

ELEMENTARY INTERACTIONS BETWEEN CHARGED AND NEUTRAL SPECIES IN PLASMAS

David Smith and Nigel G. Adams

Department of Space Research, University of Birmingham, Birmingham B15 2TT
England

Abstract - A brief overview is presented of the elementary reaction processes involving charged particles which can contribute to the chemical evolution of a plasma. Specific processes discussed include binary and ternary ion-neutral reactions, electron-ion recombination, electron attachment and ion-ion recombination. Typical rate coefficients for these processes are given and it is indicated how they vary with temperature and interaction energy, and the charged and neutral particle number densities. The information presented is intended as a starting point to the challenging problem of estimating formation and loss rates of charged and neutral species in discharge plasmas which are used for technological purposes. As an example, a case study of an O_2/CCl_4 discharge plasma is presented.

INTRODUCTION

When ionization is created in a gas, a variety of reactive species can be generated including electrons, positive and negative ions and neutral radicals, some of which initially may be internally excited. From this combination of reactive species, a plasma chemistry initiates which is especially complex for gas mixtures containing polyatomic molecules, polar molecules and electronegative species. Interest in the reactions between charged and neutral species in plasmas has a long history. Great stimulus has been brought to the subject by aeronomists (Refs.1-3), and astrophysicists and astrochemists (Refs.4-7), because of a desire to understand the processes which result in the generation of ions and molecules in planetary atmospheres and interstellar gas clouds. Now there is additional motivation because of the importance of discharge plasmas in, for example, plasma etching and plasma polymer deposition (Refs.8-12), plasma heating (Ref.13) and gas lasers (Refs.14 & 15). Thus, for plasma etching and plasma polymer deposition, the objective is to generate appropriate ions and neutral radicals under conditions which permit the efficient etching of surfaces or polymerisation on surfaces. The subject of plasma-surface interactions is very technologically important and is currently being researched with great vigour (Ref.16). The efficiency of the plasma surface processes depends in rather a complex way on the conditions within the plasma.

A good deal of information is available on how the macroscopic properties of plasmas influence the efficiency of surface etching and other surface phenomena. However the individual processes which occur in the gas phase, and which combine to determine the macroscopic plasma properties, are often not well understood. Obviously it is very desirable to understand these individual reaction processes and to appreciate how their rates are influenced by other processes occurring in parallel and by the ambient plasma conditions, in order that conditions may be optimised to create the required plasma-surface interaction. Several distinct types of gas phase ionic reactions will usually be occurring simultaneously in practical discharge plasmas, including ion-molecule reactions, electron attachment, electron-ion recombination and ion-ion recombination. Via these reactions, new ionic and neutral species will be generated which may be the most surface active species within the plasma. Neutral-neutral reactions may also be important, but a discussion of these is beyond the scope of this review. Excellent reviews are available on this topic (see Ref.17 and others therein). Figure 1 is a block diagram of the major reaction types involving only charged particles which can occur in a discharge plasma. It shows the chemical evolution of the plasma following the establishment of a discharge through a gas mixture. Note the complex network of reactions which can occur following the creation of ions and electrons and which generate more reactive species (i.e. radicals, metastables, negative ions etc) and more complex (larger) species via clustering reactions and ion-ion recombination. Some of these individual reaction types will be briefly discussed in this review. The rates of the various processes are usually very dependent on the plasma conditions, i.e. the 'temperatures' of the species, the electron and ion number densities, the total gas pressure, the magnitude of impressed electric fields (e.g. the wall sheath field) etc. It is clearly essential to appreciate the sense and magnitude of such variations in predicting overall plasma properties.

