ the ion loss becomes important. For flows above $2000 \text{ atm cm}^3 \text{ min}^{-1}$ the pressure in the flow tube becomes rather high, owing to the limited pumping speed of our roots blower, and the vacuum in the mass spectrometer section starts to deteriorate. Consequently we used buffer gas flows between 1000 and $2000 \text{ atm cm}^3 \text{ min}^{-1}$.

Figure 3 shows some typical mass spectra obtained during the study of reaction 2c. The two main peaks are clearly attributable to $^{79}\text{Br}^-$ and $^{81}\text{Br}^-$ (natural isotopic abundances 50.5 and 49.5%) but I^- is still present. Upon addition of about $0.05 \text{ atm cm}^3 \text{ min}^{-1}$ of Cl_2 , Br^- and I^- disappear while Cl^-

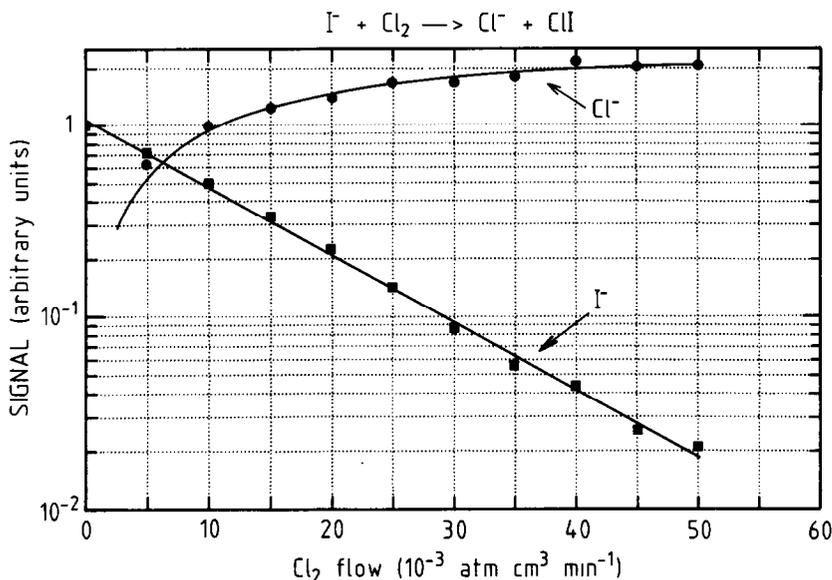


Fig. 4. Measured attenuation of I^- (■) versus Cl_2 flow and simultaneous appearance of Cl^- (●). Lines correspond to best fits.

strongly increases. In this example we can also identify the ions Cl_2^- , Cl_3^- and $BrCl_2^-$.

For each of the above-mentioned reactions we measured the attenuation of the reactant ion for a given Cl_2 flow by comparing it with the signal without the reactant gas. This procedure was repeated for each value of the reactant gas flow in order to prevent significant drift of the reactant ion production. The characteristic measuring time was about 30 s with 10^5 accumulated counts. We also checked that Cl^- was the product ion with the exception of reaction 2d.

In Fig. 4 the measured attenuation of I^- versus Cl_2 flow is displayed together with the appearance of Cl^- . When applying a least-square fitting procedure (linear for the disappearance of I^- and non-linear for the appearance of Cl^-), we found an attenuation exponential coefficient of $81.0 \text{ atm}^{-1} \text{ cm}^{-3} \text{ min}$ for the disappearance of I^- and a value of $54.0 \text{ atm}^{-1} \text{ cm}^{-3} \text{ min}$ for the correlated appearance of Cl^- . This relative disagreement can result from a strong coupling between diffusion and reaction loss (see Ferguson et al. [9] for discussion) or from some subsequent unknown ion molecule reaction.

The possibility of saturating the ion detector with too high count rates (which results in curvature of the attenuated signal plot on a logarithmic scale) was tested by checking the natural isotopic ratio of $^{35}Cl^-$ to $^{37}Cl^-$. Finally the measurements were also repeated for various flow and source conditions. We

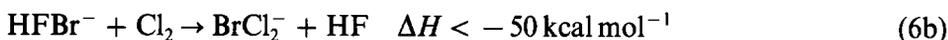
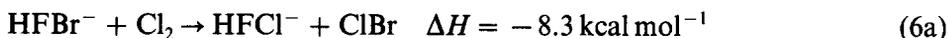
TABLE 1

