Coo-3283-7

Electronic States of B^+ Produced by Electron Bombardment of Boron
Trihalides: Some Ion-Molecule Reactions of B^+

K. C. Lin, R. J. Cotter and W. S. Koski

Abstract

Beam attenuation studies of B^+ as a function of attenuating gas pressure shows that the beam has a composition of 35% 3P and 65% 1S when produced by 70 eV electrons from BF_3 . As one proceeds in the series from BF_3 to BI_3 , the amount of excited state varies in a regular manner and B^+ ions are completely in the ground state when BI_3 is used as a target. The composition of the beam could also be varied by varying the electron energy.

The results of the attenuation studies were also confirmed by studying the cross section vs. beam energy curves for the $B^+(^1S)$ and $B^+(^3P)$ reactions with N_2O .

NOTICE

This report was prepared as an account of work sponsored by the United States Government. Neither the United States nor the United States Atomic Energy Commission, nor any of their employees, nor any of their contractors, subcontractors, or their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness or usefulness of any information, apparatus, product or process disclosed, or represents that its use would not infringe privately owned rights.

MASTER

DISTRIBUTION OF THIS DOCUMENT IS UNLIMITED

DISCLAIMER

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency Thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

DISCLAIMER

Portions of this document may be illegible in electronic image products. Images are produced from the best available original document.

Electronic States of B^+ Produced by Electron Bombardment of Boron
Trihalides: Some Ion-Molecule Reactions of B^+

K. C. Lin, R. J. Cotter and W. S. Koski

Department of Chemistry
The Johns Hopkins University
Baltimore, Maryland 21218

Earlier mass spectroscopic studies of the electron fragmentation of the boron trihalides have been carried out in our laboratory¹ and in other laboratories.² In these studies the measured appearance potentials were used to infer certain molecular properties. In general, the electron excitation curves are rather complex and the appearance potentials are obtained by some extrapolation procedure and comparison with the appearance potential of a gas whose ionization potential is accurately known. Frequently, the shapes of the measured curve and the curve for the standard differ contributing significantly to the uncertainty of the inferred appearance potentials. One of the areas in which such uncertainties contribute is in the determination of the electronic states of the B^+ ion produced by electron bombardment of the boron trihalides. Although the earlier work did not permit an accurate evaluation of the states of the B^+ , the results did indicate a possible systematic variation in the states of the B^+ ions produced from the various boron trihalides by electron bombardment. A knowledge of such information is of interest not only from the insight it may provide into the nature of the process that leads to electron fragmentation of molecules but also from a more practical point in preparing ions for use in ion-molecule studies since in the latter case it is necessary to know the electronic state of the projectile ion in order to infer quantitative information on a reaction under study. We have, therefore,

undertaken a study of the electronic states of B^+ produced by electron bombardment of the boron trihalides using the attenuation of the B^+ ion beam in a suitable gas as a function of the target gas pressure as a diagnostic tool. It was found that the fraction of the excited electronic state present in the B^+ beam varied in a systematic way as one varied the target gas in the series ranging from BF_3 to BI_3 . In addition, some preliminary measurements of the cross sections of certain ion-molecule reactions were made and found to be consistent with the conclusions drawn from the attenuation studies.

Experimental Method and Procedure

The apparatus used in this work has been described previously^{3,4} and it consists of a 180° magnetic sector mass spectrometer with a 1 cm radius of curvature in tandem with a 60° magnetic sector with an 8 in. radius of curvature. Detection of product ions is realized by counting the ions with a 17 stage electron multiplier. Gas pressures were measured with an MKS Baratron differential pressure gauge. The BCl_3 and BF_3 were obtained from the Matheson Gas Products Co. These gases were of the C.P. grade with a 99.9% purity. They were used as received. The BBr_3 and BI_3 were synthesized in our laboratory some years ago and were purified by trap to trap distillation before use.

The procedure for measuring the attenuation was to pass the beam through the attenuation chamber when the gas number density (n) was zero and to measure the ion current (I_0) reaching the detector. The gas number density was then adjusted to some finite value and the ion current (I) was measured. If two electronic states i and j are present

with total cross sections σ_i and σ_j respectively for all attenuation processes and if l is path length and f is the fractional abundance of the upper state then the attenuation is given by

$$I = (1 - f) I_0 \exp(-n\sigma_i l) + f I_0 \exp(-n\sigma_j l)$$

A semilogarithmic plot of I/I_0 vs. gas pressure permits one to resolve the two curves and determine the fractional composition of the beam.