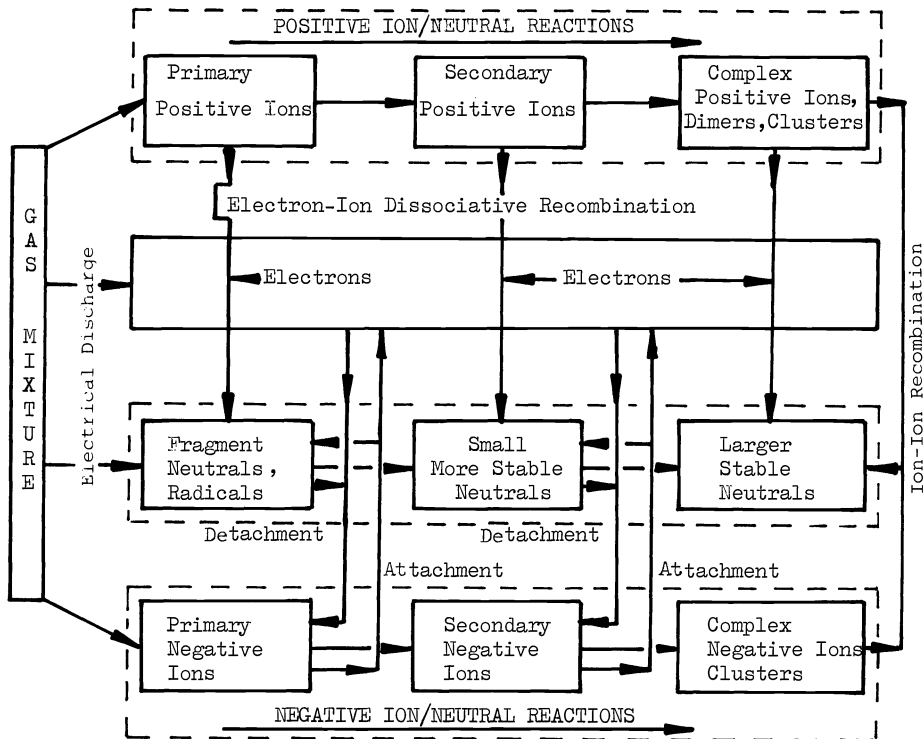


Fig.1 Chemical evolution following the creation of ionization in a gas mixture. Positive ions are generated by the primary process of collisional ionization and negative ions are generated largely by non-thermal and thermal dissociative electron attachment reactions. Reactions of the primary positive and negative ions with the abundant neutrals generate positive ions with smaller recombination energies and negative ions with larger electron detachment energies. Subsequent ion-neutral reactions can generate complex ions. Detachment reactions of negative ions can regenerate free electrons and a variety of neutral species. Electron-ion and ion-ion recombination act continuously to remove ionization and to generate both reactive (radical) and stable neutral species.

The time rate-of-change of the number density, $[n]$, of a plasma species can be described by a general continuity equation of the type:

$$\frac{d[n]}{dt} = \sum_i P_i - \sum_i L_i - D\nabla^2[n] \quad (1)$$

Production Rate
Loss Rate
Ambipolar Diffusion

Ambipolar diffusion of electrons and positive ions, and free diffusion of neutral species are always volume loss processes from active plasmas; note however, that negative ions are largely prevented from diffusing to the walls of the plasma container by the space charge wall sheaths. Clearly, an understanding of diffusion processes is very important in plasma-surface interaction studies but this also is outside the scope of this review (see Ref.18). Essential parameters in establishing the production and loss rates (P_i and L_i) due to individual reactions are their rate coefficients. A great deal of experimental work has been carried out during the last two decades to determine these coefficients and their temperature (and energy) dependences. In this review, we will discuss the essential results of these studies with specific examples, mentioning the major experimental techniques which have been used. In the following sections, we briefly discuss the individual types of reaction processes which can occur between charged and neutral species; details should be sought in the cited specialist papers and reviews.

ION-NEUTRAL REACTIONS

The rate coefficients and product ion distributions for thousands of ion-neutral reactions have been determined at or near room temperature using a variety of techniques, and a small but significant fraction of the total have been studied over appreciable temperature ranges. Both two-body (binary) reactions and three-body (ternary) association reactions are well characterised. The former reactions are usually quite exoergic and often result in more than one ion and neutral product, whilst the latter reactions are much less exoergic and result in a single 'cluster' ion product. We discuss these binary and ternary reactions separately.

Binary Reactions

These reactions, unlike neutral-neutral reactions, are usually very rapid especially at low temperatures (including room temperature) and low interaction energies. They are exemplified by



described by a rate equation of the kind $d[A^{\pm}]/dt = -k_2[A^{\pm}][B]$, where k_2 is the rate coefficient of the binary reaction. In the vast majority of these reactions, activation energy barriers do not exist; rather the opposite is true in that the ion-neutral pair are attracted to each other by an ion-dipole interaction. Hence most such reactions proceed at or near the collisional-limiting value described by the collisional rate coefficient, k_c , which is about $10^{-9} \text{cm}^3 \text{s}^{-1}$ for all reactions (Ref.19). For reactant molecules possessing large polarizabilities and/or large dipole moments, k_c will be several times this value, (Refs.20 & 21). The majority of the data have been obtained in the thermal energy regime (temperatures in the range 80-900K) using the flowing afterglow (FA; Refs.22 & 23) and selected ion flow tube (SIFT; Refs.24 & 25) techniques, and at near-thermal energies (~ 0.1 eV) using ion cyclotron resonance (ICR) techniques (Refs.26 & 27). Useful compilations of some FA and SIFT data (Ref.28) and some ICR data (Ref.29) are available. Many of the reactions studied were chosen because of their relevance to the ion chemistry of the atmosphere (Refs.1-3) and interstellar clouds (Refs.4-7). An appreciable amount of data is also available for many reactions on the variation of k_2 as a function of the ion-neutral centre-of-mass kinetic energy, E_{cm} . These data have been obtained up to E_{cm} values of a few electron volts using static drift tube (SDT) and flow drift tube (FDT) techniques (Refs.25 & 30).

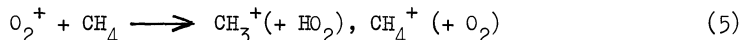
An important general observation on this class of reactions is that when they are rapid (i.e. when $k_2 \sim k_c$) then they usually do not change appreciably with reaction temperature, T , or E_{cm} (Refs.31-33). On the contrary, however, the k_2 for slow reactions usually do change with T and E_{cm} ; often k_2 first reduces with increasing T and E_{cm} , reaching a minimum and then increases towards the limiting value k_c . This feature is evident in many reactions (Ref.33), including the much studied reaction (Ref.34)



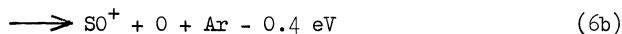
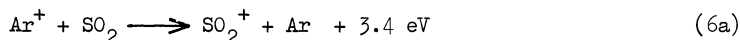
and the reaction of O_2^+ with CH_4 which at low T proceeds thus



but which at higher T and elevated E_{cm} proceeds predominantly thus:



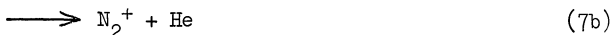
The detailed mechanisms of this reaction have been discussed in a recent paper (Ref.35). Clearly the additional energy, available as E_{cm} is increased, opens up additional, otherwise endoergic, channels. Another simpler example of this is in the reaction:



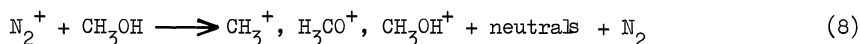
in which the endoergic channel (6b) is seen to appear at an E_{cm} close to 0.4 eV (Ref.36).

