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INTRODUCTION

Mass spectrometric studies of electrical discharges have been carried out during the past decade by several workers (1-6) in an attempt to identify the ionic precursors of a variety of neutral by-products which are formed in these systems. Such studies are expected to reveal the detailed chemistry of the many reactions that follow the formation of primary ions through the impact of energetic electrons on the neutral gas molecules, and end with the neutralization of the final form of the ion either in the gas-phase or at the electrodes or the walls of the discharge tube. Thus, the identification of these ionic reactions will, in many cases, demonstrate the mechanism of the production of the free-radicals which are the source of the neutral by-products. Further, such studies would be expected to provide information on the mechanisms of catalytic or inhibitory effects of trace quantities of certain compounds (e.g. water vapor) on the formation of these products. Processes such as charge-exchange or ion-molecule reactions which occur with large cross-sections and have been suspected to be responsible for such effects will thus be easily identified.

The complexity of electrical discharges however, often makes the interpretation of mass spectrometric data very difficult. Specifically, the variations of electric field along and across the discharge tube in certain commonly used discharges (e.g. glows) often affect the abundance distribution of the various ionic species which are observed at the mass spectrometer (2,3). This is mainly due to the complex dependence of the cross-sections of both charge-exchange and ion-molecule reactions on ion energy as determined by the electric field within the discharge tube. Further complication arises from the formation of ion-sheaths around the walls of the discharge tube, through ambipolar diffusion. These may strongly influence the sampling of the discharge by the mass spectrometer. It is therefore essential that the system under investigation be well understood before the interpretation of the data is attempted.

In this paper, the results of mass spectrometric investigations on low pressure positive corona discharges established between two coaxially placed electrodes will be discussed. This form of discharge has been chosen primarily because its electrical properties are relatively simple and well understood. Further, the ion-sheath effects at the point of sampling are minimized because of the low level of ionization in these systems.

EXPERIMENTAL

Detailed description of the apparatus has already been given (6). Figure 1 shows the schematic diagram of the apparatus. Briefly, a coaxial discharge tube is operated through a high-voltage d.c. power supply and the current is stabilized through the use of an external current limiting resistor, R. Electrons moving through the high field region present only at very close distances to the anode wire will gain energy from the field and cause ionization of the gas molecules in this region. Because of the symmetry of the electrodes, therefore, the system closely behaves as a line source of positive ions which are continuously regenerated. These ions will then move through the gas, perpendicular to the axis, undergoing various interactions before reaching the cathode. A small sampling port (10 to 100 microns in diameter) at the cathode allows a small portion of the ions to escape the discharge tube and be analyzed by a quadrupole mass spectrometer.

The form of the electric field within the discharge tube is rectangular hyperbolic before the discharge is established. As the discharge is formed, however, the presence of the positive space charge distorts this initial field, causing the

latter to attain a constant value for the major distance between the electrodes (7).

Differential pumping of the sampling region and the mass spectrometer allows operation of the discharge tube between pressures ranging from less than 1 torr to atmospheric. An electron gun placed before the mass spectrometer serves as an independent ionizing source for monitoring the composition of the neutral discharge gas when no ions are extracted from the discharge tube. For such analysis, calibration curves made on prepared gas mixtures, showing mass discrimination due to the specific flow condition are used. A rapid flow of gas is maintained through the discharge tube in order to avoid appreciable accumulation of neutral by-products of the discharge. For this purpose a linear flow velocity is maintained such as to completely renew the gas within the tube in two seconds. In systems where the concentration of the electro-negative gas (e.g. oxygen) is low, an external source of ionization through the use of a weak radioactive source (e.g. Po^{210}) is used to stabilize the discharge.

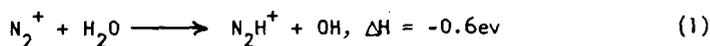
The general problem of mass spectrometric sampling from high pressure sources has recently been discussed by several workers (8). In systems where condensable gases are present, the temperature drop following the adiabatic expansion of the gas through the sampling nozzle may cause condensation if such gaseous components are present in sufficient concentrations. In the present experiments, the water content of the gases under investigation has been chosen below 5×10^{-2} mole %. Under these conditions, it can be demonstrated* that such condensations make negligible contribution to the results.

