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# Mobilities of negative halogen ions in various gases

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The mobilities of  $SF_6^-$  in He and of  $F^-$ ,  $Cl^-$ ,  $Br^-$ , and  $I^-$  in Ar, Xe, H<sub>2</sub>, N<sub>2</sub>, CO, and CH<sub>4</sub>, have been investigated over the field-strength (E/P) range of 5 to 25 V/cm Torr using time-resolved high pressure mass spectrometry and an ion source with coaxial electron entrance and ion drift fields. The reduced mobilities obtained by this method are in good agreement with those obtained in drift tubes when comparison is possible. Results are compared with "Langevin" polarization limits and with the drift properties of isoelectronic positive alkali ions measured previously.

## INTRODUCTION

Knowledge of the mobilities of negative halogen ions is important to a quantitative understanding of plasma, laser and electrical discharge physics and radiation chemistry in atmospheres containing halogenated compounds, and to the measurement of ion-molecule reaction rate constants in negative chemical ionization as well as their application to analytical negative chemical ionization. The energy or temperature dependence of drift properties may also be used to derive ion-molecule interaction potentials.<sup>1</sup> However, only little information about mobilities of negative ions is available.<sup>2-6</sup>

Recently our laboratory has investigated ion transport properties for various positive ions under chemical ionization conditions using a pulsed chemical ionization source employing coaxial electron entrance and ion exit apertures and ion drift fields.<sup>7,8</sup> Ion mobilities obtained by this method are in good agreement with results determined by drift tube measurements where comparison is possible.

In this paper, we report the reduced mobilities  $K_0$  of F<sup>-</sup>, Cl<sup>-</sup>, Br<sup>-</sup>, and l<sup>-</sup> in Ar, Xe, H<sub>2</sub>, N<sub>2</sub>, CO, and CH<sub>4</sub> over a field-strength range of 5 to 25 V/cm  $\cdot$  Torr, using small concentrations of molecules which produce negative halogen atomic ions by interaction with low energy electrons.<sup>9</sup>

## EXPERIMENTAL

#### Apparatus

Measurements were conducted using a pulsed high pressure mass spectrometer described previously.<sup>7,8</sup> A modified Varian Atlas MAT CH4-B mass spectrometer was fitted with a special ion source, constructed from oxygen-free copper and commercially gold plated. The ion source is cylindrically symmetric about the direction of ion motion. The electron entrance aperture is coaxial with the ion exit slit. Two gold plated stainless steel drift guard rings are contained in the source to establish a uniform field over an axial cross section of  $25 \text{ mm}^2$ . Adjustment of the potential on these rings and the extraction plate provides uniform electric fields over the ion drift region whose distance is 2.29 cm.

To detect negative ions efficiently, we constructed a

new detection system in which the anode of the electron multiplier is coupled to the preamplifier via a capacitance coupler.<sup>10</sup> Two separate high voltage power supplies independently provide the multiplier potential to the anode and the cathode of the electron multiplier. The cathode potential may thus be raised without affecting the multiplier gain, permitting the negative ions to strike the cathode with sufficient kinetic energy to be detected efficiently.

Gas was introduced to the ion source via two series 203 Granville-Phillips leak valves from two separate 5 liter stainless steel reservoirs. Ion source pressure was measured with a MKB Baratron 170M-44A capacitance manometer. Temperature was determined with two platinum resistors connected in series and inserted into the ion source block. The experiments presented here were all conducted at 298°K. In order to maintain this temperature, cooled nitrogen was continuously passed through two cooling chambers in the ion source block.

### Procedure

The electron gun was pulsed by unblocking for 0.1 to 0.2  $\mu$ s a biased 35% transparent stainless steel screen (the grid) between the electron entrance aperture and the filament. The Hewlett Packard Model 214A pulse generator was coupled to the grid via a 0.02  $\mu$ F capacitor. The trigger pulse from the pulse generator was used to start an ORTEC 467 time-to-pulse height converter, which was terminated by the amplified signal produced when an ion strikes the electron multiplier detector. Output pulses were sorted in a TMC 402 multichannel analyzer which is interfaced with a Varian 620L-100 minicomputer with dual floppy disks. The gases used in this study were obtained from Matheson, were all of purity greater than 99.99% except methane (99.97%) and were used as received. The fluoride ion F was made by adding less than 0.02% tetrafluoromethane (Matheson, 99.7%) to the drift gas. Methylene chloride (Fluka, 99%), iodomethane (Fluka, 99.5%) and methyl bromide (Matheson, 99.5%) were used at similar concentrations to prepare Cl<sup>-</sup>, Br<sup>-</sup>, and I<sup>-</sup>, respectively.

## **RESULTS AND DISCUSSION**

#### Mobility of SF<sub>6</sub> in He

 $SF_6$  ions are formed by attachment of thermal electrons to  $SF_6$  which was introduced into the ion source at a partial pressure of  $10^{-4}$  Torr.

