



Gas phase ion-ion recombination and electron capture reactions at atmospheric pressure
by John Allen Culbertson

A thesis submitted in partial fulfillment of the requirements for the degree of Doctor of Philosophy in
Chemistry

Montana State University

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Abstract:

Gas phase ion processes at high pressure (one atmosphere) are the basis of some of the most sensitive and selective analytical techniques for chemical analysis, ie. the electron capture detector (ECD), the atmospheric pressure ionization mass spectrometer (APIMS), and the ion mobility spectrometer. Under most conditions, ion-ion recombination (IIR) will be the dominant loss mechanism for ions in high pressure ionized gases. Therefore, it is of fundamental importance to understand IIR. In this thesis work, relative IIR rate constants were determined using an APIMS. Also, a new method was developed for the determination of the fate of molecular anions upon recombination with positive ions at atmospheric pressure. These results were used to predict the atmospheric chemistry of certain perfluorocompounds (PFC's). This method also proved to be effective for determining the electron capture (EC) rate constants of compounds that undergo dissociative EC.

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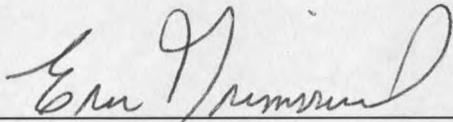
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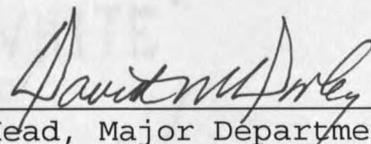
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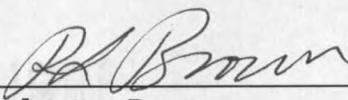
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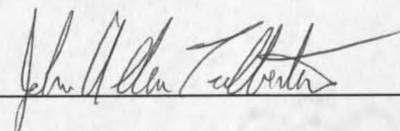
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ABSTRACT

Gas phase ion processes at high pressure (one atmosphere) are the basis of some of the most sensitive and selective analytical techniques for chemical analysis, ie. the electron capture detector (ECD), the atmospheric pressure ionization mass spectrometer (APIMS), and the ion mobility spectrometer. Under most conditions, ion-ion recombination (IIR) will be the dominant loss mechanism for ions in high pressure ionized gases. Therefore, it is of fundamental importance to understand IIR. In this thesis work, relative IIR rate constants were determined using an APIMS. Also, a new method was developed for the determination of the fate of molecular anions upon recombination with positive ions at atmospheric pressure. These results were used to predict the atmospheric chemistry of certain perfluorocompounds (PFC's). This method also proved to be effective for determining the electron capture (EC) rate constants of compounds that undergo dissociative EC.

The APIMS showed that for all ions studied, the IIR rate constant was the same, approximately $2 \times 10^{-6} \text{ cm}^3 \text{ sec}^{-1}$. The experimental apparatus developed for the determination of the fate of molecular anion upon IIR allowed for the comparison of two ECD responses for the compound being studied. The first was a normal ECD response. The second ECD response was obtained after the gas chromatographic carrier gas was passed through a reaction cell in which EC and IIR reactions occurred. The ratio of these two responses was interpreted in terms of the extent to which the molecule was lost to EC and then regenerated by IIR. The conclusions were that the molecular anions of C_7F_{14} (perfluoromethylcyclohexane) and C_6F_{12} (perfluorodimethylcyclobutane) regenerate their parent neutrals upon IIR while the molecular anion of SF_6 does not. The molecular anions of nitrobenzene and several substituted nitrobenzenes were also studied and showed varying extents of regeneration. The same experimental procedure was also used to determine EC rate constants for compounds that could not be regenerated by IIR.