RESULTS AND DISCUSSIONS

Earlier experiments (6) on corona discharges in air at atmospheric pressure clearly demonstrated the important role of trace quantities of water vapor in these systems. In nitrogen, oxygen and their mixtures, where the water content exceeded 4 to 5×10^{-2} mole %, the dominant ionic species observed at the mass spectrometer were those corresponding to hydrated proton clusters, $(\text{H}_2\text{O})_n\text{H}^+$. These species were apparently formed from the interaction of the primary ions with the water molecules in the system as they passed through the gas to the cathode. In order to determine the role of various reactions which lead to such clusters, low pressure experiments were designed with individual gaseous components (e.g. O_2 , N_2) and their corresponding mixtures with various quantities of water vapor. These experiments were expected to reveal the formation of intermediate species and their final conversion to hydrated protons.

Discharge in Nitrogen:

Experiments with nitrogen at low pressures, containing various concentrations of water vapor show several intermediates which are formed through the reactions of nitrogen ions with water. The results of a typical experiment showing the relative abundances of various species reaching the mass spectrometer as the pressure of the discharge is varied, are shown in Fig. 2. In this experiment, it can be observed that as the pressure is increased, the abundance of the primary ion, N_2^+ , is sharply reduced while those of the intermediate ions, namely, N_4^+ , N_2H^+ and H_2O^+ rise to a maximum and then decrease as the tertiary ion H_3O^+ begins to appear. This latter ion also rises to a maximum at higher pressures as its more highly hydrated forms appear. Thus the two reactions:



and

*Calculations based on the maximum number of collisions of an ion with water molecules present up to 10^{-1} mole % in an expanding gas, assuming cross-sections of 10^{-13}cm^2 , show negligible contribution to the total collisions that such an ion and molecule will undergo within the discharge system. These calculations will be published elsewhere.

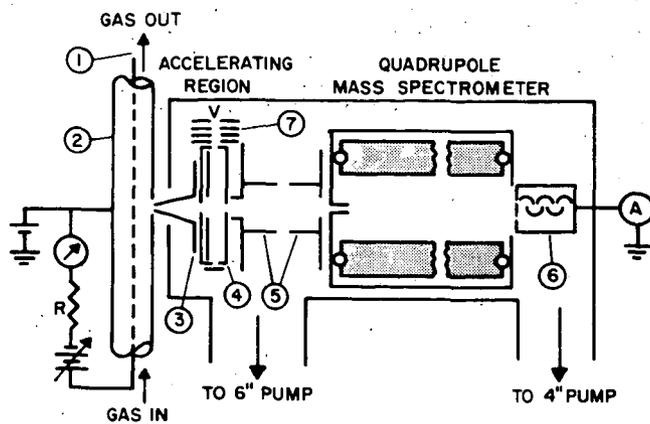


Fig. 1. Schematic diagram of the discharge tube and mass spectrometer; 1, platinum wire anode; 2, cylindrical discharge tube; 3, extraction electrode; 4, mass spectrometer ionization chamber; 5, focussing electrodes; 6, electron multiplier; 7, electron-gun assembly.

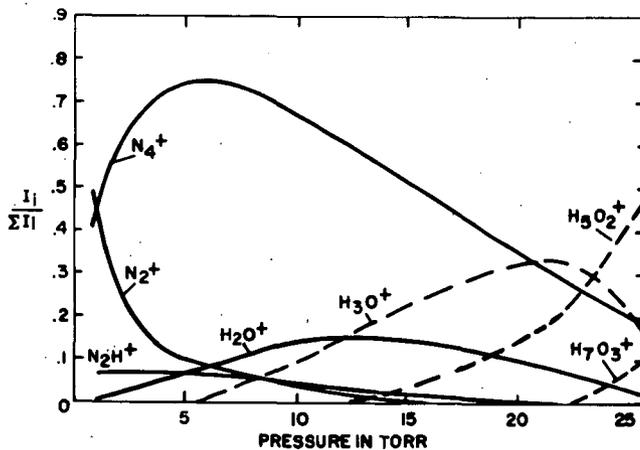
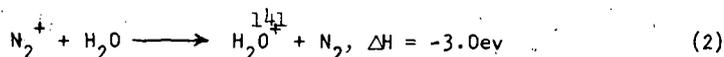
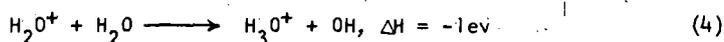
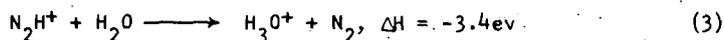


Fig. 2. Variation of the relative abundance of different ions with pressure in a positive corona discharge in nitrogen containing 2.2×10^{-2} mole % of water vapor.



