Electron attachment to boron trichloride

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Low-energy electron attachment to BCl_3 was measured using an electron swarm technique. The parent negative ion, BCl_3^-, was observed within a narrow electron range close to thermal energy. Previous negative ion measurements in BCl_3 discharges, which yielded seemingly inconsistent results, can be shown to be self-consistent based on the present observations. © *1998 American Institute of Physics.* [S0021-8979(98)01722-8]

Boron trichloride is used extensively in plasma etching applications and basic data for reaction kinetics involving BCl_3 are needed to successfully model such discharges (see Refs. 1 and 2 and references therein). Since large abundances of negative ions have been reported in radio frequency (rf) discharges of BCl_3,[3–5] accurate electron attachment cross sections for BCl_3 will facilitate such model calculations. Furthermore, the above mentioned experiments[3–5] yielded conflicting results on negative ion formation: while BCl_3^- was almost exclusively observed in Ref. 3, it was not observed in the other two studies[4,5] where Cl^- was the primary anion observed. We have conducted an electron swarm study on electron attachment to BCl_3; the measured rate constants were unfolded to obtain electron attachment cross section values for electron energies below 2 eV. Our results show that the BCl_3^- ion is formed with a peak cross section of $\approx 4\times 10^{-15}$ cm^2 in a narrow electron energy range of 0–0.1 eV, and the Cl^- ion formation cross section (for ground state molecules) in the energy range of 0–2 eV is likely to be $\leqslant 5\times 10^{-18}$ cm^2. Based on this result, we will show that the observations of Refs. 3–5 are not contradictory to each other.

The electron swarm apparatus has been described in detail previously (see Ref. 6 and references therein). In the present experiments conducted at room temperature of 295 ± 1 K, N_2 was used as the buffer gas; ultrahigh purity N_2 (99.999%) purchased from Matheson Gases and Equipment Company was subjected to liquid N_2 temperature for ≈ 5 h before use in order to freeze out condensible impurities. The BCl_3 gas was purchased from Air Products and Chemicals Company with a stated purity of 99.95%; prior to use, a BCl_3/N_2 premixture was made in a SUMMA™ canister with a specially coated inside surface. This was found to be necessary in order to minimize the loss of BCl_3 to the chamber surfaces; BCl_3 is a highly reactive and corrosive gas, which is extremely difficult to handle.

Even with these precautions, we observed an apparent time dependence of the measured electron attachment rate constant k_a. The apparent time dependence of k_a for a few density-reduced electric field values (E/N, where E is the applied electric field and N is the total gas number density) is shown in Fig. 1; this was presumably due to the loss of BCl_3 to the walls of the experimental apparatus. Assuming an exponential decay of $k_a(t)$ with increasing time, the value of E/N extrapolated to $t=0$ (corresponding to the time when no BCl_3 molecules were lost) was taken to be the actual electron attachment rate constant.[6] Such extrapolated values of k_a are shown in Fig. 2 as a function of E/N. For comparison, measurements by Buchel'nikova[7] and Petrovic[8] for BCl_3/N_2 mixtures are also shown in the same figure (both these data sets were taken from Ref. 8); the thermal electron attachment rate constant reported by Stockdale *et al.*[9] is also shown. It is clear that our results are in qualitative agreement with those of Ref. 8 especially near the low E/N values. Buchel'nikova's[7] results are clearly not compatible with any of the other measurements especially close to thermal energy.

The $k_a(\epsilon)$ at an electron energy ϵ is given by the electron attachment cross section (σ_a) at that energy times the electron velocity. The measured electron attachment rate constant $k_a(E/N)$ at a given E/N value represents the $\sigma_a(\epsilon)$ values averaged over the electron energy distribution $f(\epsilon,E/N)$ for N_2, viz.

$$k_a(E/N)=\left(\frac{2}{m}\right)^{1/2}\int_0^\infty \epsilon^{1/2}\sigma_a(\epsilon)f(\epsilon,E/N)d\epsilon. \tag{1}$$

Using the calculated $f(\epsilon,E/N)$ for N_2,[10,11] we determined the $\sigma_a(\epsilon)$ using an iterative electron swarm-unfolding technique.[11,12] The $\sigma_a(\epsilon)$ values calculated using this procedure are shown in Fig. 3 as a function of electron energy ϵ. It shows that the electron attachment cross section increases rapidly with decreasing electron energy for electron energies below ≈ 0.1 eV. The cross section has a value of $\approx 4\times 10^{-15}$ cm^2 close to thermal energy. For electron energies >0.15 eV, the cross section is $<5\times 10^{-18}$ cm^2.

