ION-MOLECULE REACTION RATES MEASURED IN A DISCHARGE AFTERGLOW

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ABSTRACT

The application of a flowing afterglow reaction technique to the measurement of thermal energy ion-molecule reactions is briefly described. The flowing afterglow system allows the measurement of reactions of ions with such unstable neutrals as O, H, N, and O_3. The reaction $O^+ + CO_2 \rightarrow O_2^+ + CO$ appears to be important in CO_2 discharges, as O_2^+ has been found to be a dominant ion in this case. The O^+, C^+, and CO^+ ions rapidly react to produce either O_2^+ or CO_2^+, the dominant ions observed in a CO_2 discharge. In an argon-hydrogen discharge, H_3^+ would be an important ion, since it is the most stable ion in that system and a reaction sequence leading to H_3^+ production is fast. Several associative-detachment reactions such as $O^- + O \rightarrow O_2 + e$ and $H^- + H \rightarrow H_2 + e$ have been found to have large rate constants and such reactions may be important in determining the negative ion concentrations in discharges.

I. Introduction and Experimental

A flowing afterglow system has been utilized for the past several years in the ESSA Laboratories in Boulder, Colorado, for the measurement of reaction rate constants at 300° K for both positive and negative ions reacting with both stable and unstable neutral species[1,2]. Figure 1 illustrates one version of the flowing afterglow tube which has been utilized. A tube of about 1 m length and 8 cm diameter serves as the reaction vessel. A gas, usually helium, is introduced at one end of the tube and exhausted at the other end at a rate of around 100 atm cc/sec, the helium pressure being typically ~ 0.3 torr. The helium is ionized by a pulsed dc discharge producing about 10^{10} He^+ ions and $He(2^3S)$ metastable atoms per cc. Positive ions are produced in most cases by adding a relatively small concentration of neutral gas into the helium afterglow by means of a small nozzle. The positive ions are products of He^+ and $He(2^3S)$ reactions with the added neutral. The reactions of these ions with a second neutral added at a second downstream nozzle are then measured. The ion composition of the afterglow is monitored by means of a frequency scanned quadrupole mass spectrometer covering the mass range 1 - 100 amu. The rate of disappearance of a reactant ion with neutral reactant addition leads directly to a reaction rate constant. Our estimate of the reliability of the rate constants so determined is ± 30% in favorable cases. Our experience in comparing our rate constants with other measured rate constants generally supports this estimate.

This experimental scheme has many variations. We have, for example, successfully used pyrex and quartz reaction tubes as well as stainless steel, and microwave and electron beam ionization as well as the dc discharge. We sometimes find it desirable to produce reactant ions by adding a suitable gas through the discharge with the helium rather than downstream in the afterglow, particularly in the case of certain negative ions such as O^- and H^-, which are readily created by dissociative attachment by fast electrons in the discharge. We sometimes use carrier gases other than helium, particularly argon.

Some of the important features of the flowing afterglow experimental technique are the following: (1) The reactant ions in many cases are known to be in their ground states, either because of the reaction which produces them or by virtue of superelastic electron collisions in the plasma prior to neutral reactant addition. Stable neutral reactant species are added without being subjected to discharge or

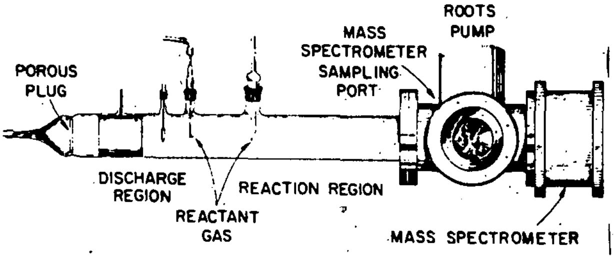

Figure 1. Flowing Afterglow Reaction System.

excitation conditions so that they can be assumed to be neither vibrationally nor electronically excited. On the other hand, some selective excitation is possible. For example, the reaction

$$O^+(^4S) + N_2(^1\Sigma) \rightarrow NO^+(^1\Sigma) + N(^4S) + 1.1\ \text{eV} \qquad (1)$$

has been measured[3] as a function of vibrational temperature from 300 - 5000°K.

(2) It is possible to add chemically unstable neutral reactants into the afterglow so that reactions such as

$$N_2^+ + O \rightarrow NO^+ + N, \qquad (2) \qquad O_2^+ + N \rightarrow NO^+ + O, \qquad (3)$$

$$O^- + O \rightarrow O_2 + e, \qquad (4)\ \text{and} \qquad O^- + O_3 \rightarrow O_3^- + O \qquad (5)$$

have been studied in this system.