INTRODUCTION

Gas Phase Ion Chemistry

During the past 25 years, gas phase ion chemistry (GPIC) has been a steadily growing research field (1), (2), (3). This is due in part to the fact that the intrinsic properties of ions and molecules are best studied in the gas phase, where solvent effects can be eliminated or carefully controlled. Also, some of the most selective and sensitive analytical techniques for chemical analysis are based upon GPIC. Such techniques include ion cyclotron resonance (ICR) mass spectrometry (MS) (4), chemical ionization (CI) MS (5), electron capture detection (ECD) (6), atmospheric pressure ionization (API) MS (7), ion mobility spectrometry (IMS) (8), and electrospray MS (9). These techniques operate over a wide pressure range, from 10^{-5} - 10^{-6} Torr for ICR, to 0.1 - 0.5 Torr for CIMS, to atmospheric pressure for ECD, APIMS, IMS, and electrospray MS. In spite of this wide pressure range, most of the instrumentation used to study the fundamentals of GPIC operate at less than 10 Torr. Such instruments typically employ a mass spectrometer to select and measure the ions of

interest. These MS-based instruments include ICR, flowing afterglow (10), selected ion flow tube (10), and pulsed electron high pressure MS (11), all of which have contributed significantly to the wealth of valuable GPIC information that exists at lower pressures. In contrast, studies of GPIC at pressures greater than 10 Torr are very few, due mainly to the lack of capable instrumentation in the past. However, there is a clear need to understand high pressure GPIC processes in order to increase the performance of analytical instruments that operate at or near atmospheric pressure (such as the ones listed above), thoroughly interpret the results obtained from such instruments, or to design new high pressure instrumentation. In addition, gas phase processes at low pressure are often significantly different from those at high pressure. Thus, predictions of GPIC at high pressure based on low pressure results often fail. This basic lack of knowledge of high pressure gas phase processes was the motivation for this thesis work. Two processes in particular, ion-ion recombination (IIR) and electron capture (EC), are the focus of this work and are discussed below.

Electron Capture

Several of the most selective and sensitive techniques for chemical analysis are based on the electron capture process. The most widely used of these, and the one used for a great deal of this thesis work, is the electron capture detector. The first description of the ECD was by Lovelock (12) in 1960. While the modern ECD is quite different from the first ones described by Lovelock, the fundamental characteristics are similar.

The ECD is very selective in that only molecules with positive electron affinities and sufficiently large electron capture cross sections are detected, which comprise a small minority of compounds. A molecule meeting these criteria may attach a low energy electron to form a molecular anion (resonance capture) or a fragment anion (dissociative capture). The mechanism of the electron capture process is discussed in the Theory section.

The ECD response is based on changes in the electron population within the detector. In most ECD's, electrons are collected at an anode that is pulsed at approximately +50 volts. The resulting current is then measured and maintained

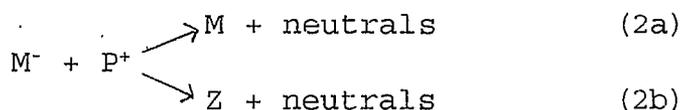
at some fixed value by adjusting the pulse frequency, thus the term, constant current ECD is used. When a compound that attaches electrons enters the detector, the electron population decreases, causing an increase in the pulse frequency. The response at the chart recorder is proportional to the change in pulse frequency. In other ECD's, such as the dual cell ECD used in this work, the anode is pulsed at a fixed frequency. Thus, a change in electron population results in a change in the current measured at the anode. This type of ECD is well suited for fundamental studies in that the dynamics of the ECD can be changed by adjusting the pulse frequency and/or pulse width.

Ion-Ion Recombination

The dominant loss mechanism for ions in most high pressure ionized gases is ion-ion recombination. Diffusion of ions to grounded surfaces or removal by carrier gas flow is typically much slower than IIR (13). For this reason, IIR is a very important reaction within the ECD, and the products of the IIR reaction may influence the ECD response to certain compounds.

Consider the following reaction sequence which can occur

within the ECD.



