To the Graduate Council:

I am submitting herewith a dissertation written by Ronald Earl Goans entitled "Electron Attachment to Molecules in Very High Pressure Gases." I have examined the final electronic copy of this dissertation for form and content and recommend that it be accepted in partial fulfillment of the requirements for the degree of Doctor of Philosophy, with a major in Physics.

L. G. Christophorou, Major Professor

We have read this dissertation and recommend its acceptance:

R. J. Lovell, R. O'brilly, F. Williams

Accepted for the Council:

Dixie L. Thompson

Vice Provost and Dean of the Graduate School

(Original signatures are on file with official student records.)
February 28, 1974

To the Graduate Council:

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Major Professor

We have read this dissertation and recommend its acceptance:

Accepted for the Council:

Vice Chancellor for Graduate Studies and Research
ELECTRON ATTACHMENT TO MOLECULES
IN VERY HIGH PRESSURE GASES

A Dissertation
Presented to
the Graduate Council of
The University of Tennessee

In Partial Fulfillment
of the Requirements for the Degree
Doctor of Philosophy

by
Ronald Earl Goans
June 1974
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ABSTRACT

In this thesis, electron capture mechanisms and reaction schemes have been developed for electron attachment to \( O_2, C_6H_6, \) and \( C_2H_5Br \) embedded in high densities of \( N_2 (P_{N_2} \leq 36 \text{ atm}), Ar (P_{Ar} \leq 56 \text{ atm}), C_2H_4 \) \( (P_{C_2H_4} \leq 22 \text{ atm}), \) and \( C_2H_6 (P_{C_2H_6} \leq 23 \text{ atm}) \). As the density of each medium increases, each is found to affect the attachment rate in a different manner, indicating the profound effect and importance of the environment on the electron attachment process. The results of a study on the capture of slow (\(< 1 \text{ eV}\)) electrons by \( O_2 \) in high pressures of \( N_2, C_2H_4, \) and \( C_2H_6 \) media are presented and discussed and a model is presented to account for the experimental observations in each case. Benzene has also been found to capture slow electrons in high pressures of \( N_2 \) and \( Ar \) media and a model is presented to account for the observed results. The finding that \( C_6H_6 \) captures electrons in the gas phase forces the conclusion that \( (EA)_B > 0 \text{ eV} \) in contrast to the accepted view that \( (EA)_B < 0 \text{ eV} \). Bromoethane has been found to capture slow (\(< 3 \text{ eV}\)) electrons in high pressures of \( N_2 \) and \( Ar \) and a reaction mechanism is presented which accounts for the relative magnitudes of the rate constants for autoionization, dissociation, and collisional stabilization. The high pressure data for electron attachment to \( O_2, C_6H_6, \) and \( C_2H_5Br \) to form the respective negative ions have been extrapolated to liquid densities to yield values of the attachment rate in the liquid state. These values generally are in reasonable agreement with those obtained by other investigators using liquid solutions.
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CHAPTER I

INTRODUCTION

I. IMPORTANCE OF ELECTRON ATTACHMENT STUDIES

The study of low energy electron attachment to molecules is of fundamental importance in both the physical and biological sciences. These processes are important in the physical sciences because many molecular parameters can be directly or indirectly determined from electron attachment studies. Such parameters include electron affinities of molecules, electron attachment rate constants and cross sections, autoionization lifetimes of transient negative ion species, bond dissociation energies, and shapes of molecular and negative ion potential energy curves. Electron attachment studies are important in biology because of the large number of low energy electrons that are produced when ionizing radiation interacts with matter. The elucidation of reaction mechanisms for these electrons is a crucial step in the development of a coherent picture of radiation biology. The importance of electron attachment studies in the physical and biological sciences is obvious, and related details have been discussed in several books [see, e.g., McDaniel (1964), Szent-Gyorgyi (1960, 1968) and Christophorou (1971a)].
II. REACTION CHANNELS OF INTEREST IN ELECTRON ATTACHMENT STUDIES

It is instructive to consider the various reaction channels available when a free electron is captured by a molecule. These are as follows:

\[ AX + e \rightarrow AX^- \]

\[ k_1 \]

where \( k_i \) (\( i = 1, \ldots, 4 \)) are the rate constants for the various channels. \( k_1 \) is the absolute rate for formation of the compound negative ion \( AX^- \).

This compound system may autoionize either elastically or inelastically with a lifetime \( \tau_a = k_2^{-1} \) as short as \( 10^{-14} \) - \( 10^{-15} \) seconds. Dissociation [Equation (I-2)] can be in competition with autoionization and is energetically possible when the incident electron energy exceeds \( D(AX) - EA(X) \) where \( D(AX) \) is the dissociation energy of \( AX \) and \( EA(X) \) is the electron affinity of \( X \). The electron affinity of a molecule is defined as the difference in energy between the neutral molecule and the negative ion when both are in their ground electronic, vibrational, and rotational states. By convention, \( EA \) is positive if the \( v = 0 \) level of \( AX^- \) lies below the \( v = 0 \) level of \( AX \), where \( v \) is the vibrational quantum number.
Channel (I-3) is the nondissociative electron attachment process resulting in the formation of the parent negative ion AX. This reaction is possible when EA(AX) > 0 eV and there is a mechanism for removing the excess excitation energy. Generally, radiative stabilization of AX is improbable and stabilization occurs through interaction with a third body, i.e.,

\[
e + AX \rightarrow AX^\ast + S \rightarrow AX^- + S^\ast + \text{energy} \quad (I-4)
\]

where S may be AX or another molecule or atom. Complete stabilization of transient ions with \(10^{-13} \leq \tau_a \leq 10^{-6}\) sec can be achieved in high pressure swarm experiments \(10^3 \leq P \leq 10^5\) Torr if the density of the stabilizing body is such that the autoionization lifetime is much longer than the time between collisions of AX and S.

III. METHODS USED TO STUDY MOLECULAR NEGATIVE IONS

Three groups of negative ions have been distinguished [Christophorou (1971a)] on the basis of the magnitude of the negative ion lifetime \(\tau_a\).

1. Extremely short lived ions \(10^{-15} \leq \tau_a \leq 10^{-13}\) sec. These ions are observed as resonances in electron scattering experiments.

2. Moderately short lived ions \(10^{-13} \leq \tau_a \leq 10^{-6}\) sec. Collisional stabilization can occur in this time interval at high pressures and the negative ions can be observed in high pressure swarm experiments.
3. Long lived negative ions \( (\tau_a \geq 10^{-6} \text{ sec}) \). The lifetimes of many of these ions can be determined under single collision conditions in a time of flight mass spectrometer (TOFMS).

The two methods used most often for observing molecular negative ions are the electron beam and the electron swarm. In the electron beam method, a nearly monoenergetic beam of electrons collides under single collision conditions with the molecule of interest. Beam experiments using a TOFMS are utilized to measure the negative ion yield \( I(\epsilon) \) and to mass analyze and find the energy dependence of the reaction products. Under appropriate experimental conditions the yield \( I(\epsilon) \) is proportional to the attachment cross section thereby giving a relative cross section spectrum. The mean autoionization lifetime of long-lived negative ions \( (\tau_a \geq 10^{-6} \text{ sec}) \) can also be determined in a TOFMS by measuring the ratio of the total current (neutral + ion) to the neutral current for various values of the accelerating potential. The TOFMS method has been improved with the development of the retarding potential difference technique (RPD) [Fox et al. (1955)]. This technique has a resolution of \( \sim 0.2 \text{ eV} \) and thereby provides a lower limit to the width of a negative ion resonance that can be measured experimentally.

The electron swarm method combined with the swarm unfolding technique (see Chapter II) is ideally suited for low energy electron attachment studies in the high pressure gas phase \((0.2 \text{ atm} \leq P \leq 100 \text{ atm})\). Such a range of pressures can be utilized to stabilize negative ions in the lifetime range
10^{-13} \leq \tau_0 \leq 10^{-6} \text{ sec. This type of experiment is important because such negative ions are undetectable in a conventional TOFMS. The high pressure swarm experiment is crucial in relating the abundant knowledge on isolated molecules (low pressure gases) to that in the condensed phase. Such studies are useful in developing an understanding of the environmental influences on reaction mechanisms accompanying the interaction of radiation with matter. Furthermore, an understanding of the role of the physicochemical properties of molecules in biological reactions requires knowledge as to how these isolated molecule properties change when the molecule is embedded in gradually denser and denser gaseous and, finally, into condensed phase environments. Through the high pressure swarm experiment one is capable of determining the pressure dependence of certain molecular parameters and, in some cases, is capable of extrapolating these values to the liquid phase.

IV. SCOPE OF THE PRESENT WORK

In this thesis, results on electron attachment to molecules embedded in high pressure gaseous media will be given. In Chapter II, we review both the analytical and experimental methods and the experimental modifications which were necessary in order to extend measurements to 55 atm. In Chapter III, we present results of a study on the capture of slow (< 1 eV) electrons to O_2 in very high pressures of nitrogen, ethylene, and ethane. In addition, we present various models for attachment in these three environments and utilize the proposed models to calculate a value for
the lifetime of $O_2^{-\ast}$. The high pressure data on $O_2$ are also extrapolated to liquid state behavior. In Chapter IV, gaseous electron attachment to benzene in dense media is presented. These data along with certain models are used to calculate the autodetachment lifetime of $C_6H_6^{-\ast}$. In Chapter V, ultrahigh pressure studies on the dissociative attachment processes in $C_2H_5Br$ are presented. In Chapter VI, the present work is summarized.
CHAPTER II

EXPERIMENTAL AND ANALYTICAL METHODS

In this chapter we review work performed with the electron swarm method and comment on the experimental modifications introduced in the present work in order to study electron attachment in ultrahigh pressure gas mixtures. Furthermore, the accuracy of the experimental data has been significantly improved by addition of a new electronics system and by modifications on the chamber. These details will be discussed first and then, the methods of determining electron attachment cross sections will be presented.