The few examples already given indicate the variety of binary reactions which can occur. We will now highlight some of the most common mechanisms including charge transfer, proton transfer, atom abstraction, molecular ion-atom reactions and associative detachment (only for negative ion reactions) and also briefly mention the reactions of internally excited ions and doubly charged ions.

Charge transfer can be dissociative or non-dissociative, e.g.



The small amount of excess energy in (7a) appears as kinetic energy in the product fragments, whereas the larger amount of excess energy in (7b) is partitioned between kinetic energy of both the N_2^+ and He and internal excitation of the N_2^+ (Ref.37). This product N_2^+ will therefore be very reactive (see later). When ions possessing large recombination energies charge transfer with polyatomic molecules, several product channels often result (Refs.38 & 39) e.g.

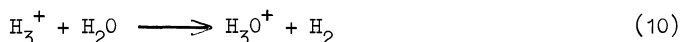


Again, the product ions and neutrals will usually be kinetically and internally excited and this will influence their reactivity in a plasma situation. Of course charge transfer is not limited to positive ions; negative ions also charge transfer (Ref.40) e.g.

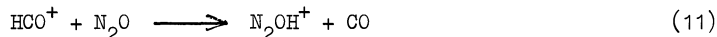


In these reactions, the product negative ion must necessarily possess a larger detachment energy than the primary ion. Hence the product ion is generally less reactive.

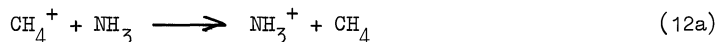
Proton transfer is invariably very rapid (i.e. $k_2 \sim k_2$) from species with small proton affinities (PA) to species with larger PA. Species with large PA include H_2O , NH_3 and most organic acids, alcohols, cyanides etc, and these will therefore usually appear in their protonated forms in ionized gases. Thus, the ions H_3O^+ , NH_4^+ , etc. are invariably present in plasma containing H_2O , NH_3 , etc, especially for example when the bulk gas is hydrogen since H_3^+ rapidly forms (via the reaction $H_2^+ + H_2 \longrightarrow H_3^+ + H$) which is a very effective proton donor e.g.



Detailed studies of proton transfer have been made using FA and SIFT (Refs.41-43) and ICR (Ref.44) techniques. These detailed studies have been used as a critical test of theories which predict values of k_c and how it varies with the dipole moments of reactant molecules (Refs.20 & 45). Some endoergic proton transfer reactions have been studied as a function of E_{cm} (Ref.46). They include the reaction :

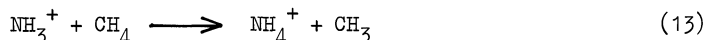


for which it has been shown that E_{cm} can initiate endoergic proton transfer. Often proton transfer is seen to compete favourably with charge transfer, e.g.

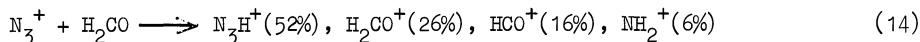


for which channel (12a) is favoured (60%) at 300 K (Ref.47).

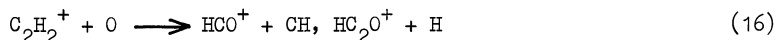
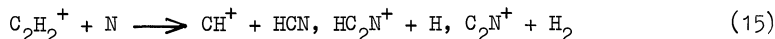
Atom abstraction is a very common mechanism. It is usually facile when the product ion has a stable closed shell e.g.



It is also commonly responsible for one of the products of multiple product rearrangement reactions (Refs.39 & 48) e.g.



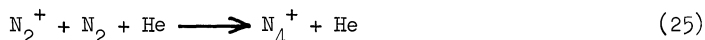
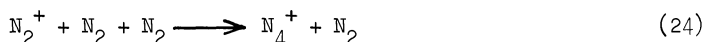
Molecular ion-atom reactions are of potential importance in discharge plasmas when the degree of collisional dissociation of molecules is relatively high, and when dissociative recombination (see later) generates appreciable concentrations of reactive atoms such as H, N, O etc. Atom reactions have not been studied to any great extent due to experimental difficulties in generating atoms in sufficiently large concentrations under controlled conditions. The available data show that these reactions can be very rapid (Refs.49-54). In reaction with hydrocarbon ions, N and O atoms have a great propensity to form the strongly bonded -CN and -CO groupings, e.g.



As is evident from these examples, branching into several product channels can occur producing several new ionic and neutral species, including other radicals. The study of atom reactions has often been directed towards atmospheric (Refs.49 & 52) and interstellar (Refs.51 & 53) chemistry. However, the importance of atoms in plasma etching is also well established (Refs.8, 11, 55) and clearly an understanding of their production and loss processes is very important in optimising plasma conditions for this process.