The accuracy of the cross section data is ultimately dependent on the accuracy of the scattering cross sections used to obtain the electron energy distribution function for N_2 see for example, Ref. 11. The uncertainties are normally higher for low electron energies. Also considering the indirect procedure that was used to make the measurements, we estimate the uncertainty of the data below 0.1 eV electron energy to be $\pm 20\%$.

In BCl_3, negative ions can be produced via three possible electron attachment processes:

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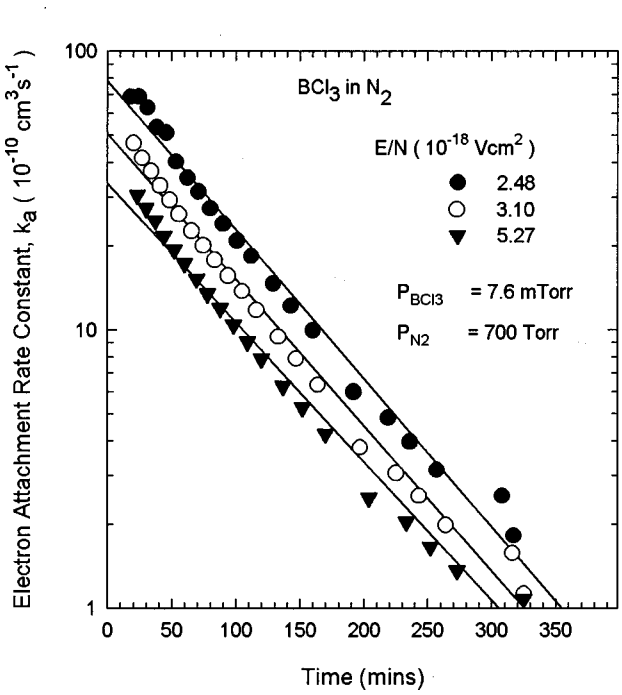

FIG. 1. Electron attachment rate constant, k_a, values for BCl_3 as a function of time following the introduction of the gas mixture into the chamber for three E/N values indicated in the figures.

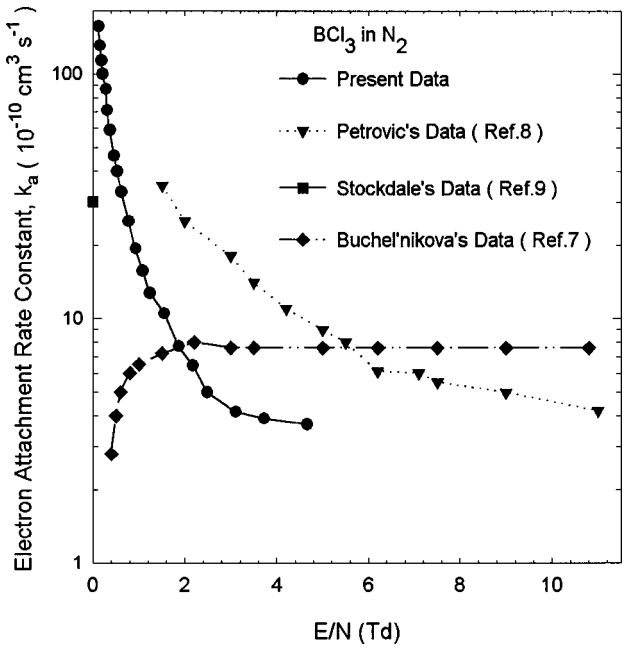

FIG. 2. Electron attachment rate constant k_a values for BCl_3 as a function of E/N. The experimental parameters were the same as those for Fig. 1. The data obtained by other groups are also shown for comparison.

$$BCl_3 + e^- \rightarrow BCl_3^{-\star}, \tag{2}$$

$$BCl_3 + e^- \rightarrow BCl_2 + Cl^-, \tag{3}$$

$$BCl_3 + e^- \rightarrow BCl + Cl_2^-, \tag{4}$$

where $BCl_3^{-\star}$ is a metastable parent anion.