appear to provide species which can further react with water through reactions (3) and (4) to form the hydrated proton:



The third and the major intermediate, namely N_4^+ which is formed through reaction of N_2^+ with neutral nitrogen molecule (9) apparently also undergoes reactions with water similar to reactions (1) and (2) to form N_2H^+ and H_2O^+ ion. These reactions are also expected to be exothermic. The relative abundance of N_4^+ ion is found to be strongly dependent on the field strength within the discharge tube. Specifically, the formation of a space-charge around the corona wire is found to strongly influence the relative abundance of N_4^+ and N_2^+ ions in the system as this space-charge substantially reduces the field strength within the discharge tube. In the experiments shown in Fig. 2, the magnitude of E/P, the pressure reduced electric field for the major distance between the two electrodes, was calculated to be about 7 volt/cm. mm Hg.

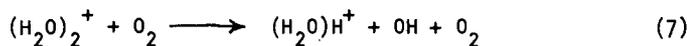
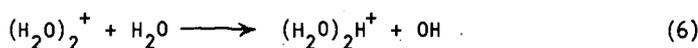
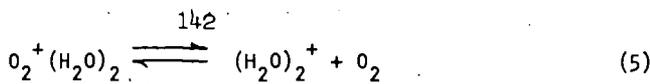
Two other intermediate species have been observed in this system. These ions, not shown in Fig. 2, are N_4H^+ and N_3H^+ . They apparently arise as a result of ion-molecule reactions involving N_4^+ and N_3^+ ions in the system with water molecules and are expected to undergo proton transfer reactions similar to reaction 3, to yield H_3O^+ .

Other ions observed were at $m/e = 32$ and 46 . These ions are believed to arise from trace quantity of oxygen which is inevitably present in this system as a result of the decomposition of water. The ion of $m/e = 32$ is apparently O_2^+ while that of $m/e = 46$ is NO_2^+ .

In a system of pure nitrogen where the water concentration was kept below 5×10^{-3} mole %, under similar discharge conditions as those presented in Fig. 2, it was observed that the intensity of N_4^+ ion rapidly increased as the gas pressure was increased, reaching a plateau after a few mm Hg pressure. This plateau corresponded to 95% of total ion intensity, with the remaining 5% being mainly due to N_3^+ ion. This result supports the earlier reference to the presence of a low E/P between the two electrodes (9) and the lack of any appreciable ion-sheath near the cathode.

Discharge in Oxygen:

Figure 3 shows the pressure dependence of the relative abundance of various ionic species in a corona discharge in oxygen. This experiment shows several marked differences from those shown for nitrogen in Fig. 2. The most striking feature is the presence of large abundances of hydrated forms of the primary ion, namely $\text{O}_2^+(\text{H}_2\text{O})_{1,2}$ and their dependence on pressure. That the abundances of these ions appear to rise to a maximum and then decrease at higher pressures with the formation of hydrated protons strongly suggests their role in the intermediate processes. This evidence together with the appearance of $(\text{H}_2\text{O})_2^+$ ions in the system, and the variation of its abundance with pressure, i.e. rising to a maximum and then reducing at higher pressures, indicates the operation of an entirely new mechanism in this system for the formation of hydrated protons. Moreover, the appearance of $m/e = 37$, $(\text{H}_2\text{O})_2\text{H}^+$ before the first member of the series suggests that a reaction other than the hydration of H_3O^+ , is responsible for the formation of this species. Since the ionization potential (I.P.) of oxygen (12.07ev) is lower than that of water (I.P. = 12.56ev), a charge-exchange reaction similar to reaction 2, for nitrogen does not appear probable. Nor is it likely that a reaction similar to that of reaction 1, to form O_2H^+ would occur, as it appears to be endothermic. It is therefore probable that the hydrated form of the primary ion, especially the species containing two water molecule may be a precursor in the formation of the hydrated proton through the reactions:



Reaction 5 is expected to be exothermic owing to the heat of hydration of H_2O^+ ion. It may also be possible, though unlikely, that any required energy for the reaction be supplied through the electric field in the discharge.

One other ionic species which may play a role in this system is O^+ . However, since the I.P. of atomic oxygen (13.61eV) is greater than that of oxygen, this species is not observed in this system as it most probably undergoes charge exchange with molecular oxygen at pressures used in these experiments. The reaction of O^+ with O_2 to give rise to O_3^+ , if it occurs at all, is not observed in these experiments since ozone has also a higher I.P. (12.8eV) than that of oxygen and therefore O_3^+ is similarly expected to undergo a charge-exchange reaction with O_2 .