(3) The difficulty of resolving concurrent reactions does not arise, as it does in mass spectrometer ion sources, and we have measured the reaction

$$CO_2^+ + H_2 \rightarrow CO_2H^+ + H \qquad (6)$$

without complication from the reaction

$$H_2^+ + CO_2 \rightarrow CO_2H^+ + H, \qquad (7)$$

since H_2 is not ionized in the flowing afterglow arrangement.

II. Thermal Energy Charge-Transfer Reactions

The flowing afterglow system is well suited to exothermic charge-transfer reaction measurements, since the neutral reactant, necessarily of lower ionization potential, does not go through the ionization region and hence is not selectively ionized as would be the case in some experimental arrangements used for ion-molecule reaction studies. For positive ions, either atomic or molecular, charge-transfer to molecular neutrals is usually fast (barring occurrence of a competitive exothermic rearrangement reaction). Very many such examples (several dozen) have been observed and very few exceptions, notably the reaction between $He^+ + H_2$, which is observed not to have a rate constant as large as 10^{-13} cm^3/ sec. For example, Ar^+, CO^+, CO_2^+, N_2^+, N^+, and H_2O^+ all charge-transfer with O_2 to produce O_2^+ with rate constants greater than 10^{-10} cm^3/sec (or cross sections greater than 20 Å^2).

This result contradicts most theoretical predictions which had assumed that charge-transfer would be slow except in unusual cases involving fortuitous energy resonances.

The situation appears the same for negative ion charge-transfer although much less data is available in this case. We have found that the reactions

$$H^- + NO_2 \rightarrow NO_2^- + H \qquad (8) \qquad OH^- + NO_2 \rightarrow NO_2^- + OH \qquad (9)$$

$$O^- + O_3 \rightarrow O_3^- + O \qquad (10)$$

and several other negative ion charge-transfer reactions have rate constants greater than 10^{-10} cm^3/sec at 300° K and previously Curran[4] had observed a number of fast negative ion charge-transfers to NO_2, and Henglein and Muccini[5] observed a fast negative ion charge-transfer with SO_2. In the absence of experimental data one would certainly predict that exothermic charge-transfer to a molecular neutral will be fairly efficient.

III. Ion-Atom Interchange Reactions

The most commonly studied ion-molecule reactions have involved changes in molecular configuration. Typical examples are

$$C^+ + O_2 \rightarrow CO^+ + O, \qquad (11)$$

whose rate constant, 1.1×10^{-9} cm^3/sec, from flowing afterglow experiments[2] agrees with an earlier value 9×10^{-10} cm^3/sec measured in a mass spectrometer ion source by Franklin and Munson[6]; the reaction

$$O^+ + CO_2 \rightarrow O_2^+ + CO \qquad (12)$$

with a rate constant of 1.2×10^{-9} cm^3/sec from both flowing afterglow[2] and mass spectrometer ion source measurements[7]; and

$$C^+ + CO_2 \rightarrow CO^+ + CO \qquad (13)$$

with a rate constant 1.9×10^{-9} cm^3/sec.

Such reactions are more often fast than slow. One of the slowest exothermic ion-molecule reactions (again barring cases where charge-transfer competes) is

$$O^+ + N_2 \rightarrow NO^+ + N, \qquad (14)$$

with a rate constant $\sim 10^{-12}$ cm^3/sec[3]. This rate constant increases[3] to about 3×10^{-11} cm^3/sec for an N_2 vibrational temperature of 5000° K and also increases with O^+ kinetic energy[8,9].

No case of a fast ion-atom interchange reaction involving the breaking of two bonds has so far been reported. The exothermic reaction

$$O_2^+ + N_2 \rightarrow NO^+ + NO \qquad (15)$$

has a rate constant less than 10^{-15} cm^3/sec, for example.

