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Dissociative Electron Attachment in Br₂ at 296°K*

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Dissociative electron attachment frequencies have been determined for bromine in the presence of helium using microwave cavity techniques. Initial ionization was produced by a single light pulse from a hydrogen flash lamp. The value for the electron attachment coefficient k determined from the attachment frequency data is $k = 0.82 \times 10^{-12} \text{ cm}^3 \text{ sec}^{-1} \pm 10\%$ at 296°K. The electron-ion ambipolar diffusion coefficient (D_{amb}) for Br₂⁺ in helium was found to be $795 \text{ cm}^2 \text{ Torr sec}^{-1} \pm 10\%$ at 296°K. The positive-ion-negative-ion ambipolar diffusion coefficient for this ion was found to be $380 \text{ cm}^2 \text{ Torr sec}^{-1} \pm 10\%$ at 296°K under the conditions where the only significant negative ion present was Br⁻.

I. INTRODUCTION

Although measurements of dissociative electron attachment in bromine have been carried out previously for electron energies in the eV region¹ little information is available concerning the rate constant for this process at thermal energies. Frost and McDowell,² however, established that electrons with an energy of approximately 0.03 eV can become attached to bromine by the reaction



The present study has been carried out to determine the magnitude of the rate constant related to process (1) for the case in which the electrons and bromine molecules are in thermal equilibrium at room temperature (296°K).

Initial ionization was created using a hydrogen flash lamp adjacent to a microwave cavity which contained the bromine vapor. The time dependence of the electron number density within the microwave cavity was measured using a microwave resonant frequency shift technique.

The equations describing the time dependence of the electron and ion densities in the afterglow are given when electron attachment and ambipolar diffusion are the main collision processes. In addition to results pertaining to electron attachment frequencies determined as a function of Br₂ pressure, data concerning positive-ion diffusion are also presented. These latter data have been obtained in order that the contribution of diffusion loss of electrons to the total electron loss frequency could be assessed separately. An examination of both

positive and negative ions has also been carried out in the afterglow after the transition from electron-positive-ion ambipolar diffusion to positive-ion-negative-ion ambipolar diffusion has occurred. As will be discussed, it is only after this transition has occurred that significant negative-ion wall currents are observed. In the Discussion (Sec. V) a comparison is made between the results for the dissociative attachment coefficient obtained in the present study and the results of Bailey *et al.*,¹ which were obtained at higher electron energies.

II. EXPERIMENTAL APPARATUS

The apparatus used for the current study has been previously described.^{3,4} Included are a microwave cavity which acts as the plasma container, and a hydrogen flash lamp adjacent to the cavity which produces the initial ionization of the bromine within the cavity. Microwave and associated equipment used in conjunction with the cavity allows the determination of the time dependence of the electron number density within the cavity after a single photoionization pulse. In addition to the measurements of the time dependence of the electron density, a quadrupole mass filter has been used to obtain the time dependence of the ion wall currents. In the present experiment the ions pass from the cavity into the quadrupole mass filter through an orifice having a 0.0076-cm diam which was drilled in a 0.0025-cm-thick nickel foil mounted between the cavity and quadrupole chamber. Collection of the ions is assisted by means of a grid located 0.14 cm from the orifice between the orifice and the quadrupole mass-filter assembly.

The design of the orifice and grid is similar to that used by Sauter, Gerber, and Oskam.⁵

The ions after passing through the quadrupole mass filter were accelerated into the first stage of a focused mesh electron multiplier. The output pulses from the multiplier were amplified and fed through a pulse-height discriminator and then counted and stored in a Hewlett Packard 5400 series multichannel analyzer used in the multichannel scaling mode. The cavity, grid, and electron multiplier were biased with respect to the quadrupole mass filter so that positive- or negative-ion wall currents could be examined separately.⁴ An ionizer was used in conjunction with the quadrupole filter to determine gas impurity levels as previously described.^{3,6} The ionizer was removed from the system prior to measurements of the ion wall current as a function of time.