Three other ions were observed in minor relative abundance in this system. These ions are OH^+ , H_2O^+ and $H_2O_2^+$. The relative yield of the OH^+ ion is shown in Fig. 3 while the yields of H_2O^+ and $H_2O_2^+$, being somewhat smaller, are not indicated. It is believed that the first two of these ions arise from an ion-molecule reaction and a charge-exchange process between O^+ and water molecule respectively, and are detected only at higher discharge pressures where such reactions compete with direct charge transfer of O^+ to oxygen molecules. $H_2O_2^+$ ion, however, may appear as a result of an efficient charge transfer process between O_2^+ ion and the trace quantities of H_2O_2 , apparently formed in the system by the recombination of hydroxyl free radicals, or the reaction, $HO_2 + H_2 \longrightarrow H_2O_2 + H$, hydrogen being supplied through the decomposition of water.

In a system of pure oxygen, where the water content was kept below 5×10^{-3} mole %, only two ions, O_2^+ and O_4^+ were observed within the pressure range investigated. The abundance of O_4^+ ion rises sharply as the pressure is increased while that of O_2^+ decreases and both reach a plateau beyond a pressure of 20 Torr in the discharge tube. The relative abundance of O_4^+ in this plateau region was found to be about 62%.

Discharge in Nitrogen Containing 0.12 mole % Oxygen:

In order to determine the role of oxygen in air discharges in the absence of water vapor, a number of experiments were carried out in nitrogen containing 0.12 mole % of oxygen. The lower limit of water vapor in these experiments was 5×10^{-3} mole %. Fig. 4 shows the results of the relative abundance of various ionic species which are detected at the cathode as the pressure of the discharge is increased. These experiments clearly trace the history of the primary ionic species, namely N_2^+ as it is converted to N_4^+ and the latter undergoes charge-exchange with the trace quantity of oxygen present in this system. Thus, beyond a pressure of 20 Torr in the discharge tube the charge carriers in this system are almost all O_2^+ . The trace amount of N_3^+ observed in the system is also all removed beyond a pressure of 15 Torr.

It is significant to note that no nitric oxide ion is observed in this system, indicating that neither the reaction $N_4^+ + O_2 \longrightarrow NO^+ + NO + N_2$, nor $O_2^+ + N_2 \longrightarrow NO^+ + NO$, occur to any appreciable extent, in spite of the fact that both these reactions are expected to be exothermic.

Experiments in which water was not excluded showed the appearance of many ionic intermediates of both pure oxygen and nitrogen and their mixtures. All these ions could be traced and their final conversion to hydrated protons followed.

Discharge in Air:

Experiments in air in the absence of water vapor (less than 5×10^{-3} mole %) were carried out in order to determine the importance of ionic species of oxides of nitrogen in these systems. The results of these experiments are shown in Figure 5.

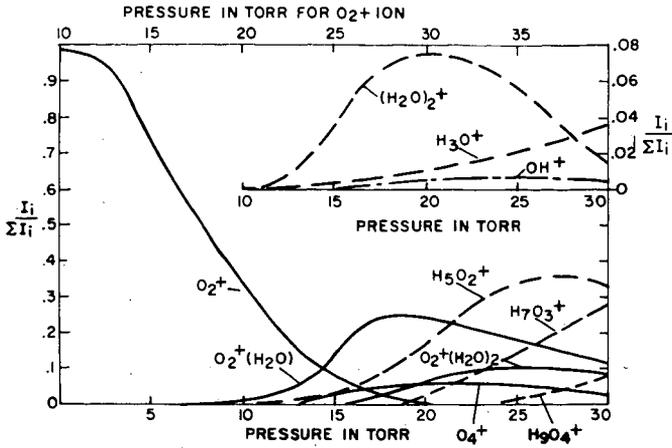


Fig. 3. Variation of the relative abundance of different ions with pressure in a positive corona discharge in oxygen containing 2.0×10^{-2} mole % of water vapor. The pressure scale for O_2^+ ion is shown on the top of the figure.