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The primary quantity measured in our experiment is the arrival time distribution (ATD) of the specified ion passing through the entire drift region. Figure 1 shows a typical ATD of  $SF_6^-$  in He at the extraction potential Eof 7.5 V/cm in the limit of low electron energy (16 eV nominal) and high ion source pressure (1.0 Torr). Under these conditions, the incident electrons are thermalized and  $SF_6^-$  is produced close to the electron entrance aperture. If these ions do not react further, they pass through the drift region towards the exit slit with a drift velocity  $v_d$  which is obtained by dividing the drift length by the mean drift times.  $v_d$  is proportional to the extraction potential E:

$$v_d = KE \quad . \tag{1}$$

The proportionality constant K is the mobility of the ion through the neutral medium.

Figure 2 shows the variation of the measured drift velocities for SF<sub>6</sub> in He with increasing E/P at a source pressure of 1.0 Torr.  $v_4$  varies linearly with E/P throughout the entire range studied, as expected for E/P < 30 V/cm Torr.<sup>11</sup> The mobility is obtained from the slope. Since the mobility of an ion is dependent upon the pressure P of the neutral species, the temperature T (K) and the pressure P (Torr), we present data in the form of the reduced mobility  $K_0$ , defined commonly as:

$$K_0 = K(760/P)(273/T) . (2)$$

For ions originating from a point source and detected through a slit of width  $\Delta y$  and infinite length, the detected ion current is given by<sup>12</sup>

$$i(t) = \left(v_d + \frac{d}{t}\right) \frac{n_0 \Delta y}{8\pi t \sqrt{D_T D_L}} \exp\left[-\frac{\left(d - v_d\right)^2}{4D_L t}\right],\tag{3}$$

where  $n_0$  is the number of ions, and  $D_T$  and  $D_L$  are the diffusion coefficients for transverse and longitudinal motion, respectively. At low fields, these become equal and are reduced to the Einstein relation:

$$D = D_L = D_T = K(kT/e)$$
, (4)

where K is in  $cm^2/Vs$ , k is the Boltzmann constant, and e is the electron charge. The solid curve through the



FIG. 1. Arrival time distribution of  $SF_6$  in He. E/P was 7.5 V/cm Torr and T was 298 K. The solid curve is the ATD calculated using Eq. (3).



FIG. 2. Dependence of drift velocities of  $SF_6$  in He on E/P. P(He) = 1.0 Torr, T = 298 K, 16 eV electrons.

distribution in Fig. 2 was calculated using this equation and demonstrates that the two profiles are in very good agreement, with the experimental profile a little broader than the calculated one. This is generally an indication of deviation from the idealized point source assumption: some electrons penetrate further, some are scattered off axis, and some ion formation may already occur between the electron entrance aperture and the filament screen. The areas under the wings of the curves which do not fit the diffusion equation are the same on both sides and correspond to  $\sim 11\%$  of the total ion count each. This observation supports our assumption that our geometry may be assumed to correspond to a point source of ions at the entrance aperture in the limit of high pressure and low electron energy. This is necessary if our results are to reflect drift velocities reliably.

The slope of Fig. 2 leads to a measured mobility of  $SF_6$  in He

 $K_0(SF_6/He, 298 \text{ K}) = 12.0 \pm 0.2 \text{ cm}^2/\text{Vs}$ ,

in good agreement with the value 12.2  $\text{cm}^2/\text{Vs}$  obtained using a drift tube mass spectrometer.<sup>13</sup>

## Mobilities of F<sup>-</sup>, Cl<sup>-</sup>, Br<sup>-</sup>, and l<sup>-</sup> in Ar

Measurements of low-field mobility of  $F^*$ ,  $CI^*$ ,  $Br^*$ , and  $I^*$  in Ar were made at 298 K. The negative halogen ions were formed by dissociative electron attachment in an argon buffer gas containing less than 0.2% of the reagent gases listed earlier. We did not observe formation of dimers or other ion clusters.

The results are given in Table I. The errors given in Table I reflect the precision of measurements (generally 0.05 or better). The literature values cited were obtained by a flow-drift tube.<sup>4</sup> The comparison between this work and literature values indicates excellent agreement except for  $F^*$ . Even for  $F^*$ , however, the discrep-

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TABLE I. Low field mobilities of negative halogen ions in Ar at 298 K.

Ion	$K_0 \ (\mathrm{cm}^2/\mathrm{V}\cdot\mathrm{s})$			
	This work <sup>2</sup>	Literatureb		
F-	$3.56 \pm 0.08$	3,33±0,17		
C1 <sup>-</sup>	$\textbf{2,89} \pm \textbf{0,06}$	$2.87 \pm 0.14$		
Br <sup>-</sup>	$\textbf{2.46} \pm \textbf{0.02}$	$2.40 \pm 0.12$		
r	$2,28 \pm 0.07$	$2.27 \pm 0.11$		

<sup>a</sup>Errors all represent the precision.

<sup>b</sup>Dotan and Albritton, Ref. 4.

ancy is still within the combined error limits of the two methods.