I. EXPERIMENTAL PROCEDURE

1. Description of the Electron Swarm Method

In the electron swarm method, electrons drift through a gas at high pressures under the influence of a uniform electric field $E$. Because of the high pressures employed, these electrons rapidly come into equilibrium with the gas and attain an energy distribution $f(\epsilon, E/P)$ which is characteristic of the gas, the temperature, and the pressure-reduced electric field $E/P$ (volt-cm$^{-1}$ Torr$^{-1}$). The electron swarm distribution is broad and is defined by $f(\epsilon, E/P) \, d\epsilon = \text{fraction of electrons in the energy interval between } \epsilon \text{ and } \epsilon + d\epsilon$. One therefore determines quantities, such as the attachment
rate, \( (\alpha w)_o \), in a high pressure swarm experiment which are averages over the electron energy distribution \( f(\epsilon, E/P) \).

In the electron swarm method employed in the present study, the attaching gas is mixed in very small proportions with another gas called the carrier gas which does not capture electrons in the energy region of interest and whose role is to establish the electron distribution function at each \( E/P \). In this study, ethylene \( (\text{C}_2\text{H}_4) \), ethane \( (\text{C}_2\text{H}_6) \), nitrogen \( (\text{N}_2) \) and argon \( (\text{Ar}) \) were used as carrier gases. The electron energy distribution functions for these gases will be discussed in a subsequent section.

The swarm method of Bortner and Hurst (1958), modified for ultrahigh pressures \( (0.5 \text{ atm} \leq P \leq 100 \text{ atm}) \), was used for measurement of electron attachment rates. The swarm apparatus as modified by Christophorou et al. (1965) is shown in Figure II-1. Briefly, in this method, electrons are produced in a plane by \( \alpha \)-particle ionization at a known distance between two parallel plate collectors. Because of the high pressures involved, these electrons \( \sim 1.5 \times 10^5 \) per \( \alpha \) particle) come into equilibrium with the gas quickly and attain the energy distribution \( f(\epsilon, E/P) \). A uniform electric field \( E \) causes the electron swarm to drift toward the positive collector. Let \( N \) be the number of electrons at a distance from the source and let \( dN \) be the number of electrons removed from the swarm by the attaching species while the swarm drifts through the distance \( dx \). We then have
SWARM APPARATUS FOR MEASUREMENT OF ELECTRON ATTACHMENT COEFFICIENT AND DRIFT VELOCITY

Figure II-1. Swarm Apparatus of Bortner and Hurst as Modified by Christophorou et al.
\[ dN = -\alpha N(x) P_A \, dx \]  \hspace{1cm} (II-1)

where \( \alpha \) is the attachment coefficient and \( P_A \) is the pressure of the attaching species. Integrating Equation (II-1) gives

\[ N(x) = N(0) e^{-\alpha P_A x} \]  \hspace{1cm} (II-2)

As the electron swarm drifts a distance \( dx \), the potential variation \( dV \) at the positive electrode is given by

\[ dV = \frac{N(x) V_0 \, dx}{d} \]  \hspace{1cm} (II-3)

where \( d \) is the distance between the \( \alpha \) source and the collector and \( V_0 \) is the change in the collector potential due to a single electron traversing the distance \( d \). The time variation of the collector potential \( V(t) \) is given by

\[ V(t) = A \left( 1 - e^{-ft/\tau_0} \right) \]  \hspace{1cm} (II-4)

where \( A = N(0) V_0 \), \( \tau_0 = d/w \) is the collection time of a swarm of drift velocity \( w \) and \( f = \alpha P_A d \).

2. Description of the Electronics System

The height of the pulse given by Equation (II-4) is measured (i) for the pure carrier gas and (ii) in a binary mixture in which the attaching gas is mixed in minor proportions with the carrier gas under identical experimental conditions and total pressure. The pulse \( V(t) \) is fed into a Tennelec
TC161D charge sensitive preamplifier and through a TC200 Tennelec linear pulse amplifier. The TC200 pulse amplifier contains a main amplifier section of gain $A'$ and wave shaping networks consisting of two differentiators and a single integrator, each with separately adjustable time constants $\tau$. The transfer function of the pulse amplifier is [see Kowalski (1973)]

$$\frac{E_o(s)}{E_i(s)} = \left(\frac{s \tau_{d1}}{1 + s \tau_{d1}}\right)\left(\frac{s \tau_{d2}}{1 + s \tau_{d2}}\right)\frac{A'}{1 + s \tau_{\text{int}}}
$$

(II-5)

where $s$ is the Laplace transform variable, $E_o(s) = \mathcal{L}[e_o(t)]$ is the transform of the output signal $e_o(t)$, $E_i(s) = \mathcal{L}[e_i(t)]$ is the transform of the input signal, and $\tau_{d1}$, $\tau_{d2}$, and $\tau_{\text{int}}$ are the first differentiator, second differentiator, and integrator time constants, respectively. The input to this amplifier is the collector signal $V(t)$ so that

$$e_o(t) = \mathcal{L}^{-1}\left\{\frac{s^2 \tau_{d1} \tau_{d2} A'V(s)}{(1 + s \tau_{d1})(1 + s \tau_{d2})(1 + s \tau_{\text{int}})}\right\}
$$

(II-6)

where $\mathcal{L}^{-1}$ is the inverse Laplace transform operator, $e_o(t)$ is the output signal in the time domain, and $V(s) = \mathcal{L}[V(t)]$. Equation II-6 can be inverted to yield

$$e_o(t) = \frac{A A'}{\tau_o \tau_{\text{int}}} \sum_{i=1}^{4} \frac{P(\alpha_i)}{Q'(\alpha_i)} \alpha_i^t e_i
$$

(II-7)
where \( P = s, \quad Q = \prod_{i=1}^{4} (s + \alpha_i) \quad \text{and} \quad \alpha_i (i=1, \ldots, 4) = 1/\tau_{d1}, 1/\tau_{d2}, 1/\tau_{d3} \)

and \( f/\tau_o \), respectively. \( e_o(t) \) may either be a bipolar or unipolar pulse depending on the relative magnitudes of the time constants. The noise can be shown [Fairstein (1961)] to be minimized when the differentiator and integrator time constants are equal. \( e_o(t) \) is then inputed into a 512 channel Nuclear Data analyzer and the output of the multichannel analyzer is printed out using a teletype. At a given \( E/P \), the pulse \( e_o(t) \) will be stored in channel \( c_1 \) for the pure carrier gas (i) and will be stored in channel \( c_2 < c_1 \) for the binary mixture (ii). From the ratio \( R = c_2/c_1 \) of the heights of the collector pulses for the binary gas mixture and the carrier gas itself, the attachment coefficient \( \alpha \) can be determined [Eldridge (1962)]. The tables of Eldridge considered the response of an amplifier with single integrator and differentiator shaping networks to the input pulse \( V(t) \). These tables may be used, however, with the more complicated situation II-6 because the ratio \( R \) is independent of the shaping networks.

The product of \( \alpha \) and the electron swarm drift velocity, \( w \) (in \( \text{cm sec}^{-1} \)), at each \( E/P \) gives the absolute rate of electron attachment, \( \alpha w \) (in \( \text{sec}^{-1} \text{Torr}^{-1} \)), at that \( E/P \). Drift velocities used in this work were taken from Christophorou (1971a) and represent averages of the best experimental data available. Attachment rates can be obtained as a function of mean energy \( \langle \epsilon \rangle \) if \( \langle \epsilon \rangle \) is known as a function of \( E/P \). \( \langle \epsilon \rangle \) is generally known as a function of \( E/P \) for the common carrier gases \( N_2, \text{Ar}, \text{and} C_2H_4 \) [Christophorou (1971a)] and can often be found from \( D_L/\mu \) data for other gases.
The electronics system used in the high pressure swarm apparatus has very little drift (< 1 channel per day) and consequently can be used to measure low attachment rates ($\sim 10^{-3}$ sec$^{-1}$ Torr$^{-1}$). Such low rates are difficult to measure because the pulses for the carrier gas and the binary mixture are nearly the same size. However, the stability of the system has allowed reasonably precise measurement of $\alpha w$ where the pulses for the binary system are more than 5 channels below the pulses for the pure carrier gas.

3. **Source Modifications**

Due to the wide range of high pressures employed it was necessary to build $\alpha$-particle sources of different dimensions. A number of these were constructed by electroplating either $^{252}\text{Cf}$ ($\alpha$-particle energies: 6.12, 6.08 MeV; half life: 2.65 yr.) or $^{239}\text{Pu}$ ($\alpha$-particle energies: 5.16, 5.15, 5.11 MeV; half life: 24390 yr.) on a thin ribbon of plutonium and locating it in a circular groove as shown in Figure II-2 at a distance $R$ from the inside edge of the annulus. The dimensions $R$ and $D$ (see Figure II-2) were decreased as the pressure was increased because an increase in pressure causes a corresponding decrease in $\alpha$-particle track length. Sources with $1.5 \leq D \leq 8.6$ cm and $0.038 \leq R \leq 0.014$ cm were found to be effective. Care was also taken to have a thin source so that the fraction of the $\alpha$-particle energy lost in the source was small. Collimation of the $\alpha$-particles is extremely important in order to have narrow pulse-height distributions; this objective was achieved...
Figure II-2. Dimensions of α Source in Inches.
by accepting only those α-particles coming from a series of equally spaced
collimating holes. The holes are arranged in a 360° pattern and the number
of holes varied from 120 for D = 8.6 cm to 24 for D = 1.5 cm. To maintain
a convenient counting rate, the source activity was increased from 0.5 μC
for the source with the largest D to ~ 5 μC for the source with the smallest
D. In general, use of sources with high activity tended to give better results.

4. Chamber Modifications

The use of high pressures required the construction of a new
ionization chamber of the same general design as that in Figure II-1, page 9.
The chamber was milled from a single piece of nonmagnetic stainless steel
to reduce outgassing and noise pickup and was structurally designed using
ASME (American Society of Mechanical Engineers) boiler standards to
support internal pressures of up to ~ 80,000 Torr. All seals were inside
welded and copper gaskets were used to facilitate bakeout. Varian flanges
and Nupro high pressure valves were used at critical points in the chamber.
Pump-out pressures were ≤ 1 × 10^{-8} Torr and the outgas rate was normally
≤ 0.2 μ/hr.