Reaction 1 is resonance electron capture by which the molecular anion, M^- , is formed. Reactions 2a/b represent the two possible pathways of the subsequent IIR between the molecular anion and positive ions. In reaction 2a, IIR results in the regeneration of the parent molecule, M , while in reaction 2b the parent molecular entity has been altered upon IIR. If the parent molecule is regenerated, it may undergo additional EC/IIR reactions. This will result in an enhanced response to that compound relative to the case in which altered neutrals are formed upon IIR (Reaction 2b). This type of behavior can give anomalous responses in gas phase coulometry (14) experiments and may also have important implications to the atmospheric chemistry of perfluorinated compounds (15), which is discussed below.

Atmospheric Fates of Perfluoro Compounds

Fully fluorinated compounds (perfluoro compounds or PFC's) represent a class of chemicals which include many

species that exhibit extreme inertness to chemical and photochemical reactions. This results in most PFC's being immune to the processes that typically remove trace chemicals from the atmosphere, ie., photodissociation and reaction with radicals (15). Therefore, PFC's may be transported through the troposphere (the first 15 km of the atmosphere) and stratosphere (15 to 50 km), to the mesosphere (50 to 90 km). Only in the mesosphere are important destructive processes for PFC's thought to exist. These destructive processes include absorption of Lyman- α radiation (121.6 nm) and reaction with free electrons. The latter means of destruction can potentially be more important than photolytic destruction for those PFC's that have relatively large EC rate constants. These EC active compounds are known to include SF₆ (16), c-C₄F₈ (15), and larger cyclic carbon based PFC's, such as C₇F₁₄ (perfluoromethylcyclohexane) (17), and C₁₀F₁₈ (perfluorodecaline) (18). Furthermore, it is known that these molecules capture thermalized electrons primarily by the resonance EC process (Reaction 1) in which the molecular anion is formed. Therefore, in determining the atmospheric chemistry of these EC active PFC's, the critical question is: what will be the neutral products formed in the subsequent recombination

of these molecular anions with positive ions, as represented in Reactions 2a/b. If the original molecule is simply regenerated in these IIR reactions, as in pathway 2a, the sequential EC/IIR reactions will have no impact on the overall atmospheric chemistry of that compound. If, on the other hand, the molecular entity is altered by the IIR reaction, as shown in pathway 2b, the atmospheric presence of that compound will be terminated by its EC reaction.

Because PFC's are not believed to destroy stratospheric ozone, they were considered environmentally friendly, and some were thus suggested as replacements for the ozone depleting chlorofluoro compounds (15). However, PFC's are expected to have extraordinarily long atmospheric lifetimes (on the order of millennia) due to their chemical and photolytic inertness, and thus significant global warming potentials (GWP) (15). The GWP is a measure of the relative efficiency of a gas to contribute to global warming (the greenhouse effect) by absorption of infrared radiation, per kilogram emitted (15). Therefore, even if relatively small amounts of PFC's are emitted into the Earth's atmosphere, they would accumulate over time and their impact could be very significant in future years.

Morris et al.(15) have predicted that for some PFC's which attach electrons rapidly, the EC/IIR process could account for at least 90% of their removal in the mesosphere if the molecule is, in fact, destroyed by its sequence of EC and IIR reactions. Based on this fact, it is clear that the need to know whether or not a PFC is regenerated upon IIR, as in Reaction 2a, is of central importance. Therefore, this thesis will focus on the fractional regeneration of several PFC's upon IIR at near atmospheric pressure. Work was also performed to determine what effects the nature of the recombining ions has on the rate constant for IIR. The same experimental apparatus used for determining the fractional regeneration of PFC's was also proven to be a very effective method for determining EC rate constants for dissociatively attaching compounds. EC rate constant for many such compounds were determined for the first time in an atmospheric pressure buffer gas.

THEORY

Chemistry and Dynamics Within the
Reaction Cell/ECD

As was mentioned in the Introduction, the chemistry and dynamics of gas phase processes at or near atmospheric pressure are quite different from those at low pressure. Therefore, in order to characterize the reaction cell/ECD apparatus, these processes must be understood.