In the polarization limit, reduced mobilities may be obtained theoretically using the relationship

$$K_{0,t} = 35.9/\sqrt{\alpha\mu} \ \mathrm{cm}^2/\mathrm{Vs}$$
, (5)

where  $\alpha$  (polarizability) and  $\mu$  (reduced mass) are in atomic units.

Table II compares experimental and theoretical mobilities in terms of the ratio  $K_0/K_{0,t}$  for a number of negative halogen ions and their positive, isoelectronic alkali ion analogs in Ar. For the positive ions, the literature values are cited from the compilation of McDaniel and Mason.<sup>1</sup> Although the measured F<sup>-</sup>, Cl<sup>-</sup>, Br<sup>-</sup>, and I<sup>-</sup> mobilities decrease with increasing ionic mass as predicted by Eq. (5), measured values are consistently 16% to 18% higher than calculated values; this has been observed frequently.<sup>14</sup> The ratios of  $K_0/K_{0,t}$  for all the negative ions are virtually identical; similarly,  $K_0/K_{0,t}$ values are essentially the same for all alkali ions.

The differences in these ratios must be ascribed to the larger ionic radius of negative ions, suggesting that failure of the point charge approximation inherent in Eq. (5) is a primary cause of the deviation of  $K_0/K_{0,t}$ from unity.<sup>13</sup>

#### Mobilities of Cl<sup>-</sup> in Ar, Xe, H<sub>2</sub>, N<sub>2</sub>, CO, and CH<sub>4</sub>

Mobilities of the Cl<sup>-</sup> ions in several gases have also been measured. No other such measurements have been reported to date for halide ion drift in the molecular gases.

Our results, including those reported previously for  $K^*$  ions, are shown in Table III and compared with the polarization limit, again in terms of  $K_0/K_{0,t}$ .  $K_0/K_{0,t}$ 

TABLE II. Ratios of measured mobilities  $(K_0)$  to those in polarization limits  $(K_{0,t})$  for a number of ions in Ar gases.

This work			Literature <sup>a</sup>		
Ion	$K_{0} (\mathrm{cm}^{2}/\mathrm{V}\cdot\mathrm{s})$	$K_0/K_p$	Ion	$K_0 \ (\mathrm{cm}^2/\mathrm{V}\cdot\mathrm{s})$	K <sub>0</sub> /K <sub>0,t</sub>
F	3.56	1,18	Na <sup>+</sup>	3.02	1.07
C1-	· 2.89	1.16	К*	2.66	1.09
Br <sup>-</sup>	2.46	1.18	Rb⁺	2.25	1.09
Г	2.28	1,17	Cs <sup>+</sup>	2.10	1,08

<sup>a</sup>McDaniel and Mason, Ref. 1.

TABLE III. Reduced mobilities of Cl<sup>-</sup> and K<sup>+</sup> ions in several gases at 298 K.  $K_0/K_{0,t}$  is the ratio of measured mobility to that in the polarization limit.

Neutral gas	Cl <sup>-</sup> (This v	vork <sup>a</sup> )	K <sup>*</sup> (Literature <sup>b</sup> )	
	$K_0(\mathrm{cm}^2/\mathrm{V}\cdot\mathrm{s})$	$K_0/K_{0,t}$	$\overline{K_0(\mathrm{cm}^2/\mathrm{V}\cdot\mathrm{s})}$	$K_0/K_{0,t}$
Ar	$2.89 \pm 0.06$	1.16	2.66	1.09
Xe	$1,27 \pm 0,05^{c}$	0.98	1.35	1,08
$H_2$	$12.93 \pm 0.5$	1.15	12.75	1.15
$N_2$	$2.52 \pm 0.04$	0.95	2.55	0.99
co	$2.37 \pm 0.03$	0.95	2.30	0.94
CH4	$2.12 \pm 0.094$	0.82	•••	•••

<sup>a</sup>Errors represent the precision.

<sup>b</sup>McDaniel and Mason, Ref. 1.

<sup>o</sup>The corresponding literature value from Thackston *et al.*, is  $1.34 \text{ cm}^2/\text{V}$  s, Ref. 6.

for  $CI^-$  in  $H_2$  is about the same as that for all the halide ions in Ar. It is less than unity for Xe and the other molecular gases.

A comparison of the mobilities of the Cl<sup>-</sup> ions with those of its positive, isoelectronic counterpart (Tables II and III) shows no obvious correlation:  $K_0/K_{0,t}$  is the same for Cl<sup>-</sup> and K<sup>+</sup> drifting in H<sub>2</sub> or CO,  $K_0/K_{0,t}$  is larger for Cl<sup>-</sup> in Ar, but smaller in Xe and N<sub>2</sub>. We believe that this indicates the need to consider all components of the intermolecular potentials<sup>15</sup> and that the observed differences at a single temperature only reflect an accidental combination of terms which determine the dependence of zero-field mobilities on temperature.<sup>16</sup>

#### ACKNOWLEDGMENT

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