These reactions are envisaged to proceed via the formation of an excited intermediate complex $(A^{\pm} \cdot B)^*$ which can either decompose back to the reactants or suffer a collision with a third body, M, which removes sufficient energy to stabilise the AB^{\pm} ion. These reactions are described by a rate equation of the kind $d[A^{\pm}]/dt = -k_3[A^{\pm}][B][M]$, where k_3 is the rate coefficient for the ternary reaction. Clearly they will be promoted by high pressures (i.e. large number densities $[M]$) and, as numerous experiments have shown, by low temperatures according to power laws of the form $k_3 \propto T^{-n}$. Values of k_3 have been measured for many reactions, in some cases over appreciable temperature ranges (Refs.31,32,76). Ternary reactions are of major importance in atmospheric ion chemistry and so association reactions of N_2^+ , O_2^+ and NO^+ with atmospheric gases have received much attention. Notable amongst these reactions are the reactions of N_2^+ with N_2 , NO^+ with N_2 and O_2^+ with O_2 (Refs. 77-82). The reactions:

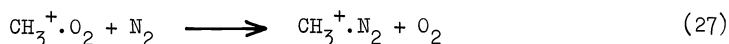


have been studied in great detail (Refs.81 & 82). k_3 for the N_2 stabilised reaction (24) is several times greater than that for the He stabilised reaction (25) within the thermal energy regime. Very recently, it has been shown that this is because stabilisation of the (N_4^+) excited intermediate complex in reaction (24) is by the rapid process of N_2 switching between the complex and the gas, and by the less efficient process of superelastic de-excitation in reaction (25) (Ref.83). The temperature dependences of k_3 for these two reactions are somewhat different as a result of these different stabilisation mechanisms ($k_3 \propto T^{-1.7}$ for reaction (24) and $\propto T^{-2.4}$ for reaction (25)). However, the temperature index n is approximately represented (in accordance with recent theoretical predictions, Refs.84-86) by $\ell/2$, where ℓ is the number of rotational degrees of freedom in the separated reactants (therefore $\ell/2 = (2 + 2)/2$ for these reactions). A detailed study of the association reactions of CH_3^+ ions has been carried out (Ref.80) in the context of a programme of measurements of reactions of interstellar interest (Refs.87 & 88). This study indicates that the measured n values are in good agreement with these recent theoretical predictions.

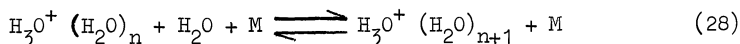
Some of the CH_3^+ association reactions are extremely fast, notably reactions involving polar molecules such as HCN and H_2O , e.g.



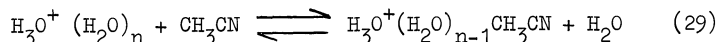
This reaction is so fast at 300 K that the effective binary rate coefficient $k_2^{eff} (= k_3[He])$ is close to the collisional rate coefficient, k_c (Ref.89). This suggests that the product ion is not a cluster ion of the type $CH_3^+ \cdot X$ as indicated, but that it is CH_4CN^+ , i.e. the more stable protonated CH_3CN . However, the ion formed in the CH_3^+ and O_2 association reaction is indeed a genuine cluster ion, since the ligand O_2 can be readily replaced by other molecules (Refs.35 & 90), viz:



Other genuine cluster ions include those in series such as NH_4^+ $(NH_3)_n$, $H_3O^+(H_2O)_n$ etc. They are formed in sequential ternary reactions:



In mixtures of gases, replacement of ligands in these cluster ions can occur (Refs.91 & 92) e.g.



The relative proportions of the various cluster ions, i.e. the equilibria in reactions such as (29), are of course determined by ΔH° , ΔS° and the temperature and pressures of the reactants in the usual way (Ref.91). Detailed discussion of many aspects of ternary association reactions including those involving negative ions and ligand replacement (switching) reactions, are given in Refs. 31, 32, 76.

ELECTRON-ION DISSOCIATIVE RECOMBINATION

Although the ion-molecule reactions discussed above can drastically modify the ionic composition of a plasma, they do not reduce the degree of ionization directly. Such can only result from the recombination of positively- and negatively-charged particles. In a plasma devoid of negative ions, the major de-ionization process is electron/positive ion neutralization either on the walls of the plasma container (following ambipolar diffusive

loss from the volume) or volume dissociative recombination of molecular positive ions with electrons, exemplified by the much-studied reaction:



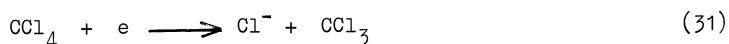
The loss of ionization by this process is described by the rate equation $d[\text{O}_2^+, e]/dt = \alpha_e \times [\text{O}_2^+] [e]$, where α_e is the dissociative recombination coefficient. The process is faster the larger the ionization density and indeed exercises a controlling influence on the degree of ionization. The neutral fragments are often radicals which may be both kinetically and electronically excited (as is the case for the oxygen atoms generated in reaction (30), Ref.93) and may therefore be very surface active.

Several groups have contributed to the measurement of α_e for many reactions (see Refs.94-96 for details). However, Biondi and his colleagues using their pulsed afterglow technique have made the major contribution (Refs.94,98-104). Other groups have measured cross-sections, σ_e , as a function of electron energy and derived α_e values (Refs.95 & 97). In general, it is found that α_e increases with the complexity of the recombining positive ion, although this is not a hard-and-fast rule (Ref.98). The α_e for reaction (30) has been determined most often, a consistent value of $2 \times 10^{-7} \text{cm}^3 \text{s}^{-1}$ being obtained at 300 K using a variety of techniques, including the recently developed flowing afterglow/Langmuir probe (FALP) technique (Ref.96). The temperature dependence of α_e for this reaction has also been determined and it is found to vary as $T^{-0.7}$ under truly thermal conditions (i.e. $T_e = T_+ = T$) within the temperature range 200 to 600 K (Ref.96, this relationship has recently been shown to be valid down to 80 K in FALP experiments) and as $T_e^{-0.7}$ up to a T_e of ~ 2000 K (for $T_+ = T = 300$ K; Refs.95 & 99). Inverse T and T_e dependences are the rule for relatively slow dissociative recombination reactions, indicating that they will be inhibited by the high electron temperatures which exist in some discharge plasmas. These experimentally determined temperature dependences are in general accord with theoretical predictions (Refs.94 & 105). The α_e at 300 K for the ions N_2^+ and NO^+ are similar to that for O_2^+ but the temperature variations are significantly different (i.e. $\alpha_e (\text{N}_2^+) \propto T^{-0.4}$, Refs.99 & 105; $\alpha_e (\text{NO}^+) \propto T^{-0.9}$, Ref.100).