The increased gas density at atmospheric pressure results in a shorter mean free path and therefore a greater collision frequency, f , between molecules. This is the fundamental difference between the high and low pressure regimes. A value for f can be obtained at any given pressure by Equation 3,

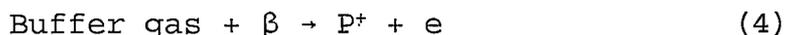
$$f = \bar{v}\sigma\sqrt{2}\frac{N}{V} \quad (3)$$

where \bar{v} is the relative mean velocity of the molecule, σ is the collision cross section, and N/V is the gas number density. A value for σ can be obtained from $\sigma=\pi d^2$ where d is the collision diameter of the molecule (19). For N_2 ($d =$

$3.7 \times 10^{-10} \text{m}$) (19) at 640 Torr and 120°C , $f = 5.2 \times 10^9 \text{ sec}^{-1}$. However, in the low pressure regime where techniques such as PHPMS and ICR are often employed to study GPIC, collision frequencies are much smaller. For example, in an ICR cell operating at 10^{-5} torr, f is approximately 100 sec^{-1} .

The high collision frequency at atmospheric pressure serves to stabilize any excited ions or molecules that are within the cell and quickly bring them to thermal equilibrium with the buffer gas. This is important because species with excess internal energy are often formed from the ionization process or other energetic reactions. Under most experimental conditions encountered at atmospheric pressure, any excited species will be thermalized in 10 collisions and a Maxwell-Boltzmann energy distribution will be achieved in about 100 collisions with the buffer gas (20).

All chemistry occurring in the reaction cell is initiated by Reaction 4, in which a beta particle, β , from a ^{63}Ni foil



collides with a buffer gas molecule to produce a positive ion, P^+ , and a secondary electron. The average kinetic energy of the beta particle is 17 keV (13) and approximately 35 eV is required to produce one P^+/e pair (21), therefore, 458 P^+/e

pairs are formed per beta. The secondary electrons are thermalized by subsequent collisions with the buffer gas. The rate of change in positive ion or electron concentration in the cell with no sample present is given by Equation 5 (22),

$$\frac{dn_e}{dt} = \frac{dn_+}{dt} = \frac{S}{V} - Rn_e n_+ \quad (5)$$

where n_e and n_+ are the electron and positive ion densities respectively, S is the production rate of electrons governed by the activity of the ^{63}Ni foil, R is the positive ion-electron recombination rate constant, and V is the volume of the cell. Applying the steady state assumption to Equation 5, the equilibrium concentration for n_e and n_+ can be calculated from Equation 6.

$$n_e = n_+ = \sqrt{\frac{S}{VR}} \quad (6)$$

With a volume of 1.5 cm^3 , R given as $3 \times 10^{-6} \text{ cm}^3 \text{ sec}^{-1}$ (23), and a 13 mCi foil ($4.8 \times 10^8 \text{ disint sec}^{-1}$), the electron density is calculated to be $1.4 \times 10^8 \text{ cm}^{-3}$. For all experiments in which the reaction cell was used, the electron density in the cell was determined experimentally using a reference compound whose electron capture rate constant is well known. This procedure will be discussed in detail in the

Results and Discussion section.

The thermalized electrons can interact with species present in the cell via Reactions 7-9.



Positive ion-electron recombination, Reaction 7, was discussed above in describing electron and ion densities. Reactions 8 and 9 are resonance and dissociative electron capture, respectively. Resonance EC results in a molecular anion, while a fragment atomic anion is produced from dissociative EC. Electron capture will occur when a molecule with a sufficiently large electron attachment cross section enters the cell. An excited intermediate negative ion, MX^* , is initially formed upon EC. The reaction will proceed to completion forming a stable anion only if MX^* is sufficiently long lived so that either the excess internal energy can be quenched through collisions to form a thermalized molecular anion or bond rupture can occur to produce a fragment anion.

The negative ions within the cell will be destroyed by ion-ion recombination, shown in reactions 2a/b. IIR will be discussed in detail in the following section. Two other

possible loss mechanisms for negative ions are ventilation out of the cell via carrier gas flow and diffusion to the wall of the cell resulting in charge neutralization. Both are considered negligible for the reasons described below.