5. Experimental Results

The carrier gases N₂ and Ar were obtained from Matheson Company
and were of a quoted purity of 99.997%. Due to the large quantities of
carrier gases needed in high pressure experiments it is uneconomical to use
gases of extreme purity. However, since traces of impurities could be
troublesome, a tank of extra pure N\textsubscript{2} (99.9995\%) was purchased and it was found that the extra purity had no effect on the attachment rates. The carrier gases C\textsubscript{2}H\textsubscript{4} and C\textsubscript{2}H\textsubscript{6} were of a quoted purity of 99.95\% and were purified extensively by use of liquid nitrogen traps. In all experiments the carrier gas was introduced first into the chamber for pulse height measurements. When this set of measurements on the pure gas was completed the gas was collected in liquid nitrogen traps and was reused in subsequent measurements on the mixture. This procedure allowed use of a carrier gas that was of exactly the same relative purity for both sets of measurements. Furthermore, it helped avoid the difficulty of distilling larger quantities of carrier gas and of containing this amount in the liquid nitrogen traps. The cost of the experiment is also significantly reduced in view of the large quantities of carrier gas needed.

The attaching gas pressures were measured with an MKS capacitance manometer; the carrier gas pressure was measured with a Wallace-Tiernan absolute pressure gauge up to 25,000 Torr and above this pressure with a strain gauge-digital voltmeter combination. The strain gauge was calibrated with the Wallace-Tiernan up to 25,000 Torr and the calibration curve was extrapolated for use in the higher regions.

Although for N\textsubscript{2} it was not necessary to correct the pressure readings for gas compressibility, such a correction was necessary in the case of C\textsubscript{2}H\textsubscript{4} and C\textsubscript{2}H\textsubscript{6}. For an ideal gas (PV = nRT)

\[ \frac{E}{P} \propto \frac{E}{N} \]  

(II-7)
where $P$ is the pressure in Torr and $N$ is the number of molecules per cm$^3$ per Torr. For a compressible gas ($PV = znRT$)

$$E/P \propto E/N \left(1/z\right) \tag{II-8}$$

where $z$ is the compressibility factor. The compressibility factor approaches unity at low pressures and decreases with increasing pressure. In the present experiment the measured pressures $P_M$ were divided by $z$ to obtain the quantity $P' = P_M/z$ for which $E/P' \propto E/N$. The compressibility factor data were taken from Walters et al. (1954) for C$_2$H$_4$ and from Maxwell (1950) for C$_2$H$_6$.

All measurements were made at room temperature (298° K) and in all experiments the carrier gas pressures were much greater (by a factor of $3 \times 10^2$ to $2 \times 10^7$) than the attaching gas pressures. For this reason, the total pressures are referred to as carrier gas pressures.

Three high voltage power supplies provided the accelerating voltage. A Keithley 240 regulated high voltage supply was used for voltages $\leq 1$ KV, a John Fluke 410 A supply for voltages 1-10 KV, and a John Fluke 430 A supply for voltages 10 KV-20 KV. The need for high fields in order to reach large values of $E/P$, especially for the highest pressures, demanded very careful filtering of the power supplies to reduce ripple. In many cases, corona and gas breakdown limited the value of $E/P$ that one could achieve. This problem was particularly critical at the highest pressures.
II. DISTRIBUTION FUNCTIONS

1. General Theory

The electron energy distribution function \( f(\epsilon, E/P) \) is a solution to the Boltzmann transport equation

\[
\frac{\partial f}{\partial t} + \mathbf{v} \cdot \frac{\partial f}{\partial \mathbf{x}} + \frac{\mathbf{F}}{m} \frac{\partial f}{\partial \mathbf{v}} = \int d\mathbf{v'} \int d\Omega \, g(\mathbf{v}, \theta) [f' \delta f' - ff']
\]

where \( f(\mathbf{x}, \mathbf{v}, t) \, d\mathbf{x} \, d\mathbf{v} \) is defined to be the number of electrons having coordinates between \( \mathbf{x} \) and \( \mathbf{x} + d\mathbf{x} \) and velocities between \( \mathbf{v} \) and \( \mathbf{v} + d\mathbf{v} \). \( \mathbf{F} \) is the external force \((= eE)\) acting on an electron of mass \( m \) in the external field \( E \). The right-hand side of Equation (II-9) is the Boltzmann collision term \( (\partial f/\partial t)_c \) which represents the rate of change of \( f \) due to collisions with gas molecules. In the collision term, electrons of velocities \( \mathbf{v} \) and \( \mathbf{v}' \) (relative velocity \( |\mathbf{v} - \mathbf{v}'| = g \)) collide with molecules with the impact parameter \( b \) and the scattering angles \( \theta, \varphi \). \( \sigma(g, \theta) d\Omega \) is the differential cross section for the scattering process while \( f = f(\mathbf{x}, \mathbf{v}, t) \) and \( f' = f(\mathbf{x}, \mathbf{v}', t) \). Primed quantities refer to velocities \( \mathbf{v}' \) and \( \mathbf{v}' \) after the collision. Details of the theory are found in Wu (1966) and in Present (1958).

In electron swarm experiments we deal with steady state conditions so that \( \partial f/\partial t = 0 \). For homogeneous gas mixtures \( \mathbf{v} \cdot \partial f/\partial \mathbf{x} = 0 \) so that Equation (II-9) becomes time and space independent. The Boltzmann transport equation is a nonlinear integro-differential equation which in
principle can be solved as an initial-value problem. It is difficult to solve exactly but several analytical and numerical methods have been developed. These methods are discussed by Chapman and Cowling (1952), by Allis (1956) and by Wu (1966).

When the system is in thermodynamic equilibrium, the Boltzmann transport equation has the well-known Maxwellian function

\[
g(v) dv = \left( \frac{2}{\pi} \right)^{3/2} \frac{m}{(kT)^{3/2}} v^2 e^{-\frac{mv^2}{2kT}} dv
\]  

(II-10)

as a solution. \(g(v)\) \(dv\) gives the fraction of electrons with velocities between \(v\) and \(v + dv\). In Equation (II-10), \(T\) is the absolute temperature and \(k\) is Boltzmann's constant. In energy space we have

\[
f(\epsilon) d\epsilon = \frac{2}{\pi^{3/2} (kT)^{3/2}} e^{-\epsilon/kT} \epsilon^{3/2} e^{-\epsilon/kT} e^{\epsilon/kT} d\epsilon
\]  

(II-11)

where \(f(\epsilon)\) \(d\epsilon\) is the fraction of electrons in the energy interval \(\epsilon\) to \(\epsilon + d\epsilon\).

Electron energy distribution functions have been calculated for only a few molecules since experimental energy-loss data are not known for most gases. A comprehensive review of distribution functions and energy-loss data can be found in Massey and Burhop (1952), Loeb (1960), McDaniel (1964), and Christophorou (1971a).
2. Electron Distribution Functions Used in the Present Work

The electron energy distribution functions used in this work for $N_2$ were calculated by Engelhardt, Phelps, and Risk (1964) by solving the Boltzmann transport equation taking into account both elastic and inelastic collisions. Christophorou, Chaney, and Christodoulides (1969) recommended these distribution functions for $N_2$ after finding that the rates measured in $N_2$ mesh in a continuous fashion if the data of Engelhardt et al. are used.

The energy distribution functions $f(\epsilon, E/P)$ for electrons drifting in argon under the influence of a uniform electric field have been evaluated by Ritchie and Whitesides (1961). They considered a numerical treatment of the space and time independent Boltzmann equation for just elastic collisions, using the momentum transfer cross sections of Barbiere (1951). Barbiere's data ignored the Ramsauer-Townsend minimum at 0.28 eV [Ramsauer (1921), Townsend (1900)]. This minimum was subsequently taken into account by Nelson and Whitesides (1968) in their revised calculations on argon. These revised distribution functions were used in the present study.

A Maxwellian distribution function has been used for $C_2H_4$ since the system is essentially in thermal equilibrium at most $E/P$'s of interest. Rates measured in $C_2H_4$ using a Maxwellian distribution mesh very well with rates obtained in $N_2$ in the region of overlapping energy, thereby validating this choice of $f(\epsilon, E/)$. The distribution function for $C_2H_6$ has not been measured; such a situation prohibits cross section analysis in ethane.
Electron energy distribution functions \( f(\varepsilon, E/P) \) are shown for the three carrier gases \( C_2H_4, N_2, \) and Ar in Figure II-3. One can observe that the distributions are broad with the half-width being of the same order of magnitude as the mean energy \( \langle \varepsilon \rangle \). By judicious choice of the carrier gas and \( E/P \), one can investigate attachment in energy regions from thermal to \( \sim 10 \text{ eV} \).

III. ANALYTICAL METHODS

1. Attachment Rate Analysis

The absolute electron attachment rate \( \alpha w \) (in \( \text{sec}^{-1} \text{Torr}^{-1} \)) is given by

\[
\alpha w(E/P) = N_o \int_0^{\infty} v \sigma_a(v) g(v, E/P) dv
\]

or, in terms of energy,

\[
\alpha w(\langle \varepsilon \rangle) = N_o \left( \frac{2}{m} \right)^{\frac{3}{2}} \int_0^{\infty} \varepsilon^\frac{3}{2} \sigma_a(\varepsilon) f(\varepsilon, E/P) d\varepsilon
\]

where \( \alpha \) is the electron attachment coefficient in units of \( \text{cm}^{-1} \text{Torr}^{-1} \), \( \sigma_a \) is the attachment cross section, \( w \) is the electron swarm drift velocity in units of \( \text{cm sec}^{-1} \), \( v \) and \( \varepsilon \) are the electron velocity and energy, respectively, and \( N_o (= 3.24 \times 10^{16}) \) is the number of attaching gas molecules per \( \text{cm}^3 \) per Torr at \( 298^\circ \text{K} \).
Figure II-3. Electron Energy Distribution Functions $f(\epsilon, E/P)$ for $\text{C}_2\text{H}_4$, $\text{N}_2$, and $\text{Ar}$. 
It is desirable to be able to calculate both the magnitude and the energy dependence of the attachment cross section $\sigma_a(\epsilon)$, given experimental information on $\alpha w$ and $f(\epsilon, E/P)$. Previously, the swarm-beam method [see Christophorou (1971a)] was used to determine $\sigma_a$ by combining the negative ion currents $I(\epsilon)$ obtained in beam experiments with attachment rates measured in swarm experiments. This procedure requires that attachment processes be the same in both the beam experiment and in the swarm and that the shape of the negative ion current be identical to the shape of the cross section. Details of this analysis were described by Christophorou et al. (1965). Another method for determining the magnitude and the energy dependence of $\sigma_a(\epsilon)$ is described by Christophorou et al. (1971b). This method is most useful for resonant attachment at thermal energies and assumes that $\sigma_a$ can be represented by

$$\sigma_a(\epsilon) = \frac{A}{\epsilon^\gamma}.$$  \hspace{1cm} (II-14)

The values $\gamma$ and $A$ are determined through a least squares analysis.