As was mentioned previously, as the complexity of the recombining positive ion species increases, so also does the magnitude of α_e . For example, the α_e for 'dimer' ions $\text{N}_2^+ \cdot \text{N}_2$, $\text{O}_2^+ \cdot \text{O}_2$, $\text{NO}^+ \cdot \text{NO}$, and $\text{CO}^+ \cdot \text{CO}$ (Ref.98) are all about $10^{-6} \text{cm}^3 \text{s}^{-1}$ i.e. up to an order-of-magnitude larger than their 'monomer' counterparts. The dependences of α_e on T_e for these dimer ions have also been studied and found to be rather similar to each other (varying from about $T_e^{-0.3}$ to $T_e^{-0.5}$, Ref.101). The α_e for complex cluster ions in the series $\text{NH}_4^+(\text{NH}_3)_n$ and $\text{H}_3\text{O}^+(\text{H}_2\text{O})_n$ have also been determined (Refs.102-104). For the ammonia ions, α_e at 300 K increased from $1 \times 10^{-6} \text{cm}^3 \text{s}^{-1}$ for NH_4^+ to $3 \times 10^{-6} \text{cm}^3 \text{s}^{-1}$ for $\text{NH}_4^+(\text{NH}_3)_4$, and whereas $\alpha_e (\text{NH}_4^+)$ varied as $T^{-0.5}$, the α_e for the cluster ions varied only very slowly with T_e (Ref.103). For the water cluster ions, α_e ranged from $2.5 \times 10^{-6} \text{cm}^3 \text{s}^{-1}$ for $\text{H}_3\text{O}^+(\text{H}_2\text{O})$ to the large value of $\sim 5 \times 10^{-6} \text{cm}^3 \text{s}^{-1}$ for $\text{H}_3\text{O}^+(\text{H}_2\text{O})_4$. and no variation of α_e with T_e was apparent (Ref.104). A trend noticeable within the body of data for dissociative recombination is that the very fast reactions (those which perhaps proceed near to their limiting values) vary only slowly with T and T_e . This is rather similar to the rate coefficients (k_2) for binary ion-molecule reactions. Because of the very large values of α_e for cluster ions, their presence in plasmas can greatly influence the ionization density. However, the reactivity of the neutral products generated from their recombination will be low, because the recombination energies of cluster ions are relatively small and the ligands released in the process are usually stable (unreactive) molecules which are returned to the gas phase in their original form.

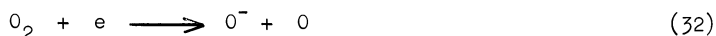
ELECTRON ATTACHMENT

In discharge plasmas containing electronegative gases such as the halogens and Freons (which are common constituents of etchant plasmas as sources of halogen atoms), then electron attachment occurs rapidly suppressing the free electron density and creating negative ions. This can drastically change both the electrical properties of the plasma and the relative importance of the various ionic reactions. For example, ion-ion recombination rather than electron-ion recombination may become the most important gas phase ionization loss process. Electron attachment is usually categorised as thermal or non-thermal and dissociated or non-dissociative. Thermal dissociative attachment is exemplified by the reaction:



since it occurs (very rapidly) at thermal energies and dissociation of the molecule occurs, producing a negative ion and a radical. Both of the products are kinetically excited possessing a total amount of energy equal to the difference between the electron affinity (EA) of Cl and the C-Cl bond dissociation energy (D_0) in CCl_4 . When $D_0 > \text{EA}$, then thermal dissociative attachment cannot occur and additional energy is required to initiate non-thermal dissociative attachment. This is the case for many molecules for which non-thermal

dissociative attachment occurs at elevated electron energies, e.g.