Ventilation

The first order rate constant for ventilation, k_v , is given by Equation 10, where F is the flow rate of the carrier

$$k_v = F/V \quad (10)$$

gas in $\text{cm}^3 \text{sec}^{-1}$ and V is the volume of the cell. With a typical flow rate of $0.34 \text{ cm}^3 \text{sec}^{-1}$ and a cell volume of 1.5 cm^3 , $k_v = 0.22 \text{ sec}^{-1}$. The rate of loss due to IIR, is given by Equation 11.

$$\text{Rate}_{\text{IIR}} = -k_{\text{IIR}} [\text{P}^+] [\text{N}^-] \quad (11)$$

The concentrations of positive and negative ions are given by $[\text{P}^+]$ and $[\text{N}^-]$ respectively. Under the experimental conditions used here, the positive ion concentration is in large excess and constant, thus, pseudo first order kinetics apply and Equation 11 can be rewritten as follows:

$$\text{Rate}_{\text{IIR}} = -k'_{\text{IIR}} [\text{N}^-] \quad (12)$$

where $k_{\text{obs}} = k_{\text{IIR}} [P^+]$. Using a k_{IIR} value of $2 \times 10^{-6} \text{ cm}^3 \text{ sec}^{-1}$ (24) and $[P^+]$ of $1.2 \times 10^7 \text{ cm}^{-3}$, determined from Equation 6, $k'_{\text{IIR}} = 24 \text{ sec}^{-1}$. As can be seen, k_{obs} for IIR is approximately two orders of magnitude larger than k_v , hence ventilation is not considered important loss mechanism relative to recombination.

Diffusion

At charge densities of approximately 10^7 cm^{-3} and above, the interaction between positive and negative charge clouds becomes sufficiently strong that the gas must be treated as a plasma, with local charge neutrality being the rule (13). Any deviation from charge neutrality induces electric fields that oppose the charge separation and tend to restore charge balance. Because the diffusion of electrons is approximately 1000 times faster than that of positive ions, there is a space charge potential that develops as the electrons attempt to diffuse to areas of lower concentration, the grounded surface of the cell wall in this case. An area of negative charge develops near the cell wall, while an area of positive charge develops in the interior of the cell volume. These space charges greatly restrain the motion of electrons towards the cell wall but have the opposite effect on the positive ions,

causing them to diffuse at about twice as fast as they would in the absence of electrons (25). Consequently, the electrons and positive ions diffuse at the same velocity and can be characterized by a single ambipolar diffusion coefficient.

The charge density in the reaction cell used in this work was typically on the order of $1 \times 10^7 \text{ cm}^{-3}$, therefore ambipolar diffusion conditions were operative. When an EC active compound was introduced into the cell, its concentration was kept sufficiently low so that electrons were in large excess of the negative ions produced from EC. Under these conditions, diffusion of negative ions to the wall of the cell is probably prohibited by the space charge described in the preceding paragraph. Thus, diffusional loss of negative ions can most likely be discounted. However, if the negative ions do diffuse to the walls as rapidly as the positive ions and electrons, the first order rate constant for that process will be given by $k_d = D_a/\Lambda^2$ (25), where D_a is the ambipolar diffusion coefficient ($D_a = 2D$, where D is the free diffusion coefficient for the ion) for the ions and electrons and Λ is the characteristic diffusion length of the ion source (25). The free diffusion coefficient can be calculated (26) using the general expression $D = 3.33 \times 10^{-3} T^2/P(\alpha M_r)^{1/2}$, where T is

temperature ($^{\circ}\text{K}$), P is pressure (Torr), α is the polarizability of the buffer gas molecule (\AA^3), and M_r is the reduced mass of the ion and buffer gas. For an ion of 100 amu in nitrogen at 393 K and 640 Torr (α for $\text{N}_2 = 1.73 \text{\AA}^3$ (19)), a value for D_a of $0.24 \text{ cm}^2 \text{ sec}^{-1}$ is obtained. Λ may be calculated by dividing the radius of the cell (0.4 cm) by π to give 0.13 cm. Therefore, the first order rate constant for diffusion of negative ions (equal to that of positive ions) would be approximately 14 sec^{-1} . Thus, even if negative ions do diffuse at the same rate as positive ions, k'_{IIR} is still about twice as large as k_d .