2. **Swarm Unfolding Technique**

Christophorou, McCorkle and Anderson (1971) developed an unfolding procedure where the known swarm electron energy distribution function is used as a "smearing" function to unfold the monoenergetic rate from the experimentally determined rates. If we denote $R(\langle\epsilon\rangle_j)$ as the experimentally determined rate at the $j$th value of the mean electron energy $\langle\epsilon\rangle$, $F(\langle\epsilon\rangle_j, \epsilon)$
as the electron energy distribution function corresponding to that mean energy and \( M(\epsilon) \) as the monoenergetic rate at energy \( \epsilon \), then

\[
R(\langle \epsilon \rangle_j) = \int_0^\infty M(\epsilon) F(\langle \epsilon \rangle_j, \epsilon) \, d\epsilon .
\]  

(II-15)

The iterative solution for \( M(\epsilon) \) starts by approximating \( M(\epsilon) \) by \( R_{\text{exp}}(\langle \epsilon \rangle_j) \).

The initial form for \( M(\epsilon) \) is introduced into Equation (II-15) and the right-hand side is evaluated at every mean energy \( \langle \epsilon \rangle \). This integral will be denoted by \( R_{\text{cal}}(\langle \epsilon \rangle_j) \). Relative weighting factors are then defined by

\[
w(\langle \epsilon \rangle_j) = \frac{R_{\text{exp}}(\langle \epsilon \rangle_j)}{R_{\text{cal}}(\langle \epsilon \rangle_j)}
\]

(II-16)

with the auxiliary condition that \( w(\langle \epsilon \rangle_j) = 1 \) when \( R_{\text{cal}}(\langle \epsilon \rangle_j) = 0 \). The new value of \( M(\epsilon) \) is determined through

\[
M_{\text{new}}(\epsilon) = M_{\text{old}}(\epsilon) \left[ \sum_j w(\langle \epsilon \rangle_j) F(\langle \epsilon \rangle_j, \epsilon) \right] / \left[ \sum_j F(\langle \epsilon \rangle_j, \epsilon) \right].
\]

(II-17)

The new value of \( M(\epsilon) \) is introduced into Equation (II-15) and the procedure is repeated until the residuals defined by

\[
\sum_j \left[ R_{\text{exp}}(\langle \epsilon \rangle_j) - R_{\text{cal}}(\langle \epsilon \rangle_j) \right]^2
\]

are minimized. When the residuals reach a minimum value, the weighting factors \( w(\langle \epsilon \rangle_j) \) approach unity and the function \( M(\epsilon) \) does not change.
with successive iterations. The number of iterations required for convergence is often large (> 3000) due to the large widths of the \( F(\langle \epsilon \rangle, \epsilon) \) distribution functions. The ratio \( R \) defined by

\[
R = \frac{\sum_j \left[ R_{\text{exp}}(\langle \epsilon \rangle_j) - R_{\text{cal}}(\langle \epsilon \rangle_j) \right]^2}{\sum_j [R_{\text{exp}}(\langle \epsilon \rangle_j)]^2}
\]

(II-18)

is a measure of the validity of the convergence and often was \( \leq 1 \times 10^{-4} \) for calculations in this thesis. The final value of \( M(\epsilon) \) is assumed to be close to the true monoenergetic rate of electron attachment, that is, the rate that would be measured had all the electrons in the swarm had the same energy. \( M(\epsilon) \) can be used to calculate the attachment cross section \( \sigma_a(\epsilon) \) from

\[
\sigma_a(\epsilon) = \frac{M(\epsilon)}{N_o \langle \epsilon \rangle \epsilon^2}
\]

(II-19)

where \( N_o \) is the number of attaching gas molecules per \( \text{cm}^3 \) per Torr at the temperature \( T \), \( m \) is the electron mass, and \( M(\epsilon) \) is in units of \( \text{sec}^{-1} \text{ Torr}^{-1} \). The swarm unfolding procedure has been found to be superior to all previous methods of calculation of \( \sigma_a(\epsilon) \) and, for that reason, has been used throughout this thesis for the calculation of the attachment cross section.
ATTACHMENT OF SLOW ELECTRONS TO $O_2$ IN HIGH PRESSURE GASES

The $O_2^{−\infty}$ negative ion is moderately short lived ($10^{-12} \leq \tau_a \leq 10^{-6}$ sec) and consequently can be collisionally stabilized in a high pressure swarm experiment. The nature and density of various stabilizing bodies has been found to have a profound effect on the attachment of electrons to $O_2$. These results will be discussed below and the high pressure rates will be extrapolated to yield approximate liquid state attachment rates.

I. ELECTRON ATTACHMENT TO $O_2$ IN HIGH DENSITIES OF $N_2$

Previous work on electron attachment to $O_2$ in a $N_2$ environment ($300 \leq P_{N_2} \leq 10,000$ Torr) has been discussed by McCorkle, Christophorou, and Anderson (1972) and by Christophorou (1972). The results obtained by these investigators have been scrutinized further and some of the early measurements have been repeated using more precise measurement techniques. Equipment modifications (see Chapter II) have also allowed an extension of this work up to $N_2$ pressures of 27,500 Torr ($\sim 36$ atms). The attachment rates, $(\alpha w)_o$, extrapolated to zero $O_2$ pressure, $P_{O_2}$, are presented in Figure III-1. The function $\alpha w_o(\langle \epsilon \rangle)$ is seen to increase with increasing $N_2$ density and to become steeper at low energies with increasing $P_{N_2}$. The maximum value of $\alpha w$ is attained at thermal energies...
Figure III-1. Attachment Rate ($\alpha w_o$) as a Function of Mean Electron Energy for $O_2$ in $N_2$.

(*) Data of McCorkle et al.; (△) and (○) Present Results.
\( \langle \epsilon \rangle \approx 0.04 \text{ eV} \). In Figure III-2, the thermal attachment rate is presented and is seen to increase much faster than would be predicted on the basis of a pure three-body mechanism (see section IV).

McCorkle, et al. obtained the attachment rate cross section by unfolding attachment rate data using the swarm unfolding technique (see Chapter II, page 23). The cross sections \( \sigma_a(\epsilon) \) determined in this manner showed two characteristic features: (i) a gradual shift of \( \sigma_a(\epsilon) \) toward thermal energies with increasing \( P_N \) and (ii) structure in \( \sigma_a(\epsilon) \) for \( P_N \leq 1000 \text{ Torr} \). The structure was attributed to electron attachment from the \( v = 0 \) vibrational level of \( O_2 \) to the \( v' = 4 \) and \( v' = 5 \) levels of \( O_2^- \). The shift in \( \sigma_a(\epsilon) \) toward thermal energies was ascribed to a perturbation of the \( O_2^- \) potential energy curve by \( N_2 \) during close collisions.

A sample calculation of \( \sigma_a(\epsilon) \) was performed using the high pressure data at \( P_{N_2} = 20,000 \text{ Torr} \) and is presented in Figure III-3. As in the previous work, the calculation was made using the swarm unfolding technique. The energy range over which \( (\omega w)_0 \) can be measured is somewhat limited at the higher \( N_2 \) pressures. This restriction in the \( \langle \epsilon \rangle \) range and the additional increase in experimental error (estimated to be \( \pm 10\% \) to \( \pm 20\% \)) at high \( P_{N_2} \) makes a determination of \( \sigma_a(\epsilon) \) somewhat unreliable. Due to these difficulties, the cross section should be considered as only an estimate. However, it does support the earlier finding that \( \sigma_a(\epsilon) \) is shifted to lower energies with increasing \( P_{N_2} \).
Figure III-2. Attachment Rate ($\alpha w$) in $\text{N}_2$ ($\bigcirc$), $\text{C}_2\text{H}_4$ ($\bullet$) and $\text{C}_2\text{H}_6$ ($\triangle$) as a Function of Carrier Gas Pressure.

The Data Plotted are for $E/P_{298}$ Values Equal to 0.03 V cm$^{-1}$ Torr$^{-1}$ for $\text{N}_2$ and 0.1 V cm$^{-1}$ Torr$^{-1}$ for $\text{C}_2\text{H}_4$ and $\text{C}_2\text{H}_6$. These E/P Values Correspond to $\langle \epsilon \rangle = 0.05$ eV.
Figure III-3. Calculation of $\sigma_a(\epsilon)$ for $O_2$ in $N_2$ at $P_{N_2} = 20,000$ Torr.
II. ELECTRON ATTACHMENT TO $O_2$ IN HIGH DENSITIES OF $C_2H_4$

Electron attachment to $O_2$ in dense ethylene environments has been investigated over the pressure range $750 \leq P'_{C_2H_4} \leq 17,000$ Torr using the swarm technique. The pressure dependence of the thermal attachment rate is presented in Figure III-2, page 29, and is seen to be quite different from that for $O_2$ in gaseous $N_2$. Figure III-4A presents $(\alpha \omega)_o$, the attachment rate for $P_{O_2} \rightarrow O$, as a function of $E/P'_{298}$ and Figure III-4B shows the same quantity as a function of mean electron energy $\langle \epsilon \rangle$ for a number of total pressures $P'$. The kinetic equations which predict this behavior will be discussed in section IV. The energy scale has been calibrated by using $\langle \epsilon \rangle = \frac{3}{2} e \frac{D_{L}}{\mu}$ (ratio of lateral diffusion coefficient to electron mobility) obtained from the $D_{L}/\mu$ data of Walker (1973). These values replace the $\langle \epsilon \rangle = \frac{3}{2} e \frac{D_{L}}{\mu}$ data (ratio of longitudinal diffusion coefficient to electron mobility) of Wagner, et al. used previously by Christophorou (1971a). The two sets of data are shown in Figure III-5 as a function of $E/P'_{298}$.

There was no unfolding of the $\alpha \omega(\langle \epsilon \rangle)$ data because the electron distribution functions in $C_2H_4$ are not known experimentally. However, the change in the energy dependence of $(\alpha \omega)_o$ at low energies is consistent with the results for the $O_2-N_2$ mixtures which show that $\sigma_a(\epsilon)$ becomes sharper with increasing $P_{N_2}$.