The Br₂ vapor pressure in the microwave cavity was regulated by controlling the temperature of a bromine storage finger connected to the microwave cavity. The vapor pressure of Br₂ in the system was measured by correlating the storage finger temperature with data concerning the Br₂ vapor pressure as a function of temperature.^{7,8} A second method of measuring the Br₂ pressure involved the use of the bromine optical extinction coefficient. A 10-cm-long optical absorption cell was mounted on a cavity side arm so that by measuring the optical absorption at 4150 Å, the Br₂ concentration in the cavity could be separately determined.⁹⁻¹¹ It was experimentally noted that no significant effect on the observed optical absorption at 4150 Å resulted from adding helium as a buffer gas for helium pressures up to 50 Torr. This observation is in agreement with the findings of Britten and Davidson¹² and also those of Evans.¹⁰ Both of these methods of measuring the bromine vapor pressure were checked against the value of the Br₂ pressure obtained using a capacitance manometer in the absence of a buffer gas. The agreement between the three above-described methods was within ±10% over the Br₂ pressure range used to obtain the electron attachment frequency data. For ion-diffusion measurements, where Br₂ pressures in the presence of helium were as low as 5×10⁻³ Torr, the partial pressure of the bromine vapor was determined primarily from the temperature of the bromine storage finger. However, Br₂ pressures in the 5×10⁻³ Torr region were also measured with the capacitance manometer in the absence of a buffer gas. Agreement between the manometer readings and the pressures obtained from the temperature data⁷ were within about 15%. The pressure of the helium which was used to thermalize the electrons and also to reduce diffusion losses was measured with a capacitance manometer. The pressure *p* in this study rep-

resents the actual measured pressure in Torr at 296 °K.

Baker analyzed reagent-grade bromine was put into the system after double fractional distillation. The only significant impurity detected in the bromine was chlorine at about 2 parts in 10⁴. Matheson research-grade helium was used with a total impurity content of about 2 parts in 10⁶. The principal impurity in the helium was neon. The ultimate pressure achieved in the cavity and gas handling system was 5×10⁻⁹ Torr after a 24 h bakeout at 300 °C.

III. DATA ANALYSIS

The equations governing the decay of electrons, positive ions, and negative ions in the afterglow have been derived by Biondi¹³ and by Oskam.¹⁴ The effect on the electron ambipolar diffusion as a result of negative-ion buildup in the afterglow also has been discussed.^{3,15} If the charged particles in the plasma container are distributed in a fundamental diffusion mode and if electron attachment together with electron and ion ambipolar diffusion are the main collisional processes involved, then the time dependence of the electron density is as follows:

$$\frac{\partial n_e}{\partial t} = - \left(\frac{D_{ae}}{\Lambda^2} + \nu_a \right) n_e = - \nu_T n_e. \quad (2)$$

In Eq. (2), n_e is the electron number density, D_{ae} is the electron ambipolar coefficient, ν_a is the electron attachment frequency, and Λ is the characteristic diffusion length of the plasma container. In the present case $\Lambda^2 = 0.235 \text{ cm}^2$. In Eq. (2), ν_T is the total electron density decay frequency. As will be discussed it is possible for D_{ae} (and thus ν_T) to be time dependent. The electron attachment frequency is related to the electron attachment coefficient k by

$$\nu_a = k n_g, \quad (3)$$

where n_g is the molecular bromine number density. If conditions are such that $\nu_a \gg D_{ae}/\Lambda^2$ so that $\nu_a \approx \nu_T$, then Eq. (2) has the solution

$$n_e \approx n_e(0) e^{-\nu_a t}. \quad (4)$$

Most of the electron attachment data has been determined where Eq. (4) is presumably valid. However, in order to determine the error in omitting the diffusion term in Eq. (2) the value for D_{ae} has been separately assessed. D_{ae} is related to the positive-ion ambipolar diffusion coefficient by¹⁴

$$D_{ae} \approx D_{a+}(1 + \alpha). \quad (5)$$

Here D_{a+} is the positive-ion ambipolar diffusion coefficient and α is the ratio of the negative-ion number density to the electron number density. The quantity α increases in the afterglow due to

the buildup of negative ions as a result of electron attachment and also as a result of electron loss by both attachment and diffusion. Equation (5) is reasonably accurate for values of α less than about 20 and applies to the case in which the electrons and ions are in thermal equilibrium. Once a value for D_{a+} is determined separately as described below, the contribution to the total electron loss frequency ν_T due to electron ambipolar diffusion can be determined.^{3,6,16}