Ion-Ion Recombination

J.J. Thomson and E.R. Rutherford (27) were the first to recognize the importance of ion-ion recombination in 1896. Rutherford (28) made the first attempts to measure IIR rate constants in 1897 followed by Langevin (29) in 1903. However, these early experiments are thought to have very little validity due to the lack of vacuum and gas purification techniques at that time. It was not until the late 1930's that experiments became more reliable and the existence of three distinct pressure regimes in which the mechanism of IIR differ

was discovered (30).

Figure 1 shows how the IIR rate constant varies with pressure. At pressures below about 1 Torr, IIR occurs via a bimolecular mechanism. The rate constant for this process bears no dependence on pressure and typical experimental values are in the range of $9 \pm 5 \times 10^{-8} \text{ cm}^3 \text{ sec}^{-1}$ (30). Above about 1 Torr a termolecular mechanism takes over. From this pressure up to approximately 1 atm the IIR rate constant increases linearly with pressure. This behavior was predicted by Thomson (31) in 1924 and was first verified experimentally

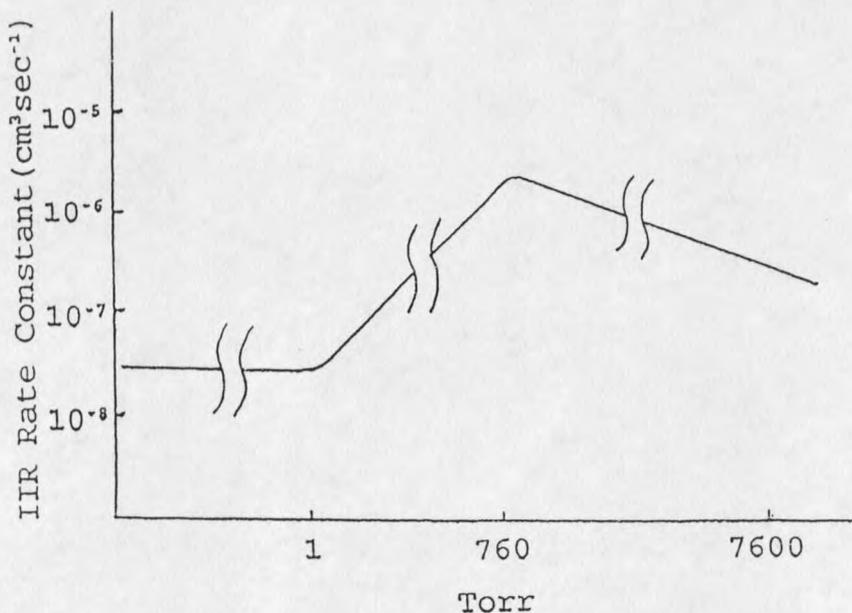


Figure 1. Plot of ion-ion recombination rate constant versus pressure.

by Sayers (32) and Gardener (33) in 1938. Near 1 atm the IIR rate constant reaches a maximum value of about $2 \times 10^{-6} \text{ cm}^3 \text{ sec}^{-1}$ and then begins to decrease with increasing pressure. This phenomena was shown experimentally by Machler (34) and is explained by a theory proposed early on by Langevin (29) which states that the rate of IIR is limited by the speed at which the oppositely charged species can diffuse together.

Since the experiments of this thesis work were performed at or near atmospheric pressure, the termolecular mechanism for IIR will be discussed in greater detail below.

Termolecular Ion-Ion Recombination

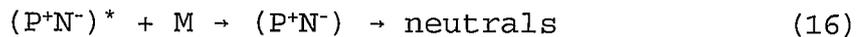
Thomson (31) proposed the first theory to explain the recombination of ions in a high pressure ionized gas. This theory provided the fundamental basis for all subsequent recombination theories.