Since the BCl_2–Cl bond energy is ≈4.59 eV [calculated from the heats of formation of BCl_n (where $n=1-3$) and Cl[13]] and the electron affinity of Cl^- is ≈3.6 eV,[3] the reaction (3) is endoergic by ≈1 eV. Thus, Cl^- formation via reaction (3) is not energetically possible for electron energies below ≈1 eV. The threshold for Cl_2^- formation via reaction (4) is somewhat higher. In fact, Stockdale *et al.*[9] observed these ions at electron energies higher than 1 eV, where the Cl_2^- signal was less intense than the Cl^- signal.

On the other hand, reaction (2) is energetically possible for electrons with close to zero energy since the electron affinity of BCl_3 is 0.33 eV,[14] also see Ref. 2. Of course, $BCl_3^{-\star}$ will undergo autodetachment if it is not collisionally stabilized within its lifetime. Due to its pyramidal structure,[15] $BCl_3^{-\star}$ can be expected to be long lived; this was confirmed by Petrovic *et al.*[8] when they observed the BCl_3^- anion in a mass spectrometer which indicates a lifetime in the microsecond range. Our measurements also confirmed the longevity of this parent anion since we did not observe a significant increase in the measured k_a values when the buffer gas (N_2) pressure was doubled. In fact, Stockdale *et al.*[9] observed the BCl_3^- anion in an electron swarm experiment under total pressures in the 5–15 Torr range and did not observe a pressure dependence.

We did not observe a significant formation of Cl^- or Cl_2^- ions (which are expected to form at electron energies above 1 eV as discussed above) in our electron energy range of 0–2 eV (see Fig. 3). The cross section values for reactions (3) and (4) have not been reported. The data of Petrovic *et al.*[8] shown in Fig. 2 have recently been analyzed by Morgan,[16] who also concluded that the electron swarm data of Ref. 8 can be explained solely due to the parent ion formation process of Eq. (2). We estimate the cross sections for dissociative electron attachment processes given by Eqs. (3) and (4) to lie below the lowest detectable cross section for our apparatus, i.e., $\leqslant 5\times10^{-18}$ cm^2.

Now let us discuss the implications of these observations for discharges containing BCl_3. Gottscho and Gaebe[3] studied negative ion formation in a 50 kHz rf parallel plate reactor configuration operating at 100 mTorr. They reported BCl_3^- to be the dominant anion in the plasma; they showed that the photodetachment signal did not change appreciably at wavelengths above the cutoff for the Cl^- ion (≈340 nm) up to ≈700 nm, and thus Cl^- formation must have been negligible.[3] These observations are seemingly in contradiction to three subsequent studies on negative ion formation in BCl_3 discharges: Petrovic *et al.*[8] observed only Cl^- ions when they extracted negative ions from a dc glow discharge (pressure≈500 mTorr) of BCl_3. (As mentioned above they observed the BCl_3^- anion only when they extracted negative ions from an electron swarm.) Overzet and Luo[4] extracted negative ions from a rf discharge (pressure range 25–700 mTorr; rf frequency is presumably 13.6 MHz) to a mass spectrometer and found no evidence of any BCl_3^- ions; they reported the observation of Cl^-, BCl_4^-, $B_2Cl_4^-$, and $B_2Cl_5^-$ ions. Fleddermann and Hebner[5] studied negative ions in an inductively coupled plasma (ICP) reactor operated at 13.6 MHz using a photodetachment technique; they observed only the Cl^- ion in the discharge.