IV. Associative Detachment Reactions

A number of associative detachment reactions have been recently measured to be fast in the flowing afterglow system (i.e. $k > 10^{-10}$ cm^3/sec), including:

$$O^- + O \rightarrow O_2 + e \qquad (16) \qquad\qquad H^- + H \rightarrow H_2 + e \qquad (17)$$

$$OH^- + O \rightarrow HO_2 + e \qquad (18) \qquad\qquad OH^- + H \rightarrow H_2O + e \qquad (19)$$

$$O^- + H_2 \rightarrow H_2O + e \qquad (20) \qquad\qquad O^- + CO \rightarrow CO_2 + e \qquad (21)$$

and

$$O^- + NO \rightarrow NO_2 + e. \qquad (22)$$

Phelps and Moruzzi[10] have been making similar measurements in drift tube experiments at Westinghouse and have measured reactions, (20), (21), and (22). The flowing afterglow and drift tube results agree within better than a factor of two in each case. Several exothermic associative detachment reactions do not occur at measurable rates ($k < 10^{-12}$ cm^3/sec), an example being

$$O^- + N_2 \rightarrow N_2O + e + 0.2\ eV. \qquad (23)$$

V. Ion-Molecule Reactions in Discharges

One obvious application of measured rate constants to the qualitative interpretation of the ion composition of a gas discharge is the case of the CO_2 discharge ion composition studied by Dawson and Tickner[11]. Dawson and Tickner observed the dominant ions in a glow discharge in CO_2 to be O_2^+ and CO_2^+. This is quite reasonable in view of the known occurrence of reactions (11), (12), and (13) above, together with the fast charge-transfer of CO^+ with CO_2 to produce CO_2^+. The results of these reactions are graphically illustrated in Fig. 2 (from Fehsenfeld, et al., J. Chem. Phys. 45, 23 (1966)), which shows that all of the ions, C^+, O^+, and CO^+, do convert to O_2^+ and CO_2^+ by reaction with CO_2 in the ~ 6 milliseconds reaction time in the flowing afterglow. If molecular oxygen were added, one would expect the dominant ion to become O_2^+ alone, since CO_2^+ is known to charge-transfer rapidly with O_2[12].

In a like manner Fig. 3, showing ion composition in an Argon-H_2 afterglow[13], suggests that the ion-molecule chemistry is such that the dominant ion is H_3^+, and this would very likely be true for certain active discharge conditions as well.

An example of the possible importance of associative detachment reactions in discharges was noted by Massey[14], who speculated that the low negative ion density in oxygen discharges (relative to iodine discharges for example) might be due to electron detachment by reaction (16). In iodine the analogous reaction, $I^- + I \rightarrow I_2 + e$ is endothermic. In view of the subsequent finding that reaction (16) is indeed fast ($k_{16} = 1.9 \times 10^{-10}$ cm^3/sec), Massey's suggestion takes on renewed interest. The same argument could be applied to H_2 discharges in view of the rapidity of reaction (17), $k_{17} \sim 10^{-9}$ cm^3/sec.

VI. Conclusions

The growing body of quantitative ion-molecule reaction rate data now available should allow in favorable cases prediction and in many cases correlation of observed ion compositions of gas discharges with known ion-molecule chemistry.

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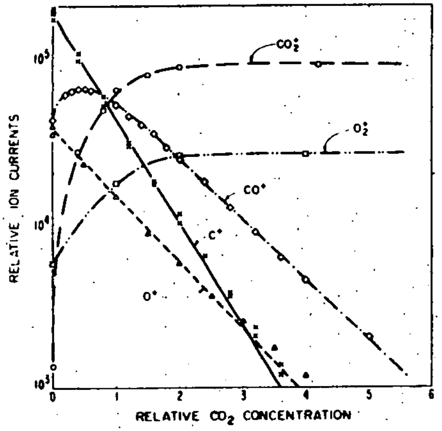

Figure 2. Ion Reactions with CO_2.

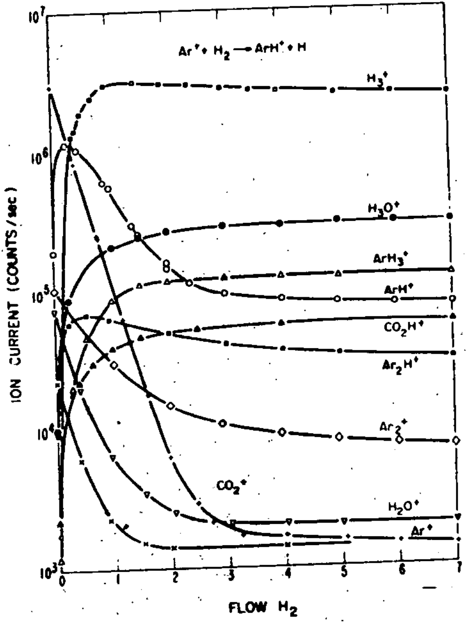

Figure 3. Ion Reactions in an Ar-H_2 System.