Thomson's theory considers two ions, one of charge e and the other of charge $-e$. These ions are assumed to be in thermal equilibrium with the gas, therefore, the average kinetic energy per ion is $3kT/2$, where T is the temperature of the gas. The mutual potential energy of the ion pair is given by the Coulomb expression $-e^2/r$, where r is the separation

distance of the ions. The basis of the Thomson theory is that if the total relative energy of the ion pair ever becomes negative, recombination will occur. In other words, the kinetic energy of relative motion of the ions, W , must become less than the energy required to separate the ions by an infinite distance, ($W < e^2/r$), if recombination is to result (25). This condition cannot be met unless one of the ions collides with a third body. In the absence of third body collisions, the relative kinetic energy of the ions increases at the same rate as their mutual potential energy decreases, hence there is no net change in the total relative energy. However, if within a critical distance, r_c , one of the ions collides with a neutral, resulting in the return of that ion to the average thermal energy, the ions will become entrained in a closed orbit about each other and recombination will result. The critical radius comes from $3kT/2 = e^2/r_c$ and is given by Equation 13.

$$r_c = 2e^2/3kT \quad (13)$$

Thomson's mechanism of recombination can be written in graphical notation by the reaction scheme shown below (35).



Reaction 14 represents the ions approaching each other and entering a hyperbolic unbound orbit, denoted as $(P^+N^-)^*$. If one of the ions does not collide with a neutral while in this orbit, the ions will bypass each other and continue on their hyperbolic trajectory (Reaction 15). However, if an ion-neutral collision does occur, the ion pair may lose relative kinetic energy and become entrained in a bound elliptical orbit which results in recombination, shown by Reaction 16.

Thomson assumed that each ion is surrounded by a sphere of radius r_c , and that the sum of the number of collisions per second of oppositely charged ions within the ion sphere will equal the recombination rate. The number of ions entering the sphere is given by $\pi r_c^2 n^\pm [(v_m^+)^2 + (v_m^-)^2]^{1/2}$ where n^\pm is the number of positive or negative ions per cm^3 and v_m represents the mean velocity of the ions. Then, if w is the probability that a collision between an ion and a neutral will occur within the sphere, the number of recombination events per cm^3 per sec is given by Equation 17.

$$R = \pi r_c^2 n^+ n^- [(v_m^+)^2 + (v_m^-)^2]^{1/2} (w^+ + w^-) \quad (17)$$

The probability, w , is given (25) by $1 - \frac{\lambda^\pm}{2r_c} (1 - e^{-2r_c/\lambda^\pm})$ where λ^\pm is the mean free path of the ion. Substituting this quantity for w and dividing by $n^+ n^-$ gives the ion-ion recombination rate constant in $\text{cm}^3 \text{sec}^{-1}$.

Thomson's theory has several shortcomings, such as; neglecting the possibility of weakly bound ion pairs dissociating by subsequent collisions; that one ion-neutral collision within the critical radius may not result in unit probability of recombination; ignoring ion pairs with ionic separations greater than r_c ; and failing to correctly predict the pressure dependence of the rate of IIR at pressures above about 2 atm. Subsequent theories (36), (37), (38), (39) have corrected for these problems and addressed other microscopic details of the physics involved in IIR. These theories are beyond the scope of this thesis. It should be noted however, that Thomson's theory still provides the best quantitative agreement with experimental results in the 0.1 to 1 atm pressure range and the mechanism shown in reactions 14-16 is still the fundamental way in which IIR is described.

EXPERIMENTAL

The Reaction/Dummy Cell Apparatus

A schematic of the reaction/dummy cell apparatus is shown in Figure 2. The flowing sections describe main components of the apparatus.