The ion ambipolar diffusion coefficient can be determined from the time dependence of the ion wall currents. The ion wall current Γ is proportional to the gradient of the ion concentration within the plasma container. The gradient, however, is proportional to the volume ion density for a given mode distribution.¹⁴ If a constant fraction of the ions reaching the walls of the microwave cavity plasma container pass through the orifice to the quadrupole mass filter, then the observed ion wall counting rate will be proportional to the volume ion number density within the cavity.^{4,15,17,18} The ion decay rate under the conditions when ambipolar diffusion is the main process by which ions decay in the afterglow, is related to D_{a+} as follows:

$$\frac{\partial n_+}{\partial t} = -\frac{D_{a+}}{\Lambda^2} n_+ . \quad (6)$$

In Eq. (6), n_+ represents the number density of the positive ions present. Equation (6) is valid for the case when the ions are in a fundamental mode distribution.

The values for the positive- and negative-ion ambipolar diffusion coefficients have been derived for the case where electrons, one type of positive ion, and one type of negative ion occur in the afterglow.^{13,14} These are as follows:

$$D_{a+} \approx 2D_+ , \quad (7)$$

$$D_{a-} \approx 2D_-(1 + \alpha)(D_+/D_e) . \quad (8)$$

In Eqs. (7) and (8), D_+ , D_- , and D_e are the free-positive-ion, negative-ion, and electron diffusion coefficients, respectively. D_{a-} is the negative-ion ambipolar diffusion coefficient. Equations (7) and (8) are valid for small values of α (say $\alpha < 20$). These equations apply only for the case where the electrons and ions are in thermal equilibrium. Under the conditions where essentially all of the electrons have been removed by attachment and diffusion so that $\alpha \rightarrow \infty$, the ambipolar diffusion coefficients for both the positive and negative ions have the following form^{3,4}:

$$D_{a+} = D_{a-} = 2D_+D_-/(D_+ + D_-) . \quad (9)$$

Thus ion diffusion in the afterglow as indicated by Eqs. (7)–(9) is as follows: In the early afterglow the positive ions will exhibit an essentially constant

diffusion coefficient [Eq (7)]. For low values of α (say $\alpha \approx 1$) encountered in the initial afterglow, D_{a-} will be small because D_+/D_e is of the order of 10^{-3} (see Ref. 13). Once the electrons have disappeared in the afterglow the positive-ion diffusion coefficient will drop to that value indicated by Eq. (9) and the negative-ion ambipolar diffusion coefficient will increase with increasing values of α to a maximum limiting value also represented by Eq. (9). The transition from electron–positive-ion ambipolar diffusion to positive-ion–negative-ion ambipolar diffusion has been discussed.^{17–19}

IV. RESULTS

A. Photoionization

Two possible ionization processes take place during the initial photoionization within the microwave cavity with the hydrogen flash lamp utilized. These are as follows:



Process (10) has a threshold energy of 10.5 eV while process (11) has a threshold of 10.3 eV.²⁰ With the known relative ionization cross sections²⁰ for these processes together with the energy distribution of the flash lamp determined with a vacuum ultraviolet spectrometer it was found that processes (10) and (11) should occur with roughly equal probability. Initial electron densities of about $5 \times 10^8/\text{cm}^3$ were obtained with 10- μsec lamp pulses. Lower initial number densities were utilized for ion diffusion studies. The total initial positive-ion concentration is estimated at about twice the initial free-electron concentration assuming equal contributions from processes (10) and (11).