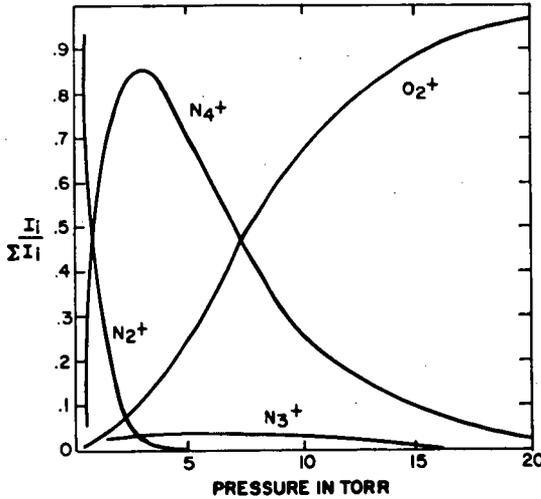


Fig. 4. Variation of the relative abundance of different ions with pressure in a positive corona discharge in nitrogen containing 1.2×10^{-1} mole % of oxygen and less than 5×10^{-3} mole % of water vapor.

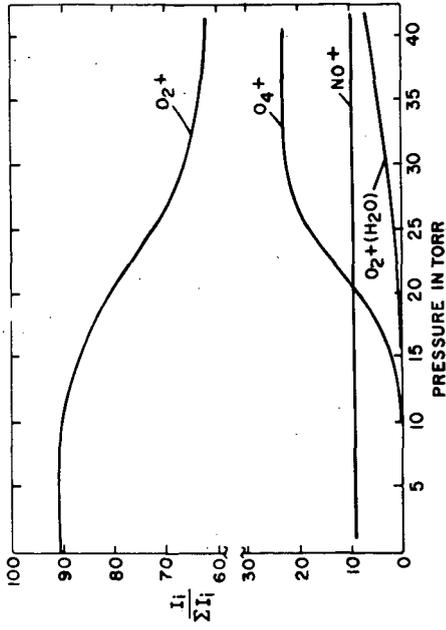
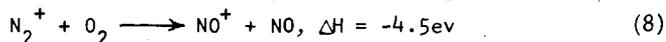


Fig. 5. Variation of the relative abundance of different ions with pressure in a positive corona discharge in air with water concentration below 5×10^{-3} mole %.

As expected from the previous sections, O_2^{145+} ion appears as the most abundant ion in this system. Also as expected, O_4^+ ion appears in the system and as the pressure is increased, it becomes an important charge carrier and its relative abundance eventually reaches a plateau. The appearance of the ion $O_2^+(H_2O)$, hydrated form of molecular oxygen ion, in this system, indicates the high affinity of this ion for hydration as the gas contained less than 5×10^{-3} mole % water in the discharge tube.

Nitric oxide ion was the only oxide of nitrogen found in the system under the experimental conditions used here. Its relative abundance remained constant as the discharge pressure was varied between 2 to 40 Torr. The presence of NO^+ in these experiments and its absence in experiments carried out in nitrogen containing 0.1 mole % of oxygen, indicates that these ions are probably formed through the reaction



Assuming that O_2^+ arises either through charge-exchange with N_2^+ ion or by direct electron impact on neutral oxygen molecule, one can use the data in these experiments to obtain a relative ratio of the rate-constants for the charge-exchange reaction of N_2^+ with oxygen to that of ion-molecule reaction (8). This ratio is found to be equal to 8, a value which is lower than the ratio of the published values of these rate-constants (10). This indicates that possibly other reactions such as $N^+ + O_2 \longrightarrow NO^+ + O$ and $O^+ + N_2 \longrightarrow NO^+ + N$ or others involving neutral atomic species also contribute to the total yield of NO^+ ion.

CONCLUSIONS

Mass spectrometric studies of low pressure positive d.c. corona discharges in atmospheric gases containing trace quantities of water vapor show a complex series of reactions with each component leading to the formation of hydrated protons in the system. In the case of nitrogen, intermediate species N_2H^+ and H_2O^+ are presumably formed through ion-molecule reaction and charge-exchange of N_2^+ and N_4^+ with water molecules. These species later form the hydrated proton through proton transfer reactions in subsequent collisions with water molecules. In moist gaseous oxygen, it appears that the hydrated form of the primary ion $O_2^+(H_2O)_2$, plays an important role in the conversion of the charge carriers to hydrated protons. It is suggested that this transformation may occur through the formation of the intermediate $(H_2O)_2^+$ which has been found in this system. In experiments where water vapor is excluded from the system, a concentration of 1.2×10^{-1} mole % oxygen can transform, through charge-exchange reactions, all ionic species of nitrogen to O_2^+ at a discharge pressure of 20 Torr, and that ion-molecule reactions leading to the formation of oxides of nitrogen are by far less probable within the pressure range investigated.

ACKNOWLEDGMENTS

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