In the case of $C_2H_4$ it was necessary to consider the pressure dependence of the electron drift velocity $w$, first noted by Huber (1969), in
Figure III-4. (a) $\alpha W_0$ as a function of $E/P_{298}$ and (b) as a function of $\langle \epsilon \rangle$ for $O_2$ in $C_2H_4$ environments.
Figure III-5. $\langle \epsilon \rangle$ as a Function of $E/P_{298}$ for C$_2$H$_4$.

(•) 3/2 $D_1/\mu$ Data of Walker. (○) 3/2 $D_1/\mu$ Data of Wagner et al.
the determination of \( \alpha w \). Huber reported that \( w \) decreased slightly (~7%) over the pressure range from 455 to 6072 Torr. These decreases are just slightly above his experimental error (~5%) but they are real and have been confirmed by measurements at the Oak Ridge National Laboratory [Gant, Christophorou, and Pittman (1973)]. Huber's data were used over the range \( 455 \leq P' \leq 6072 \) Torr and values obtained from a linear extrapolation were used for \( P' \geq 6072 \) Torr.

### III. ELECTRON ATTACHMENT TO \( \text{O}_2 \) IN HIGH DENSITIES OF \( \text{C}_2\text{H}_6 \)

Electron attachment to \( \text{O}_2 \) in a dense ethane environment has been investigated for ethane pressures in the range \( 750 \leq P'_2 \leq 17,500 \) Torr. In Figure III-2, page 29, the thermal attachment rate is presented as a function of ethane pressure. The rates in ethane are seen to be quite different, especially at high pressures, from those obtained for \( \text{O}_2\text{-N}_2 \) and for \( \text{O}_2\text{-C}_2\text{H}_4 \) mixtures. Figure III-6A presents \( \alpha w \) as a function of \( E/P'_2 \), and Figure III-6B shows \( \alpha w \) as a function of \( \langle \epsilon \rangle \) for a number of ethane pressures. The energy scale was calibrated using the \( D_L/\mu \) data of Walker (1965, 1973). The drift velocities used in the calculation of \( \alpha w \) were those determined by Huber (1969). As for ethylene, \( \sigma_{\text{a}}(\epsilon) \) could not be determined because \( f(\epsilon, E/P) \) is unknown.
Figure III-6. Attachment Rate ($\omega w_0$) for O$_2$ in C$_2$H$_6$ as a Function of (a) $E/P_{298}$ and (b) $\langle \epsilon \rangle$. 
IV. REACTION SCHEMES FOR ELECTRON ATTACHMENT TO $O_2$

IN HIGH DENSITIES OF $N_2$, $C_2H_4$ and $C_2H_6$

From the previous discussion, it is evident that electron attachment to $O_2$ depends strongly on the nature and density of the gaseous environment. Kinetic mechanisms which are consistent with the experimental data will be outlined below.

1. $O_2-N_2$ Mixtures

The pressure dependence of the attachment rate has been explained by Christophorou (1972) in terms of a model whereby $N_2$ is assumed (i) to act as a stabilizing third body in distant collisions and (ii) to be involved in close collisions which seriously perturb the $O_2^-$ potential energy curve.

We can postulate two reaction mechanisms to account for these observations:

\[(i) \quad e + O_2 \xrightarrow{k_1} O_2^- \quad (III-1)\]

\[O_2^- \xrightarrow{k_2} O_2 + e\]

\[O_2^- + N_2 \xrightarrow{k_3} O_2^- + N_2 + \text{energy}\]

\[\xrightarrow{k_4} O_2 + N_2 + e\]
Mechanism (i) is identical to a three-body reaction whereby \( N_2 \) acts to stabilize \( O_2^- \). Mechanism (ii) postulates the formation of a transient complex \([O_2^- - N_2]\) which can either autoionize or form \( O_2^- \) upon collision with a second \( N_2 \) molecule. Using the above reaction scheme we have

\[
(\alpha w)_o = k_1 \left( \frac{k_3 n_{N_2}}{k_2 + (k_3 + k_4)n_{N_2}} \right) + \frac{k_5 n_{N_2} \{k_7 n_{N_2}\}}{k_6 + (k_7 + k_8)n_{N_2}} \tag{III-3}
\]

where \( k_i (i = 1, \ldots, 8) \) are the rate constants for the processes considered and \( n_{N_2} = P_{N_2} \) is the number density of \( N_2 \) molecules. In Equation (II-3), \( k_1 \) is the absolute rate of electron attachment to \( O_2 \) to form \( O_2^- \) and \( k_3 n_{N_2}/(k_2 + (k_3 + k_4)n_{N_2}) \) is the probability that the electron remains attached to the \( O_2 \) molecule. In the second term in Equation (III-3), \( k_5 n_{N_2} \) is the rate for the formation of the complex and \( k_7 n_{N_2}/(k_6 + (k_7 + k_8)n_{N_2}) \) is the probability that the electron remains on the \( O_2 \) molecule. Consideration of these processes together therefore gives Equation (III-3). Under
the assumption that $k_2 \gg (k_3 + k_4)n_{N_2}$ and $k_6 \gg (k_7 + k_8)n_{N_2}$ we have

$$(\alpha w)_o = A P_{N_2} + B P_{N_2}^2 \quad (III-4)$$

or

$$\frac{(\alpha w)_o}{P_{N_2}} = A + B P_{N_2} \quad (III-5)$$

where $A = k_1k_3/k_2$ and $B = k_5k_7/k_6$.

A plot of $(\alpha w)_o/P_{N_2}$ vs. $P_{N_2}$ indicates good agreement with the predictions as exemplified by Equation (III-5). Such a plot is shown in Figure III-7 for the pressure range $300 \leq P_{N_2} \leq 25,000$ Torr. In this pressure range, the experimental data support the predictions of the proposed model. From a least squares fit to the data in Figure III-7 we obtained

$$A = 88.3 \text{ sec}^{-1} \text{Torr}^{-2} \quad (III-6)$$

$$B = 0.025 \text{ sec}^{-1} \text{Torr}^{-3}$$

2. **$O_2-C_2H_4$ Mixture**

Electron attachment to $O_2$ in ethylene environments has been analyzed on the basis of the following reaction scheme

$$\begin{align*}
e + O_2 & \xrightarrow{k_1'} O_2^- \\
O_2^- & \xrightarrow{k_2'} O_2 + e \\
O_2^- + C_2H_4 & \xrightarrow{k_3'} O_2^- + C_2H_4 + \text{energy}
\end{align*} \quad (III-7)$$
Figure III-7. $(aw)_0/P_{N_2}$ for $\langle \epsilon \rangle = 0.05$ eV.
Under the assumption that the probability of stabilization per collision is unity, we have

$$\frac{1}{(aw)_0} = \frac{1}{k_1} + \frac{k_2'}{k_1'k_3'} \frac{1}{P'_C_2H_4}$$

(III-9)

where \(n_{N_2}\) is the ethylene number density, proportional to \(P'_C_2H_4\). It is convenient to rewrite Equation (III-8) as

$$\frac{1}{(aw)_0} = \frac{k_1'k_3' n_{C_2H_4}}{k_2' + k_3' n_{C_2H_4}} \frac{P'_C_2H_4}{k_2' + k_3' P'_C_2H_4}$$

(III-8)

The experimental data on \((aw)_0\) vs. \(P'_C_2H_4\) are plotted in the manner suggested by Equation (III-9) in Figure III-8 for \(E/P'_{298} = 0.1 \text{ Vcm}^{-1} \text{Torr}^{-1}\). The results are seen to be consistent with Equation (III-9). From a least squares fit to six such plots in the \(E/P'_{298}\) range from 0.1 to 0.5 \text{ Vcm}^{-1} \text{Torr}^{-1} (corresponding to 0.048 \leq \langle \epsilon \rangle \leq 0.064 \text{ eV}) we obtained

$$\frac{1}{k_1'} = 0.43 \times 10^{-7} \text{ sec Torr}$$

$$\frac{k_2'}{k_1'k_3'} = 0.46 \times 10^{-3} \text{ sec Torr}^2$$

whereby \(k_1' = 2.33 \times 10^7 \text{ sec}^{-1} \text{Torr}^{-1}\) and \(k_2'/k_3' = 1.07 \times 10^4 \text{ Torr}^2\).

3. **O\(_2\)-C\(_2\)H\(_6\) Mixtures**

The reaction scheme discussed in the previous section for O\(_2\)-C\(_2\)H\(_4\) mixtures can be assumed to be operative for the O\(_2\)-C\(_2\)H\(_6\) mixtures
Figure III-8. $1/(\alpha w)_0$ as a Function of $1/P_{298}$ for $O_2$ in $C_2H_4$.

The Data are for $E/P_{298} = 0.1 \text{ V cm}^{-1} \text{ Torr}^{-1}$.  

also. Hence

\[
e + O_2 \xrightarrow{k_1} O_2^{-*}
\]

\[
O_2^{-*} \xrightarrow{k_2} O_2 + e
\]

\[
O_2^{-*} + C_2H_6 \xrightarrow{k_3} O_2^- + C_2H_6 + \text{energy}
\]

whereby we have

\[
\frac{1}{(aw)_0} = \frac{1}{k_1} + \frac{k_2}{k_1k_3} \frac{1}{P'_{C_2H_6}}.
\]

Figure III-9 shows a plot of \(1/(aw)_0\) vs. \(1/P'_{C_2H_6}\) for \(E/P'_{298} = 0.1\) Vcm\(^{-1}\) Torr\(^{-1}\). The experimental results are consistent with Equation (III-11) for \(P'_{C_2H_6} < 5000\) Torr, but for \(P'_{C_2H_6} \geq 5000\) Torr the rates are seen to increase faster than predicted by Equation (III-11). The data in Figure III-9 have been fitted by a least squares analysis yielding

\[
1/k_1' = 3.2 \times 10^{-8} \text{ sec Torr}
\]

\[
k_2''/k_1'k_3' = 6.4 \times 10^{-4} \text{ sec Torr}
\]

Using these values, we calculated the rates \((aw)_0\) that would be predicted from the mechanism shown in Equation (III-10) and subtracted these rates from the measured ones to yield a residual rate \((aw)_{ox}\). The residual rates are plotted as a function of \(P'_{C_2H_6}\) in Figure III-10. From a least squares analysis of the residual rates in Figure III-10 we obtained a slope of 4.7.
Figure III-9. $1/(\alpha W)_0$ as a Function of $1/P_{298}$ for $O_2$ in $C_2H_6$.