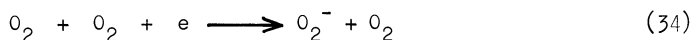
The threshold energy for this reaction is 4.5 eV and a peak in the cross section for the process, σ_a , occurs at an electron energy of 6.7 eV. Peaks in σ_a are a common feature of non-thermal dissociative attachment reactions, and are usually within the electron energy range from a few tenths of an eV to several eV (Ref.106). The rate coefficients, β , for thermal attachment reactions can however be measured directly. An appropriate rate equation for these reactions which defines β is $d[e]/dt = \beta[e][M]$, where $[M]$ is the attaching gas number density. The β have been measured for a large number of gases using a variety of techniques. The theory of electron attachment and much of the earlier experimental work is reviewed in the book by Massey (Ref.107) and a considerable amount of early data is given in the reviews by Christophorou (Refs.106 & 108). More recent work is reported in (Refs.109-111). Measurements show that β for thermal attachment reactions involving ostensibly similar molecules can differ by several orders-of-magnitude. For example, the β at 300 K for CCl_4 (reaction (31)) is $4 \times 10^{-7} \text{ cm}^2 \text{ s}^{-1}$ (Refs.109,111), i.e. close to the theoretical upper limit of $5 \times 10^{-7} (300/T)^{0.5} \text{ cm}^2 \text{ s}^{-1}$ (Ref.112), whereas for CF_3Cl , β is $7 \times 10^{-14} \text{ cm}^2 \text{ s}^{-1}$ at 300 K (Ref.113). For the very rapid thermal attachment reactions, β usually decreases with increasing temperature and σ_a decreases with increasing electron energy (Refs.111, 114-117). However for the slower reactions β is often observed to increase dramatically with increasing temperature (Refs.111,115, 118); for example the β for CCl_2F_2 and CHCl_3 increase by more than an order-of-magnitude for a temperature increase from 200 to 600 K, as a recent FALP study has indicated (Ref.111). This phenomenon is attributed to the existence of activation energy barriers in the reactions which control the rate of their exoergic reactions. Such barriers occur because the negative ion-radical repulsive curve does not cross the neutral (molecular) curve at its minimum but rather at a higher energy point within the vibrational/rotational manifold (Ref.118). Thus the internal excitation of the molecule which occurs at higher temperatures effectively removes the energy barrier and promotes the attachment reaction. Energy in the free electron is not so effective because of the usually small Franck-Condon factors associated with the vertical transitions necessary to access the repulsive curve. In fact, elevated electron energies often reduce the σ_a (and β) (Refs. 106, 116), which is an important consideration in some discharge plasmas.

A particularly interesting reaction which has received much attention is:



At 300 K, SF_6^- is the only observed product and it is known that on production, the $(\text{SF}_6^-)^*$ is metastable with respect to electron ejection and can be stabilised in collisions with atoms or molecules. Thus, production of the stable SF_6^- ion in collision-dominated experiments, is a non-dissociative, ternary attachment process, whereas $\text{SF}_5^- + \text{F}$ production (channel (33b)) is binary dissociative attachment which becomes relatively more important at higher temperatures. The increasing importance of channel (33b) with increasing temperature is attributed to an activation energy barrier of magnitude 0.43 eV (Refs.111, 119). The overall β for reaction (33) is very large and there is some evidence for a maximum ($\beta_{\text{max}} = 4.8 \times 10^{-7} \text{ cm}^2 \text{ s}^{-1}$) between 400 and 500 K. This is probably a manifestation of the sharp resonance in the attachment cross section at very low electron energies (Refs.106, 120). It is also evident from attachment studies at high temperatures that β for SF_6 decreases rather quickly with increasing temperature until above 2000 K, SF_6 is rather a poor electron scavenger (Ref.121). Paradoxically, the analogous tungsten hexafluoride, WF_6 , does not attach thermal electrons ($\beta < 10^{-11} \text{ cm}^2 \text{ s}^{-1}$, as indicated from a recent FALP study) but above ~ 2000 K it is a better electron scavenger than SF_6 . (Ref 121).

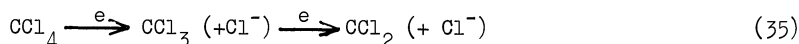
Other ternary electron attachment reactions are well characterised (Ref.122) e.g.



These reactions are relatively slow except at high pressures and generally result in negative ions with small detachment energies. In the presence of electronegative species therefore, they will generally undergo charge transfer (i.e. in reactions such as (9)). Reaction (34) is very important in the stratosphere since it initiates much of the negative ion chemistry (Refs.1,2).

The wide variations in the β for electron attachment reactions makes it mandatory that each reaction be considered in the context of the medium in which it is occurring. Some reactions are promoted and others are inhibited by high temperatures. What is certain is that when they occur they can profoundly influence the plasma. The negative ions that are formed will be trapped within the plasma by space charge fields and can then undergo ion-ion recombination (see below) or be destroyed in associative detachment reactions. The neutral radicals formed in attachment reactions will however often be able to reach the

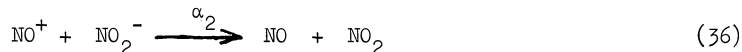
container walls and be very active there. Finally it is interesting to note that in reactions such as



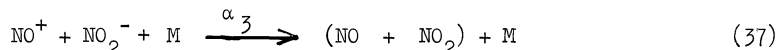
more than one radical may be produced from a single molecule in sequential reactions (Ref.111).

ION-ION RECOMBINATION

Ion-Ion (or ionic) recombination is the general term used to describe the neutralization of positive ions by negative ions producing neutral particles. There are two distinct mechanisms, the binary process of mutual neutralization, e.g.



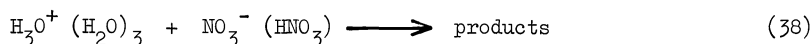
and the ternary process, e.g.



In the mutual neutralization process, the electron is transferred from the negative ion to the positive ion at a pseudocrossing of the reactant/product potential curves and the reaction energy appears as both kinetic and internal energy of the separating neutrals (Refs. 123 & 124). In fact, for reaction (36), it has shown that at thermal interaction energies, the energy released largely appears as electronic excitation of the NO (Ref.125). In the ternary process, the reaction energy is carried away, at least in part, by the third body M (as kinetic and/or internal energy), and as indicated the neutral product may be a compound molecule. It must be stated at the onset that little is known about the products of any but the simplest ionic recombination reactions (Refs. 124 & 126).