We point out that all of the above observations are con-

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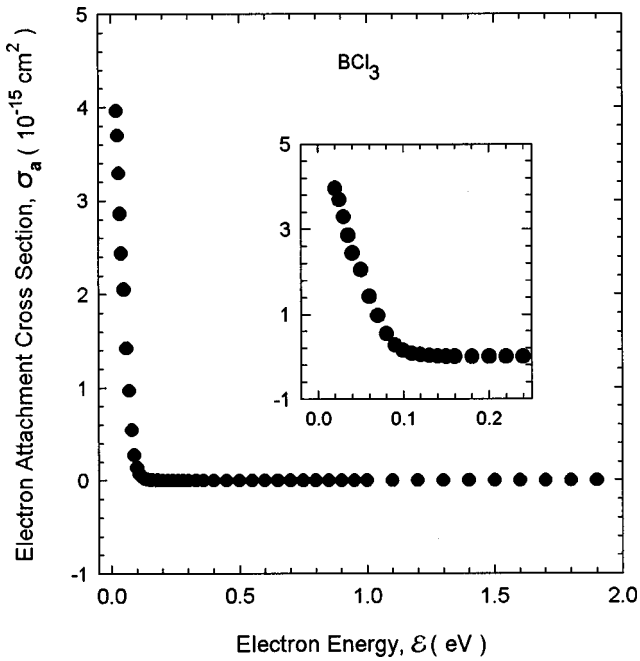

FIG. 3. Swarm-unfolded electron attachment cross section $\sigma_a(\epsilon)$ as a function of the electron energy ϵ. The cross section values up to 0.2 eV are shown in the inset.

sistent when it is noted that the cross section for BCl_3^- ion formation is sharply peaked at electron energies within $\approx$0.1 eV (see Fig. 3), i.e., extremely low energy electrons are needed to form this anion efficiently. Also, the BCl_3^- ion can be detached easily by energetic electron impact due to its small electron affinity of 0.33 eV. Energetic electrons are always present in the high-frequency[4,5] and dc[8] discharges. However, in the low frequency discharge at 50 kHz of Ref. 3, the electron energy distribution relaxes completely during each half cycle, and there is ample time for slow electrons to attach producing BCl_3^- ions before the electrons are reheated in the next half cycle, where those BCl_3^- ions are detached by energetic electrons. Negative ions of any kind were not observed[3] in that half cycle.

As mentioned earlier, we estimate the cross sections for *dissociative electron attachment* to BCl_3 to be $\leqslant 5 \times 10^{-18}$ cm^2; these cross sections have not been reported previously. The question arises as to whether processes other than the weak dissociative electron attachment to a ground electronic state of BCl_3 contributed to the efficient fragment ion formation observed in Refs. 4, 5, and 8. In all those studies[4,5,8] fairly high-energy electrons were produced and it is possible that substantial amounts of secondary species such as radicals and their byproducts were produced by electron impact; subsequent electron attachment to such byproducts may lead to the formation of the observed fragment ions. Another possibility is enhanced electron attachment to electronically excited states of BCl_3: We have previously shown that highly excited states of molecules have many orders of magnitude larger cross sections for dissociative electron attachment compared to the corresponding ground state molecules (see Ref. 17 and references therein); this process only yields fragment negative ions. Therefore, it is quite likely that a significant fraction of Cl^- observed in the above mentioned high-frequency rf and dc discharge experiments was due to enhanced electron attachment to highly excited states of molecules produced in the discharge. In order to assess this possibility, we plan to conduct experiments on laser-excited BCl_3 in the future.

It is important to note that BCl_3^- was the only anion observed in the low-frequency study of Gottscho and Gaebe.[3] Electron attachment to the ground electronic state of BCl_3 was truly realized only in their experiments,[3] i.e., abundant BCl_3^- formation and insignificant fragment ion formation consistent with our present measurements. The very fact that abundant quantities of BCl_3^- ion was observed implies that the molecular dissociation must not have been severe.[3] As was pointed out by Gottscho and Gaebe,[3] at their low discharge frequencies (which were below the ion plasma frequency) much of the power was dissipated by ion conduction processes such as heating of the electrodes and gases in the sheaths; the ratio of power dissipated by electron processes relative to ion processes was estimated to be roughly 0.03.[3] Therefore, it is unlikely that either molecular dissociation or excitation to high-lying states occurred to a significant extent via energetic electron impact in their experiments.[3] On the other hand, such electron impact induced processes dominate in the high-frequency and dc discharges[4,5,8] where only the fragment anions (and secondary anions resulting from ion-molecule reactions[8]) were observed.

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