The Data are for $E/P_{298} = 0.1 \text{ V cm}^{-1} \text{ Torr}^{-1}$. 
Figure III-10. The Residual Attachment Rates, $(\alpha \omega)_{\text{ox}}$, vs. $P_{\text{C}_2\text{H}_6}$. 

$(\alpha \omega)_{\text{ox}}$ ATTACHMENT RATE (10^6 sec⁻¹ Torr⁻¹) 

ETHANE PRESSURE (Torr) 

$P_{\text{C}_2\text{H}_6}$. 
It is evident that electron attachment to $O_2$ in ethane cannot be explained entirely by the reaction scheme in Equation (III-10) but must require one which depends more strongly on $P'_C_{2}H_{6}$. One possible explanation of the rate dependence could be due to electron clustering, i.e.

$$e + (C_2H_6) + O_2 \rightarrow O_2^- + C_2H_6$$  \hspace{1cm} (III-12)

which, on the basis of the slope of Figure III-10, must involve four to five $C_2H_6$ molecules.

\section*{V. AUTOIONIZATION LIFETIME OF $O_2^{-\ast}$}

The analysis in section IV-2 provides an excellent method for determining the absolute rate of electron attachment, $k_1$, and the critical pressure, $P'_c = k_2/k_3$, at which the rate for autoionization is equal to the rate for stabilization. The latter quantity is useful in determining the lifetime $\tau(O_2^{-\ast})$ of the negative ion and can be found from the inverse plots even if the critical pressure were not reached in the experiment. If we have the general stabilization reaction with the negative ion $X^{-\ast}$ and the stabilizing body $S$, then

$$X^{-\ast} + S \rightarrow X^- + S + \text{energy}$$  \hspace{1cm} (III-13)

If we assume that the probability of stabilization of $X^{-\ast}$ per collision is unity, we can estimate the rate of stabilization at the critical pressure $P'_c$ of the stabilizing body $S$. The frequency of collisions $\nu_c$ between $X^{-\ast}$ and $S$ is
\[ \nu_c = v \frac{c}{L} n_c \]  

(III-14)

where \( v \) is the relative velocity of \( X^- \) and \( S \), \( n_c \) is the number density of \( S \) at the critical pressure, and \( \sigma^c_L \) is the classical Langevin cross section for spiraling collisions between \( X^- \) and \( S \) given by

\[ \frac{c}{\sigma^c_L} = \frac{2\pi (e^2 \alpha)}{v M_x} \frac{1}{2} \]  

(III-15)

In Equation (III-15), \( \alpha \) is the static polarizability of \( S \), \( e \) is the electronic charge, and \( M_x \) is the reduced mass of \( X^- \) and \( S \). From Equations (III-14) and (III-15) we have for the average lifetime between collisions

\[ \tau_c = \nu_c^{-1} = \frac{1}{2\pi n_c} \frac{(M_x)}{e^2 \alpha} \frac{1}{2} \]  

(III-16)

From Equation (III-16) we can approximate the lifetime of \( X^- \), \( \tau(X^-) \), by \( \tau(X^-) \approx \tau_c \). If the quantum mechanical expression for spiraling collisions, \( \sigma^q_L = 4\pi/v (e^2 \alpha)^{1/2} /M_x \) [Vogt and Wannier (1954)], is used, then the lifetime is one half that calculated on the basis of Equation (III-16).

For the \( O_2^- - C_2H_4 \) system we calculated a lifetime \( \tau_c(O_2^-) \) of \( 1.9 \times 10^{-12} \) sec using \( \alpha_{C_2H_4} = 42.6 \times 10^{-25} \) cm\(^3\), taken from the work of Landolt and Bornstein (1951), and \( P_c = 10,700 \) Torr. Therefore, \( \tau(O_2^-) = k^{-1} = 1.9 \times 10^{-12} \) sec. This value is in agreement with an earlier estimate by Christophorou (1972) and with a value deduced recently by Linder and Schmidt (1971) using electron scattering methods.
VI. EXTRAPOLATION TO THE LIQUID STATE

1. \(O_2-N_2\) Mixtures

At 25,000 Torr the \(N_2\) density is 0.04 gm/cm\(^3\) which is a factor of \(\sim 20\) lower than the density of liquid nitrogen. If it is assumed that the model proposed in section IV is valid over the entire density range up to the liquid regime we find that

\[
(\omega_0) (\epsilon \approx 0.04 \text{ eV}) = 0.74 \times 10^{10} \text{ sec}^{-1} \text{ Torr}^{-1}
\]

for \(O_2\) in liquid \(N_2\). This value compares favorably with \((\omega_0) = \sigma_a v = 1.1 \times 10^{10} \text{ sec}^{-1} \text{ Torr}^{-1}\) obtained from using \(\sigma_a = \pi \lambda^2\), where \(\lambda = 2\pi \hbar/\epsilon\) is the de Broglie wavelength for a 0.04 eV electron. This observation may indicate that the proposed model holds reasonably well over the entire range of \(N_2\) densities up to that of the liquid.

2. \(O_2-C_2H_4\) Mixtures

The analysis in Figure III-8, page 41, is an excellent way to predict liquid density behavior from attachment studies in the high pressure gas phase. The lowest data point in Figure III-8 is very close to the \(y\) axis and the intercept of the straight line can thereby be determined quite precisely, giving \((\omega_0)\) for \(P_{C_2H_4} \rightarrow \infty\). From an extrapolation of the gas data one obtains \([\omega_0]_{\text{intercept}} = 2.3 \times 10^7 \text{ sec}^{-1} \text{ Torr}^{-1} = 4.3 \times 10^{11} \text{ sec}^{-1} \text{ M}^{-1}\). At the density of liquid ethylene Equation (III-9) predicts that \([\omega_0]_{\text{liquid}} = 3.3 \times 10^{11} \text{ sec}^{-1} \text{ M}^{-1}\).
There appear to be no data on the attachment of electrons to \( O_2 \) in liquid ethylene but Bakale and Schmidt (1973) have reported a rate of \( 5 \times 10^{11} \) sec\(^{-1} \) M\(^{-1} \) for \( O_2 \) in neopentane and a rate of \( 5.2 \times 10^{11} \) sec\(^{-1} \) M\(^{-1} \) for \( O_2 \) in neohexane, both at 296°K. Richards and Thomas (1971) have reported a rate of \( 1.5 \times 10^{11} \) sec\(^{-1} \) M\(^{-1} \) for \( O_2 \) in n-hexane at 193°K. These values are in reasonable agreement with the one we predicted for \( O_2 \) in liquid \( C_2H_4 \). This agreement may indicate that the process of thermal electron capture by \( O_2 \) in \( C_2H_4 \) is well understood over the entire density range. The ethylene molecule simply acts as a stabilizing third body over the density range from the low pressure gas to the liquid regime.

3. \( O_2-C_2H_6 \) Mixtures

The simplicity of the ethylene behavior is not evident for the case of ethane and it was not possible to formulate a model to describe the behavior of \( (\alpha \omega)_o \) in high densities of \( C_2H_6 \). Because of this, it was not possible to predict \( (\alpha \omega)_o \) for \( O_2 \) in liquid ethane.

VII. THREE-BODY RATE COEFFICIENTS

The three-body coefficients for the reactions

\[
e + O_2 + N_2 \rightarrow O_2^- + N_2 + \text{energy} \quad (\text{III}-17)
\]
\[
e + O_2 + C_2H_4 \rightarrow O_2^- + C_2H_4 + \text{energy} \quad (\text{III}-18)
\]
\[
e + O_2 + C_2H_6 \rightarrow O_2^- + C_2H_6 + \text{energy} \quad (\text{III}-19)
\]
have been determined from the linear portions of the \( (\alpha \omega)_o \) vs. \( P'_{x} (x = N_2, C_2H_4, \text{and } C_2H_6) \) graphs for a number of mean energies \( \langle \epsilon \rangle \). These coefficients as well as the ones determined earlier by McCorkle et al. (1972) for the reaction

\[
e + O_2 + O_2 \rightarrow O_2^- + O_2 + \text{energy}
\]  

(III-20)

are plotted in Figure III-11 as a function of \( \langle \epsilon \rangle \). The energy scale for reactions (III-17) and (III-20) was established by determining \( \langle \epsilon \rangle \) from the known distribution functions for \( N_2 \) [see Christorou (1971a)]. The energy calibration for (III-18) and (III-19) has been discussed earlier in sections II and III. In Figure III-11 the solid curves are the early results of Chanin et al. (1962). McCorkle et al. (1972) argued that the energy scale used by Chanin et al. was in error and replotted (broken curve in Figure III-11) this data using mean energies obtained from the known electron distribution functions in \( N_2 \). The replotted data are seen to be in good agreement with the results of McCorkle et al. and on the basis of this agreement it was suggested that a similar correction might be necessary in the case of Equation (III-20).

However, no correction was made because the distribution functions for pure \( O_2 \) are not known.

From the analysis of the three-body coefficients one can conclude that \( C_2H_4 \) and \( C_2H_6 \) have comparable efficiencies in stabilizing \( O_2^- \). No other information on the three-body coefficients for reactions (III-18) and (III-19) exist as a function of \( \langle \epsilon \rangle \). Thermal (\( \sim 300^\circ K \)) values equal to
Figure III-11. Three-body Attachment Coefficients as a Function of $\langle \epsilon \rangle$ for $e + O_2 + O_2 \rightarrow O_2^- + O_2 + \text{energy}$; $e + O_2 + N_2 \rightarrow O_2^- + N_2 + \text{energy}$; $e + O_2 + C_2H_4 \rightarrow O_2^- + C_2H_4 + \text{energy}$; $e + O_2 + C_2H_6 \rightarrow O_2^- + C_2H_6 + \text{energy}$.