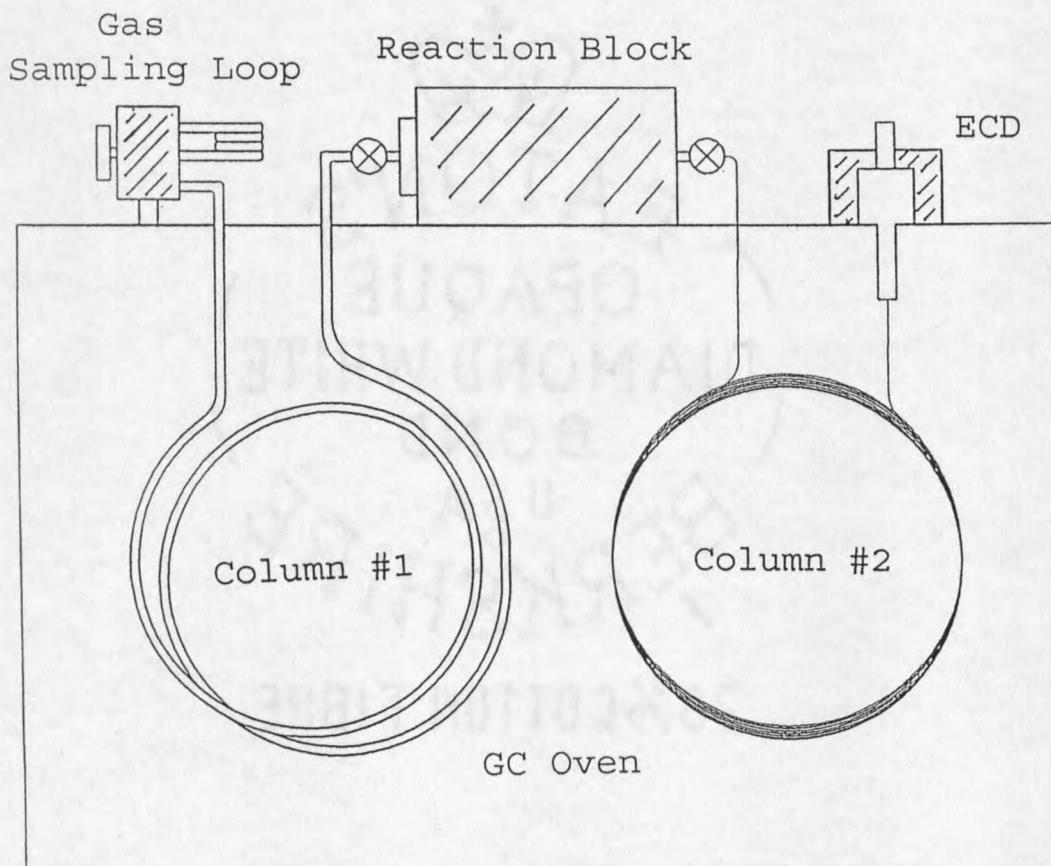


Figure 2. Schematic of reaction/dummy cell apparatus.

The Reaction/Dummy Cell

The reaction/dummy cell, shown in Figure 2, was constructed from a stainless steel block with dimensions of 8 cm(L) x 4cm(W) x 5cm(H). Within the block are two cylindrical cells 1.9 cm long and 1 cm in diameter, resulting in a volume of 1.5 cm³ each. The wall of the reaction cell was formed by a 13 mCi ⁶³Ni-on-Ni foil, while that of the dummy cell was a non-radioactive Ni foil. The GC carrier flow could be selected to pass through either the reaction or dummy cell by use of an eight-way switching valve (Carle Model 2013), while the cell not selected was continuously purged with nitrogen. The temperature of the cell block was maintained between 30 and 180°C by a cartridge heater and thermocouple feedback loop controlled by an Omega temperature controller (Model CN370). To ensure the temperature of the gas within the cell was actually the same as the temperature of the cell block, a separate thermocouple was inserted into the cell cavity and the temperature was measured by a separate temperature readout device. It was determined that the temperature of the gas was always within ±2°C of the temperature of cell block.

For some experiments it was necessary to reduce the thermal electron population in the reaction cell so that no