Both experimental and theoretical studies of ionic recombination have a long history (Refs. 127 & 128). The early experimental work was concerned with studies of the ternary process which is the dominant ionization loss process in high pressure electronegative gases. This process is recognised by an increasing effective binary rate coefficient, α_2^{eff} , with increasing pressure, [M]. Hence, a ternary recombination coefficient, α_3 , can be defined by $\alpha_2^{\text{eff}} = \alpha_3[\text{M}]$, and the appropriate rate equation is $d[\text{A}^+, \text{B}^-]/dt = -\alpha_2^{\text{eff}}[\text{A}^+][\text{B}^-]$ (the α_2 for the binary process is defined similarly). The magnitude of α_2^{eff} is relatively insensitive to the nature of the reactant ions and of the third body, varying from about $10^{-7} \text{cm}^3 \text{s}^{-1}$ at low pressures to a maximum of about $10^{-6} \text{cm}^3 \text{s}^{-1}$ for pressures within the range 0.1 to 1 atmosphere (Ref.129). These results are in general accord with theoretical predictions (Ref.128) which also predict a rather rapid inverse temperature dependence for the efficiency of the process ($\sim T^{-3}$), although there is very little experimental data with which to test this prediction (Ref.127). It must be said that in none of the early measurements of α_2^{eff} was the nature of the ions actually determined by mass analysis, but it is highly probable that with the poor vacuum techniques available and at the ambient high pressures, the reactant ions were most probably cluster ions. This was certainly the case for the recent measurements of α_2^{eff} in high pressures of NH_3 and H_2O (Ref.130) and SF_6 (Ref.131). Other experiments under 'cleaner' conditions do indicate some variation of α_2^{eff} with the nature of reactant ions and the third body gas (Refs.132 & 133). It is interesting to note that ternary ionic recombination dominates the loss of ionization in the Earth's lower atmosphere (Refs.133 & 134).

At low pressures, ionic recombination is only via the binary process. Until the advent of the merged beam technique, little was known about this process but, following the development of this technique, a good deal of data relating to the cross sections for mutual neutralization for a variety of ions was obtained for centre-of-mass energies, E_{cm} from about 0.1eV to 200 eV (Ref.124). From the cross section data at low E_{cm} thermal energy rate coefficients, α_2 , were estimated. The α_2 obtained by this procedure for reaction (36) was more than an order-of-magnitude larger than theory predicted (Ref.123). This discrepancy is almost certainly related to the difficulty of defining E_{cm} at low energies in merged beam experiments. Subsequently, the first reliable survey of mutual neutralization reactions under truly thermal conditions was made using the FALP technique (Refs.126 & 135). The α_2 values at 300 K for many reactions have been shown to be $\sim 5 \times 10^{-8} \text{cm}^3 \text{s}^{-1}$ which is close to the theoretical predictions for simple ions (Ref.123) and, somewhat surprisingly, almost independent of the complexity of the positive and/or negative ions. Thus for reaction (36), $\alpha_2 = 6.4 \times 10^{-8} \text{cm}^3 \text{s}^{-1}$ and for the cluster ion reaction:



$\alpha_2 = 5.7 \times 10^{-8} \text{cm}^3 \text{s}^{-1}$. Clearly, these α_2 are much smaller than typical electron recombination coefficients, especially those for cluster ion reactions. Therefore the conversion of electrons to negative ions in a plasma will act to reduce the rate of loss of ionization. A study of the temperature dependence of α_2 for reaction (36) has shown that

it varies as $T^{-\frac{1}{2}}$ in accordance with theory (Refs.134 & 135).

As mentioned before, the neutral products of these neutralization reactions involving complex ions cannot often be predicted with confidence. However, it is certain that they will introduce new species, often radicals, into a plasma. For example, in the reactions of any molecular positive ion with halide ions (e.g. F^+ , Cl^-) the corresponding halogen atoms are very likely to be produced which, unlike their parent negative ions, can diffuse to the container walls. Finally, it is interesting to consider the reaction of a large cluster positive ion with a large cluster negative ion, e.g.



Here the possibility arises that the detachment energy of the negative ion will exceed the recombination energy of the positive ion. Then electron transfer will be endoergic and a coalescence of the two ions is possible generating a large neutral species (perhaps a 'zwitterion' and perhaps initiating polymerization). This process has been invoked as a possible starting point for the production of aerosols in the lower atmosphere (Ref.136).

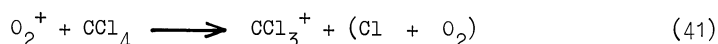
SUMMARY

Having discussed the individual ionic reaction processes, it is perhaps instructive to consider how these processes, occurring sequentially and in parallel, combine to influence the bulk properties of a plasma. This is a problem of much greater magnitude than the understanding of individual reactions. In a real plasma situation, a large number of reactions will generally be occurring, the rate coefficients for which (even if all of the reactions could be identified) would not all be known for the specific conditions of temperature, pressure etc. However, as a beginning, the "typical values" for k_2 , k_3 , α_e , α_2 referred to in the preceding sections can be used, permitting, the most important processes to be identified. Following this, specific rate coefficients could then be measured accurately in experiments specifically designed for this purpose.