See Text for Explanation of Symbols.
3.1 \times 10^{-30} \text{ cm}^6 \text{ sec}^{-1} \ [\text{Stockdale et al. (1967)}], 1.7 \times 10^{-30} \text{ cm}^6 \text{ sec}^{-1} \ [\text{Bouby et al. (1967)}], \text{ and } 2.5 \times 10^{-30} \text{ cm}^6 \text{ sec}^{-1} \ [\text{Bouby et al. (1970)}] \text{ have been reported but these values probably correspond to } \langle \epsilon \rangle \geq 0.05 \text{ eV. From the present data in Figure III-11 it is seen that the three-body coefficient has a value of } 1.54 \times 10^{-30} \text{ cm}^6 \text{ sec}^{-1} \text{ at } \langle \epsilon \rangle = 0.05 \text{ eV.}
CHAPTER IV

ATTACHMENT OF SLOW ELECTRONS TO $\text{C}_6\text{H}_6$ IN HIGH PRESSURE GASES

I. INTRODUCTION

An extensive series of experiments have been performed using the high pressure swarm apparatus to determine whether benzene ($\text{C}_6\text{H}_6$) attaches slow electrons (≤ 0.3 eV) in the gas phase at moderate carrier-gas densities ($2000 \leq P \leq 10,000$ Torr). Previously, Compton et al. (1966) discovered a compound negative ion resonance state (CNIR) in $\text{C}_6\text{H}_6$ using slow electrons with $\epsilon \sim 1.4$ eV. Christophorou and Blaunstein (1969) also examined electron attachment to $\text{C}_6\text{H}_6$ at 400 Torr in a swarm experiment and placed an upper limit of $\sim 1 \times 10^3$ sec$^{-1}$ Torr$^{-1}$ to the attachment rate at 400 Torr. The benzene negative ion has been observed to exist in the liquid state by several investigators [Tuttle and Weissman (1966), Hoijtink and Zandstra (1960), Gardner (1966), and Giling and Kloosterboer (1973)]. In view of these findings, it seemed desirable to examine the possibility that $\text{C}_6\text{H}_6$ attaches slow electrons in the gas phase at moderate densities.

II. EXPERIMENTAL DIFFICULTIES

Benzene has been found to attach slow (≤ 0.3 eV) electrons in dense $\text{N}_2$ environments over the range $2000 \leq P_{\text{N}_2} \leq 10,000$ Torr. In order to confirm these results and to clear up certain experimental difficulties,
additional experiments using Ar, C_2H_4, and a mixture of N_2 and C_2H_4 as carrier gases were also performed. These experiments will be described later in this chapter. Benzene is very difficult to study because of its low attachment rate (\sim 10^3 \text{ sec}^{-1} \text{ Torr}^{-1}) and because of the possibility that this rate might arise from impurities contained in the sample. The measurement of such low rates, however, is well within the capability of the experimental system (see Chapter II). Because of this reason and because of the fact that no other investigators have observed C_6H_6^- in the gas phase, we felt that it would be prudent to examine the possibility that contaminants could contribute significantly to the attachment rate.

Oxygen is always a suspect as a contaminant because the liquid benzene initially contains dissolved O_2. Before beginning measurements on C_6H_6, O_2 is removed from the sample by freezing the solution to \sim -70°C in a dry-ice-acetone bath and pumping until there is a vacuum of 1 \times 10^{-6} Torr above the liquid. C_6H_6 is then frozen at liquid N_2 temperatures until a vacuum of \sim 5 \times 10^{-7} Torr is attained. Measurements on samples prepared in this way agree within \pm 20\% from sample to sample. In view of these precautions it seems unlikely that O_2 contributes significantly to the attachment rate. This contention is supported by the observation that the rates for attachment to C_6H_6 are much different from those measured previously for attachment to O_2 (see Chapter III).
It also seemed desirable to examine the possibility that electron attaching contaminants could be introduced from the walls of the chamber and from the tubing leading from the sample container to the chamber. These hypotheses were tested by leaving the benzene in the tubing and the chamber for three to five hours before initiating the experiment. Rates measured following this procedure were entirely consistent with those obtained in the usual manner. It seems very unlikely that contaminants could be introduced from the walls since the system is pumped out to \( \sim 1 \times 10^{-8} \text{Torr} \) at the conclusion of each experiment and the outgas rate is \( < 0.2 \mu/\text{hr} \).

The benzene samples used were obtained from James Hinton and Company and were of a quoted purity of 99.999%. Additional experiments were performed to test whether the 0.001% impurity contributed measurably to the rate. The sample was heated to various temperatures in the range from 25°C to 70°C under the hypothesis that the impurity would have a different partial pressure at each temperature and would presumably cause a temperature dependence to the attachment rate. The results of these experiments were entirely consistent with the results at room temperature. In order for a 0.001% impurity to cause a measured rate of \( \sim 1 \times 10^3 \text{sec}^{-1} \text{Torr}^{-1} \) it must have an attachment rate of \( \sim 1 \times 10^8 \text{sec}^{-1} \text{Torr}^{-1} \) at 2000 Torr. In view of the pressure dependence of the attachment rate (see Figure IV-1) the process would have to be a nondissociative one. It seems unlikely that a nondissociative process could have such a high rate.
Figure IV-1. Attachment Rate \((\alpha\omega)_0\) for \(C_6H_6\) in \(N_2\) as a Function of (a) \(E/P_{298}\) and (b) \(<\epsilon>\), at the Indicated \(N_2\) Pressures.
and such a short lifetime ($\sim 10^{-13}$ sec) as estimated in section IV. In view of these findings we concluded that benzene is indeed the attaching species.

III. EXPERIMENTAL RESULTS

1. C$_6$H$_6$ in N$_2$

A. Absolute Rate of Electron Attachment to C$_6$H$_6$ in High Densities of N$_2$

The attachment of slow electrons ($\lesssim 0.3$ eV) to C$_6$H$_6$ has been observed in C$_6$H$_6$-N$_2$ mixtures for $5 \leq P_{C_6H_6} \leq 10$ Torr and $P_{N_2} > 2000$ Torr. Figure IV-1 presents the attachment rate $(\omega)_{o}$ for $P_{C_6H_6} \rightarrow 0$, as a function of the pressure-reduced electric field, $E/P_{298}$, and the mean electron energy ($\langle \epsilon \rangle$). The rates were found to be independent of $P_{C_6H_6}$ within experimental error. The rates in Figure IV-1 are seen to increase with increasing $P_{N_2}$ and to reach their maximum at a given $P_{N_2}$ at thermal ($\approx 0.04$ eV) energies. Figure IV-2 shows $(\omega)_{o}$ as a function of $P_{N_2}$. The rates are seen to increase linearly with $P_{N_2}$ for $P_{N_2} < 6000$ Torr and to increase at a less than linear rate for $P_{N_2} > 6000$ Torr. Furthermore, the higher the $\langle \epsilon \rangle$, the higher the N$_2$ range over which $(\omega)_{o}$ increases linearly with $P_{N_2}$. This is a result of the fact that the lifetime, $\tau(C_6H_6^{-*})$, of C$_6$H$_6^{-*}$ decreases with $\langle \epsilon \rangle$. The calculation of $\tau(C_6H_6^{-*})$ will be discussed in section IV.
Figure IV-2. Attachment Rate \((\alpha w)_0\) for \(C_6H_6\) as a Function of 
\(P_{N_2}\) for the Indicated \(<\epsilon>\).

The Broken Lines are a Linear Least-Squares Fit to the Data for \(P_{298} \leq 6000\) Torr.
B. Electron Attachment Cross Sections

Absolute cross sections, $\sigma_a(\epsilon)$, for the attachment of electrons to $C_6H_6$ to form $C_6H_6^-$ have been calculated using the swarm unfolding technique discussed in Chapter II. The results are presented in Figure IV-3 for $P_{N_2} = 2000$ Torr and for $P_{N_2} = 9500$ Torr. Results similar to these were obtained at intermediate pressures. The peak energy ($\sim 0.04$ eV) is relatively pressure independent. The full width at half maximum varies from $0.026$ eV at 2000 Torr to $0.042$ eV at 9500 Torr with some indication that it increases with increasing $P_{N_2}$.

C. Three-Body Rate Coefficients

The three-body rate coefficients for the reaction

$$e + C_6H_6 + N_2 \rightarrow C_6H_6^- + N_2 + \text{energy} \quad (IV-1)$$

have been determined from the linear portion of the $(\alpha \omega)_0$ vs. $P_{N_2}$ curves in Figure IV-2 (dotted lines). These values are energy dependent and are presented in Figure IV-4.

2. $C_6H_6$ in $C_2H_4$, in Ar, and in $C_2H_4-N_2$ Mixtures

In order to verify the attachment results for $C_6H_6-N_2$ mixtures, electron attachment studies were undertaken with $C_6H_6$ in $C_2H_4$ for $P_{C_2H_4}' \leq 13,000$ Torr. However, it was impossible to detect any attachment in such mixtures. In view of the results presented for $C_6H_6$ in high densities of $N_2$, this was entirely unexpected. Additional experiments on
Figure IV-3. $\sigma_\alpha(\epsilon)$ as a Function of $\langle \epsilon \rangle$ for $C_6H_6$ in $N_2$ for $P_{N_2} = 2000$ Torr and $P_{N_2} = 9500$ Torr.
Figure IV-4. Three-body Attachment Coefficients as a Function of \( \langle \epsilon \rangle \) for \( e + \text{C}_6\text{H}_6 + \text{N}_2 \rightarrow \text{C}_6\text{H}_6^- + \text{N}_2 + \text{energy} \).
C$_6$H$_6$ in argon and in N$_2$-C$_2$H$_4$ mixtures were then performed to resolve the question of electron attachment to benzene.

Figure IV-5 shows the attachment coefficient, $\alpha$, as a function of $P_{C_6H_6}/P_{Ar}$ for $P_{Ar} = 5000$ Torr and 10,000 Torr. Results are presented for $0.002 \leq E/P_{298} \leq 0.005$. These $E/P$'s correspond [Christophorou (1971a)], to mean energies of 0.25, 0.31, 0.35, and 0.38 eV, respectively. The marked decrease in $\alpha$ with increasing $P_{C_6H_6}/P_{Ar}$ indicates that C$_6$H$_6$ causes a severe perturbation in the argon distribution functions. The data in Figure IV-5 will be considered to be very approximate and will not be analyzed further. These data do, however, provide concrete verification that C$_6$H$_6$ attaches low energy electrons.