Present measured rate constants with existing data and associated Langevin rate constants

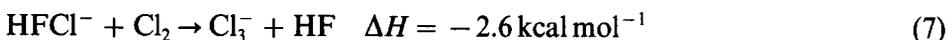
Reaction	Number of measurements	$k_{\text{meas.}}$ ($10^{-10} \text{ cm}^3 \text{ s}^{-1}$)	Existing data	$k_{\text{Lang.}}$ ($10^{-10} \text{ cm}^3 \text{ s}^{-1}$)
$\text{I}^- + \text{Cl}_2 \rightarrow \text{Cl}^- + \text{ClI}$	5	5.5 ± 0.5	–	7.4
$\text{F}^- + \text{Cl}_2 \rightarrow \text{Cl}^- + \text{ClF}$	2	8.0 ± 0.1	8.8 (ref. 11)	12.9
$\text{Br}^- + \text{Cl}_2 \rightarrow \text{Cl}^- + \text{ClBr}$	5	3.3 ± 0.1	–	8.1
$\text{HFBr}^- + \text{Cl}_2 \rightarrow \text{products}$	3	5.5 ± 0.4	–	7.7

have verified the independence of the derived rate constant on the flow tube pressure in the range 0.5–1.0 Torr for all reactions except for reaction 2b, the result of which is in good agreement with the data of Babcock and Streit [11].

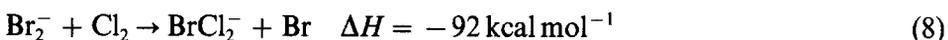
Reaction 2d was measured after the use of CF_4 in the experiment when the source produced a strong signal of HFBr^- together with the desired Br^- signal. However, it was not possible to unambiguously identify the product ions. The possible reactions are:



We observed reaction 6a but the branching ratio with respect to reaction 6b should not be greater than 10% in view of the small HFCl^- signal detected. Moreover, this product ion quickly disappears when Cl_2 flow increases, probably through the reaction



The product ion signal of reaction 5b, BrCl_2^- , strongly increases with the Cl_2 flow but is indistinguishable from the signal coming from other possible reactions involving Br_2^- and Br_3^- . For instance, one has to consider the possibility of



In Table 1 the derived rate constants with the standard deviations observed during independent measurements are summarized. The reaction 2b has already been measured by Babcock and Streit [11] and their value for the rate constant k agrees quite well with the one obtained in this work. By considering the relative uncertainties in the measurements of the pressure and the total flow in the tube, the time of flight and the determination of the true density of the reactant gas, we believe our mean accuracy to be 35%.

Also shown in Table 1 are the Langevin capture rate constants using an electric dipole polarizability of $4.57 \times 10^{-24} \text{ cm}^3$ for Cl_2 as calculated from the refractive index [12]. It is worth noticing however that these Langevin values

only give a rough indication of the rate constant while nothing is said about the reaction process itself. This should require *ab initio* quantum mechanical calculations on the collisional system for the four studied reactions.

Rather high two-body reaction rate coefficients have been measured between halide ions and Cl_2 . This suggests that the use of two independent ion sources is probably unavoidable for the simultaneous detection of HNO_3 and N_2O_5 in the active chemical ionization method. Indeed, in a unique ion source working alternately with, for instance, Cl_2 and CF_3I as ion parent gas it would not be possible to prevent a parasitic Cl^- production via the reaction 2a. One can suppose that this contamination problem will occur with every ion parent gas leading to halide ion production by electronic dissociative attachment.

It has also been observed that the determination of a rate constant or a reactant density through the observation of the product ion signal of a selected reaction can appreciably differ from the determination of the same quantity by the observation of the signal decrease of the parent ion. For stratospheric ion mass spectrometry at altitudes below 40 km it is expected that the problem of ion diffusion is less crucial owing to higher pressures in the flow tube. However, one has to check whether the NO_3^- population we intend to measure will not be affected in possible subsequent ion/molecule reactions. The domain of ion/molecule reactions involving halogen anions and their parent gases is quite complex. The high electron affinities of the reactants give rise to rather high reaction rates and also lead to the formation of stable polymer ions such as Cl_3^- , BrCl_2^- , I_2^- , etc. (see Babcock and Streit [11] for a discussion on their structural stabilities). A general study of the ion/molecule reactions involving all these species would imply, in our opinion, the use of a selected ion flow tube experiment (see Smith and Adams [13]) in order to prevent any interference between them.

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