To conclude this short review, we present a brief (and undoubtedly oversimplified) case study of a simple discharge plasma situation as an illustrative summary of the reaction processes which may contribute to bulk plasma ion chemistry. No discussion is given of the parallel neutral chemistry which must undoubtedly occur. For our example, we have chosen a discharge plasma created in an O_2/CCl_4 mixture since this has been used as an etchant for some metal (Ref.9) and semiconductor (Ref.8) surfaces. Figure 2 summarises the ion chemistry. As can be seen primary ionization in the discharge creates several positive ion species, including O^+ , O_2^+ and fragment ions of CCl_4 such as CCl_2^+ , CCl_3^+ , and negative ions O^- and Cl^- are produced in thermal and non-thermal dissociative attachment reactions with the O_2 and CCl_4 . A variety of neutral radicals (e.g. O , CCl_3) are also produced both by the direct dissociation of the O_2 and CCl_4 and in the attachment reactions. If the pressure is sufficiently high, then O_2^- can also be formed by ternary attachment. Now many more reactions can occur; which reactions are dominant depends on such parameters as the O_2/CCl_4 ratio, the ionization density and the temperature. When $[O_2] \gg [CCl_4]$, then the O^+ is rapidly converted to O_2^+ :



The O_2^+ can then react with the CCl_4 thus



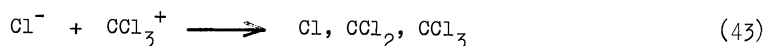
When $[CCl_4] \gg [O_2]$, then the primary, O^+ , CCl^+ and CCl_2^+ will react directly with CCl_4 finally producing CCl_3^+ . At sufficiently high pressures, ion clusters might be produced such as $O_2^+ \cdot O_2$ and $CCl_3^+ (CCl_4)_n$ although at high temperatures these probably cannot be formed. In parallel with these ion molecule reactions, recombination processes will be occurring. Dissociative recombination will most effectively remove the more complex positive ions, since the α_e are much larger for these species, and therefore this will favour the smaller ions as major plasma constituents. By this process reactive neutrals (radicals) are generated as indicated in Fig.2.

It seems certain that Cl^- will be the major negative ion species in the plasma since it is relatively unreactive. However, it can undergo associative detachment with the chlorine atoms which will probably be present in abundance:



The Cl_2 generated in this process can react with the O^- and O_2^- producing Cl_2^- (although O_2^- can also be rapidly destroyed in charge transfer reactions with oxygen atoms which must also be present). If the Cl^- number density is sufficiently large (and it should be remembered that diffusive loss of negative ions will be slow), then ion-ion recombination

with the ambient positive ions can occur, e.g.



This represents another route for the production of Cl atoms.

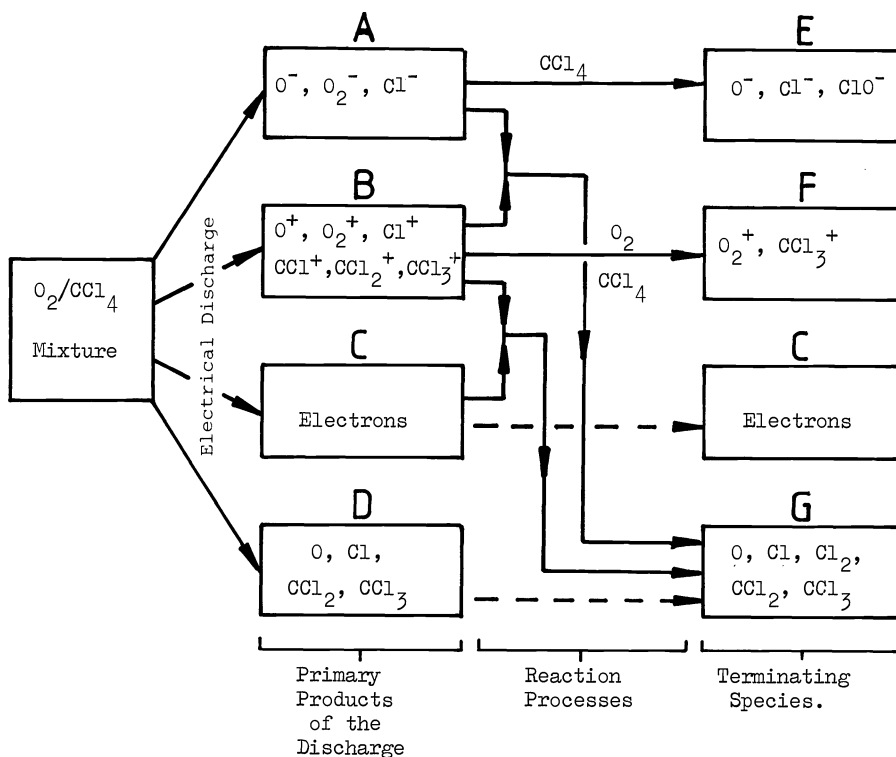


Fig.2 Some reactions which can occur when an electrical discharge is passed through a mixture of O_2 and CCl_4 . These include: ion-ion neutralization (Box A+Box B), electron-ion recombination (Box B+Box C), negative ion reactions with O_2 and CCl_4 (Box A \rightarrow Box E) and positive ion reactions with O_2 and CCl_4 (Box B \rightarrow Box F). Not indicated, to avoid confusion on the diagram, are associative detachment reactions which can occur between negative ions and neutral radicals (Box A+Box D); for example, the Cl_2 in Box G is formed via the associative detachment reaction (42) given in the text. The terminating species include some of the primary species created in the discharge and others formed in subsequent reactions. These terminating species could be expected to be present in appreciable concentrations in the plasma.

We conclude this brief review of elementary processes on an optimistic note. A rapid development of plasma diagnostic techniques, and of techniques with which individual reaction processes can be studied, has taken place in recent years. This will surely lead to a rapid advancement in the understanding of the chemistry of complex plasma media. Whilst much of the motivation results from technological needs, scientific curiosity can also be satisfied by studying this very interesting subject.

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