B. Electron Density Decay Data

The time dependence of the electron number density in the afterglow is shown in Fig. 1. The helium pressure was 20 Torr for most of the data shown. However, for the lowest Br₂ pressures studied, a helium pressure of 50 Torr was used in order that electron loss by diffusion be kept small compared to that by attachment during the early afterglow. A plot of the total attachment frequency ν_T as a function of Br₂ pressure is shown in Fig. 2. If an assumption is made that losses by electron ambipolar diffusion and other processes can be neglected so that $\nu_a \approx \nu_T$, then the attachment coefficient k can be determined from the values of ν_T as a function of Br₂ pressure by use of Eqs. (3) and (4). A value for k of $0.82 \times 10^{-12} \text{ cm}^3/\text{sec}$ is obtained from the entire straight-line plot as presented in Fig. 2. The error for k is estimated at $\pm 10\%$. The constancy of the value obtained for k

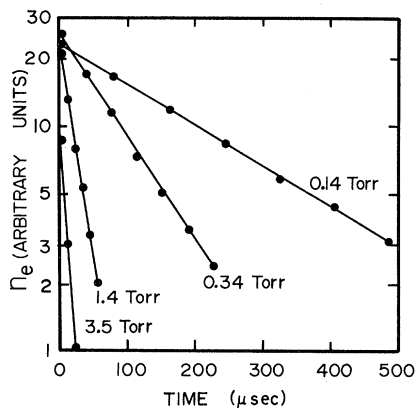


FIG. 1. Electron density decay for different bromine concentrations in helium. For the lowest bromine pressure shown a helium pressure of 50 Torr was used. For the other runs shown a helium pressure of 20 Torr was used.

over the pressure range studied supports the assumption that electron loss by processes other than attachment are small. With the electron number densities used for these measurements, recombination of electrons and positive ions is expected to be negligible. This was substantiated by the fact that the decay frequency did not significantly change for a given Br_2 pressure when the initial ionization was varied over a factor of 4.

C. Diffusion of Ions in Afterglow

In order to separately evaluate the contribution of electron diffusion to the total electron loss frequency in the afterglow [Eqs. (2) and (5)], the positive-ion diffusion coefficient was determined by measuring the ion wall current. For these measurements the Br_2 pressure was low so that α would remain relatively low in the early afterglow.

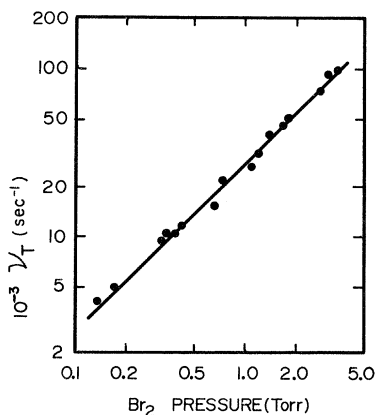


FIG. 2. Total electron decay frequency ν_T observed as a function of bromine pressure.

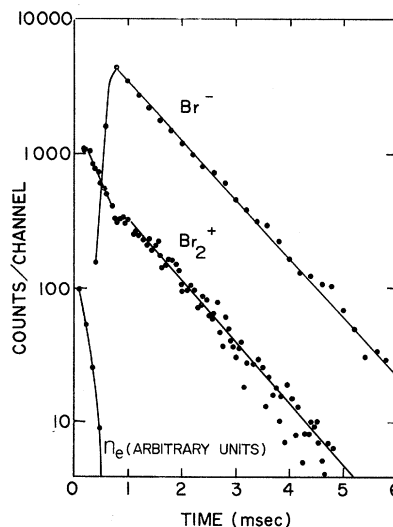


FIG. 3. The time dependence of the Br_2^+ and the Br^- ion wall currents for a bromine pressure of 5×10^{-3} Torr and a helium pressure of 1.4 Torr. The time dependence of the electron number density is also shown.

In studying the positive-ion species in the afterglow, it was determined that Br_2^+ was the predominate ion species present. As previously discussed, it was expected that Br^+ would be present with concentrations essentially identical to those for the Br_2^+ species. The initially observed Br^+ concentration was between one and two orders of magnitude below that of Br_2^+ . However, from a previous study it was found that Br^+ reacts rapidly in the early afterglow.⁴ The reaction which appears to occur is as follows:



This reaction was found to occur readily for the

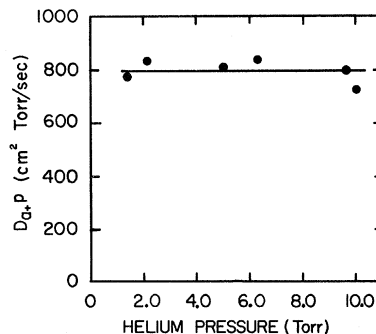


FIG. 4. Determined values for $D_{\alpha^+} p$ for the Br_2^+ ion diffusing in helium for the various helium pressures shown. The data shown have been corrected for the effect on diffusion due to the small amounts of Er_2 present. Br_2 pressures in the range 5×10^{-3} – 2×10^{-2} Torr were used for these measurements.

conversion of I^+ to I_2^+ in a study of iodine ion reactions carried out by Hogness and Harkness.²¹ The time dependence of the Br₂⁺ wall counting rate is shown in Fig. 3. The value of $D_{a+}p$ in the early afterglow has been determined from the initial portion of positive-ion decay curves as shown in Fig. 3 by use of Eq. (6) with the assumption that the loss of this ion occurs mainly as a result of diffusion processes. The values for $D_{a+}p$ thus obtained for the Br₂⁺ ion are shown in Fig. 4 for various helium pressures. The initial ionization has been kept low enough so that recombination losses were negligible compared to loss by diffusion.^{22,23} The constancy of $D_{a+}p$ obtained over the pressure range studied shows that the Br₂⁺ ion decays mainly by diffusion. The data yield an average value of $D_{a+}p = 795 \text{ cm}^2 \text{ Torr/sec}$ for the Br₂⁺ ion diffusing in helium at 296 °K with an estimated error of about $\pm 10\%$. For the lower helium pressures used, it was necessary to correct the observed values for $D_{a+}p$ because of the fact that the ions are diffusing in a mixture of bromine and helium. This correction is made using Blanc's law²⁴ together with the Einstein relationship $\mu/D = e/kT$. In making this correction, the value of $D_{a+}p$ for Br₂⁺ diffusing in bromine has been taken as twice the value found for the positive-ion-negative-ion ambipolar diffusion coefficient as defined by Eq. (9). The value of $D_{a+}p = 12.6 \text{ cm}^2 \text{ Torr/sec}$ previously obtained for the Br₂⁺ ion diffusing in bromine⁴ (where the predominate negative ion was also Br⁻) is strictly equal to one-half the initial value as described by Eq. (7) only if $D_+ = D_-$. The correction amounted to less than 10% of the measured values for $D_{a+}p$ as shown in Fig. 4 except for the data obtained at a helium pressure of 2.2 Torr. At this pressure a 23% correction was required because of the relatively high Br₂ pressure (0.02 Torr) used.

It is of interest to determine the identity of the negative-ions present in the afterglow, and to compare the positive-ion ambipolar diffusion coefficient with the negative-ion ambipolar diffusion coefficient after the transition to positive-ion-negative-ion ambipolar diffusion has occurred. It is only after this transition that appreciable negative-ion diffusion to the cavity walls takes place. Under the conditions used to obtain the data shown in Fig. 3, the Br⁻ ion is the only significant negative ion in the afterglow.²⁵ As the transition from electron-positive-ion ambipolar diffusion to positive-ion-negative-ion ambipolar diffusion takes place, a decrease in the positive-ion decay rate occurs. The slower decay shown in Fig. 3 for the positive ions after the transition has taken place is predicted by Eq. (9). It is of interest to note that if $D_+ \approx D_-$, then the value for D_{a+} after the transition should be one-half the value for D_{a+} prior to the