Results and Discussion

A typical set of attenuation curves for B^+ produced from electron bombardment of BF_3 at various electron energies is given in Fig. 1. It is clear that more than one electronic state is present and an examination of the intercept obtained by extrapolating the linear part of the curve shows that it decreases in value as the electron energy decreases. Consequently, one can vary the amount of excited state of B^+ by lowering the electron energy and at energies close to the threshold the ground state predominates. If one is interested in obtaining as high an ion intensity as possible, as one may be in the use of the B^+ ion beam to study ion-molecule reactions, this approach to eliminating the excited state is not an attractive one because of the concomitant decrease in overall B^+ intensity. Attempts to reduce the amount of excited state by collisional deactivation by increasing the pressure in the ion source has been a successful technique in some other systems⁷ but this approach failed to eliminate the upper electronic state present in the B^+ case. The addition of paramagnetic impurities has also

been used with some success to eliminate the excited electronic states in some ion beams⁸ but this approach was not applicable here because of the high reactivity of the boron trihalides. Consequently, we explored the possibilities using the other boron trihalides. Fig. 2 gives the B^+ attenuation in N_2O gas when 70 eV electrons are used with the series of boron trihalides ranging from BF_3 to BI_3 . It is apparent that the curvature in the attenuation curves is most pronounced in the BF_3 case and decreases as one proceeds through the series and in the case of BI_3 , the curve is a straight line to within experimental error indicating the presence of a single electronic state in the B^+ beam. The percent excited state present in the B^+ beam can be estimated from the intercepts of the extrapolated portions of the attenuation curves. This fraction plotted vs. electron energy is shown in Fig. 3 for three members of this series. The appearance potential obtained from the BF_3 case is compatible with the presence of B^+ in the first excited state (3P) assuming the products are $B^+(^3P) + F_2 + F$ and that the F_2 and F are in ground electronic states. The other electronic state present is the ground state (1S) judging from the results obtained for some ion-molecule reactions of B^+ in this state. No higher electronic states of B^+ were indicated by the attenuation curves.

In order to get additional evidence in support of the validity of the conclusions drawn from the attenuation data, we have made some measurements of the reactions of $B^+(^1S)$ and $B^+(^1S, ^3P)$. The cross section measurements for the charge transfer reaction $B^+(N_2O, B)N_2O^+$ are given in Fig. 4. When B^+ is in its ground state, the energy defect for the reaction is considerably greater than for the case where B^+ is in the 3P

state in which case an almost resonant process might be expected. In the former case, one obtains a small cross section rising with energy and going through a broad maximum. In the case of B^+ produced from BF_3 , the beam composition was 35.5% 3P and 64.5% 1S and the cross section curve goes through a sharper and larger maximum displaced to the lower energy compared with the $B^+(^1S)$ curve. This is the expected behavior for a charged transfer process where energy defect is changed in the manner indicated. In the case of B^+ from BF_3 , if one subtracts the contribution of the ground state and then normalizes the curve, one obtains the third cross section curve in Fig. 4 which represents the charge transfer reaction of the $B^+(^3P)$ state with N_2O . It is clear that electronic excitation of the projectile ion increases the cross section of the charge transfer reaction considerably.

In addition to the charge exchange reaction with N_2O , the mass transfer processes $B^+(N_2O, N_2)BO^+$, $B^+(N_2O, N, B)NO^+$ and $B^+(N_2O, N_2, B)O^+$ were observed and are summarized graphically in Fig. 5. All of these reactions are expected to be endothermic and the observations are in harmony with this expectation. The excited state reactions of B^+ behave as expected in comparison with the ground state reactions. For example, the maxima of the cross section curves and the apparent threshold values are shifted to lower energies when B^+ is in the excited state.

It is clear, therefore, that the results of the ion-molecule reactions investigations are compatible with the attenuation studies and that one can vary the amount of excited in the B^+ ion beam either by varying the bombarding electron energy or by selecting the appropriate boron trihalide as the target gas.

Acknowledgement

This work was done under the auspices of the U.S. Atomic Energy Commission.

References

1. W. S. Koski, Joyce J. Kaufman and C. F. Pachucki, J. Am. Chem. Soc., 81, 1326 (1959).
2. J. Marriott and J. D. Craggs, J. Electronics and Control, 3, 194 (1957).
3. E. R. Weiner, G. R. Hertel and W. S. Koski, J. Am. Chem. Soc., 86, 788 (1964).
4. R. W. Rozett and W. S. Koski, J. Chem. Phys., 49, 2691 (1968).
5. B. R. Turner, J. A. Rutherford and D. M. J. Compton, J. Chem. Phys., 48, 1602 (1968).
6. R. C. C. Lao, R. W. Rozett and W. S. Koski, J. Chem. Phys., 49, 4202 (1968).
7. E. Lindemann, R. W. Rozett and W. S. Koski, J. Chem. Phys., 56, 5490 (1972).
8. R. J. Cotter and W. S. Koski, J. Chem. Phys., in press.

B^+ Attenuation with N_2O

B^+ from BF_3 , BCl_3 , BBr_3 and BI_3

20μ Pressure in the source; B^+ B.E. 17.5 eV