transition. From the slope of the two straight-line segments of the Br₂⁺ decay curve it was determined that $D_{a+}p$ for the Br₂⁺ ion prior to the transition is about twice that value observed after the transition. The value of $D_{a+}p$ for the Br₂⁺ ion diffusing in helium after the transition is equal to $380 \text{ cm}^2 \text{ Torr/sec} \pm 10\%$. (A small systematic error may be involved because of the fact that the Br₂⁺ decay may not be exponential immediately after the transition.¹⁹) Thus it appears that the values for D_+ and D_- are comparable. As indicated by Eq. (8), the initial negative-ion diffusion is small, but increases with time as α increases. As the transition is reached, a constant value for D_{a-} should be observed giving rise to an essentially exponential decay as shown in Fig. 3. From Eq. (9), the value for D_{a-} after the transition should be identical to the value for D_{a+} under the condition where only one type of positive ion and one type of negative ion occur in the afterglow. The value of $D_{a-}p$ for the Br⁻ ion diffusing in helium after the transition was found to be $374 \text{ cm}^2 \text{ Torr/sec}$ for the data shown in Fig. 3. The values obtained for $D_{a+}p$ and $D_{a-}p$ were essentially identical over a factor of about 7 in helium pressure variation so long as the Br₂ pressure was kept low enough that processes other than diffusion were not important concerning the removal of the Br⁻ ion species.²⁵ Where necessary, the data obtained after the transition for $D_{a+}p$ and $D_{a-}p$ was again corrected for the effect on diffusion due to the small amounts of Br₂ present in the helium.

D. Evaluating Effects of Diffusion on Electron Decay Frequency Data

With the known value for $D_{a+}p$ in the early afterglow prior to the transition to positive-ion-negative-ion ambipolar diffusion, and with an initial value for α , the diffusion contribution to the total electron loss frequency for the data shown in Figs. 1 and 2 can be separately assessed. As it was determined that roughly equal amounts of processes (10) and (11) are produced during photoionization, initial values for α of unity are expected. The initial value of α can be estimated using the initial decay frequencies of the electrons and ions under the condition where the electrons are lost mainly by diffusion. Under such a condition, the value of ν_T (Eq. 2) obtained early in the afterglow divided by the initial decay frequency of the ions (Eq. 6) yields a value for α given by

$$\frac{[D_{a+}(1+\alpha)/\Lambda^2]}{(D_{a+}/\Lambda^2)} = (1+\alpha) \quad (13)$$

From the data shown in Fig. 3 (obtained under conditions where the electron loss is mainly by diffusion) an initial value for α of 1.1 is obtained. Similar initial values for α are obtained at higher

helium pressures.

The procedure by which the diffusional contribution to the total electron loss frequency is evaluated using Eqs. (2) and (5) has been described.^{3,6,16} For the lowest points shown in Fig. 2 the error involved in omitting the diffusion effects for the determination of ν_a is about 10%. This error applies in following the electron number density to about 0.1 of its initially observed value as shown in Fig. 1. The data points shown in Fig. 2 for Br₂ pressures above 0.3 Torr exhibit an increasingly smaller error as a result of neglecting electron loss by diffusion. For a Br₂ pressure of 1.0 Torr and greater, a reduction in the helium pressure from 20 to 4 Torr caused no measureable change in the total electron decay frequency. Thus electron loss by diffusion appears to be essentially negligible for all the data shown except the lowest two points plotted in Fig. 2. If the diffusion loss is accounted for, the lowest two points shown in Fig. 2 fall well within the random experimental error of the straight-line plot as shown in the figure.

V. DISCUSSION AND CONCLUSIONS

It is of interest to compare the value obtained for the dissociative attachment rate coefficient k with the data reported by Bailey *et al.*¹ for electrons at somewhat higher energies. If an assumption is made that the attachment cross section σ_a is con-

stant over most of the thermal electron velocity distribution used for the current study, then $\sigma_a \approx k/\bar{v}$ where \bar{v} is the average electron velocity. With a Maxwellian distribution the attachment cross section for Br₂ is $\sigma_a \approx 0.8 \times 10^{-19}$ cm² at 296 °K. With a simple extrapolation back to thermal energies, a plot of the observed cross section as a function of electron energy yields a value for σ_a of the order of 10^{-19} cm² from the earlier data.¹ It was found by Blewett²⁶ that formation of Br⁻ (by dissociative electron attachment²⁷) was dependent upon electron energy having a peak value at about 2.8 eV and dropping at lower energies to less than 10% of the peak value at essentially thermal energies. If an assumption is made that the cross section at thermal energies is 0.1 of that for the peak value found by Bailey¹ then Bailey's peak value of 1.6×10^{-18} cm² would yield a value of 1.6×10^{-19} cm² for σ_a at thermal energies. Agreement between these extrapolated values and the presently obtained value of 0.8×10^{-19} cm² is reasonable because of the assumptions involved.

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