Figure IV-6 shows the results of an experiment on the attachment of electrons to C$_6$H$_6$ to form C$_6$H$_6$ in a mixture of C$_2$H$_4$ and N$_2$. In this study, $P_{C_6H_6} = 8$ Torr, $P_{total} = 5000$ Torr and $100 \leq P_{C_2H_4} \leq 500$ Torr. The data in Figure IV-6 were taken at an $E/P_{298}$ of 0.022 V cm$^{-1}$ Torr$^{-1}$. At this $E/P_{298}$, the drift velocity of electrons in C$_2$H$_4$ is equal to that for electrons in N$_2$ within experimental error ($w_{N_2} = 1.94 \times 10^5$ cm sec$^{-1}$), and hence no correction is needed as the partial pressure $P_{C_2H_4}/P_{N_2}$ is changed.

The distribution function for electrons in N$_2$ and in C$_2$H$_4$ is approximately Maxwellian at this $E/P$, thereby requiring no correction for mixture composition.

The results in Figure IV-6 indicate that C$_6$H$_6$ does attach electrons in C$_2$H$_4$-N$_2$ mixtures but that $(\omega \nu)$ is a sharply decreasing function of
Figure IV-5. Attachment Coefficient $\alpha$ as a Function of $\frac{P_{C_6H_6}}{P_{Ar}}$ for Total Pressures of 5 and $10 \times 10^3$ Torr and $E/P_{298}$ Values 2, 3, 4, and $5 \times 10^{-3}$ V cm$^{-1}$ Torr$^{-1}$. 
Figure IV-6. Attachment Rate as a Function of Percent of C\textsubscript{2}H\textsubscript{4} in a Mixture of C\textsubscript{6}H\textsubscript{6}, C\textsubscript{2}H\textsubscript{4}, and N\textsubscript{2} at a Total Pressure of 5000 Torr and an E/P\textsubscript{298} of 0.022 V cm\textsuperscript{-1} Torr\textsuperscript{-1}.

The C\textsubscript{6}H\textsubscript{6} Pressure was Fixed at 8 Torr.
A mechanism which explains this decrease will be described in the next section.

IV. DISCUSSION

1. Reaction Scheme for Electron Attachment to $\ce{C6H6}$ in High Densities of $\ce{N2}$

It is possible to explain the results on $\ce{C6H6-N2}$ mixtures in terms of the following model:

\[ \text{e} + \ce{C6H6} \xrightarrow{k_1} \ce{C6H6}^- \]  
(IV-2)

\[ \ce{C6H6}^- \xrightarrow{k_2} \ce{C6H6} + \text{e} \]  
(IV-3)

\[ \ce{C6H6}^- + \ce{N2} \xrightarrow{k_3} \ce{C6H6}^- + \ce{N2} + \text{energy} \]  
(IV-4)

whereby

\[ \alpha w = \frac{k_1 k_3 n_{\ce{N2}}}{k_2 + k_3 n_{\ce{N2}}} \]  
(IV-5)

where $n_{\ce{N2}}$ is the nitrogen density, proportional to $P_{\ce{N2}}$. Equation (IV-5) can be put into the form

\[ \frac{1}{\alpha w} = \frac{1}{k_1} + \frac{k_2}{k_3} \frac{1}{P_{\ce{N2}}} \]  
(IV-6)

The $\ce{C6H6}$ attachment data have been plotted in Figure IV-7 in the manner...
Figure IV-7. $1/(\alpha w)_0$ as a Function of $1/P_{298}$ for $C_6H_6$ in $N_2$ for the Indicated Values of $\langle \epsilon \rangle$. 
suggested by Equation (IV-6) and it is seen that the data are consistent
with the proposed model. The intercept \(1/k_1\) is seen to be independent of
\(\langle \epsilon \rangle\) and the slope \(k_2/k_3\) is seen to increase with increasing \(\langle \epsilon \rangle\). A least
squares fit to the data in Figure IV-7 yields 
\[ k_1 = 5 \times 10^4 \text{ sec}^{-1} \text{ Torr}^{-1} \]
and the values \(k_2/k_3\) that are presented in Table IV-1.

2. **Autodetachment Lifetime**

The analysis in the previous section is an excellent way to obtain
the critical pressure \(P_c = k_2/k_3\) at which the rate of autoionization equals
the rate of stabilization. \(P_c\) can be determined from the least squares fit
without actually having been reached experimentally. This is fortunate
since it is impossible to obtain reliable data in the ultrahigh pressure regime.
From Table IV-1, \(P_c\) is seen to vary from 44,000 Torr to 200,000 Torr. In
order to estimate the autodetachment lifetime we calculate the average time,
\(\tau_c\), between collisions of \(X^\pm(C_6H_6^\pm)\) and \(S(N_2)\) as given in Equation (III-16).
Using Equation (III-16), the values of \(P_c\) in Table IV-1, and the assumption
that the probability of stabilization per collision, \(p\), is unity, we determined
the lifetimes listed in column 4 of Table IV-1. These are seen to lie in the
pico and subpicosecond range. \(\tau(C_6H_6^\pm)\) is found to be energy dependent as is
shown in Figure IV-8. If \(p < 1\), the average time for stabilizing \(C_6H_6^\pm\) in
collisions with \(N_2\) will be greater than \(\tau_c\); therefore

\[ \tau(C_6H_6^\pm)_{p < 1} > \tau(C_6H_6^\pm)_{p = 1} \]  \hspace{1cm} (IV-7)

The lifetimes in Table IV-1 are seen to be lower limit estimates.
<table>
<thead>
<tr>
<th>$\langle \epsilon \rangle$ (eV)</th>
<th>$k_1$ (sec$^{-1}$ Torr$^{-1}$)</th>
<th>$k_2/k_3$ ($\equiv P_c$) (Torr)</th>
<th>$\tau_a (C_6H_6^-)$ (sec)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.040</td>
<td>$5 \times 10^4$</td>
<td>$4.4 \times 10^4$</td>
<td>$10.4 \times 10^{-13}$</td>
</tr>
<tr>
<td>0.063</td>
<td>$5 \times 10^4$</td>
<td>$5.5 \times 10^4$</td>
<td>$8.3 \times 10^{-13}$</td>
</tr>
<tr>
<td>0.087</td>
<td>$5 \times 10^4$</td>
<td>$7.0 \times 10^4$</td>
<td>$6.5 \times 10^{-13}$</td>
</tr>
<tr>
<td>0.109</td>
<td>$5 \times 10^4$</td>
<td>$9.2 \times 10^4$</td>
<td>$5.0 \times 10^{-13}$</td>
</tr>
<tr>
<td>0.131</td>
<td>$5 \times 10^4$</td>
<td>$1.25 \times 10^5$</td>
<td>$3.6 \times 10^{-13}$</td>
</tr>
<tr>
<td>0.181</td>
<td>$5 \times 10^4$</td>
<td>$2.0 \times 10^5$</td>
<td>$2.3 \times 10^{-13}$</td>
</tr>
</tbody>
</table>
Figure IV-8. Variation of the Autodetachment Lifetime of $C_6H_6^{-\ast}$ with Mean Electron Energy $\langle e \rangle$. 
3. Extrapolation to the Liquid State

The analysis in part 2 is also seen to be an excellent way to determine $k_1$, the absolute rate of electron attachment to $C_6H_6$ in the limit $P_{N_2} \to \infty$. $k_1$ is the attachment rate that would be measured if the $N_2$ density were great enough so that every negative ion were stabilized. This rate should be very close to that expected for electron attachment in the liquid state, that is

$$[(\omega w)_o]_{\text{intercept}} \approx [(\omega w)_o]_{\text{liquid}}$$

(IV-8)

For liquid $N_2$ and $\langle \epsilon \rangle = 0.04 \text{ eV}$ we have $[(\omega w)_o]_{\text{liquid}} = k_1 = 5 \times 10^4 \text{ sec}^{-1}$ Torr$^{-1} = 1 \times 10^9 \text{ sec}^{-1} \text{ M}^{-1}$. No measurements have been made of the rate of attachment of electrons to $C_6H_6$ in liquid nitrogen but a thermal attachment rate $\leq 1 \times 10^9 \text{ sec}^{-1} \text{ M}^{-1}$ has been reported by Bakale et al. (1972) for $C_6H_6$ in liquid n-hexane. This value is in good agreement with the present finding.

4. Importance of the Experimental Results with $C_2H_4$

The drastic decrease in the attachment rate, $(\omega w)_{\text{mix}}$, with increasing $P_{C_2H_4}$ (Figure IV-6, page 63) indicates that collisional detachment is an important mechanism to consider in the model presented earlier. In order to include collisional detachment we must have, in addition to Equations (IV-2)-(IV-4), the reactions:

$$C_6H_6 + N_2 \xrightarrow{k_7} C_6H_6 + N_2 + e$$

(IV-9)
Consideration of Equations (IV-2) to (IV-4) and (IV-9) to (IV-11) gives for the attachment of electrons to \( C_6H_6 \) in \( N_2-C_2H_4 \) mixtures:

\[
\frac{\{k_3P_{N_2} + k_7'P_{C_2H_4}\}}{(\alpha w)_{mix} = k_1k_2 + (k_3 + k_7)P_{N_2} + (k_3' + k_7')P_{C_2H_4}}.
\]  

(IV-12)

Under the assumption that \( k_3P_{N_2} \gg k_3'P_{C_2H_4} \) we have:

\[
\frac{(\alpha w)_{N_2}}{(\alpha w)_{mix}} \approx 1 + \frac{k_7'P_{C_2H_4}}{k_2 + (k_3 + k_7)P_{N_2}}.
\]  

(IV-13)

where \((\alpha w)_{N_2}\) is the rate for the \( C_6H_6-N_2 \) system and \((\alpha w)_{mix}\) is the rate for the \( C_6H_6-N_2-C_2H_4 \) system. The previous assumption is valid since, experimentally, the rates for attachment to \( C_6H_6 \) in \( N_2 \) environments are much larger than those in \( C_2H_4 \) environments. At \( P_{\text{total}} = 5000 \) Torr, the rates for the \( C_6H_6-N_2 \) system are still well within the three-body region so that \( k_2 \gg (k_3 + k_7)P_{N_2} \). Therefore,
(\omega N_2)_N \approx 1 + \frac{k_7'}{k_2} \frac{P_{C_2H_4}}{(\omega)_{\text{mix}}} \quad \text{(IV-14)}

Figure IV-9 shows the data plotted in the manner suggested by Equation (IV-14). It can be seen that the data provide good agreement with the revised model. A linear least squares fit to the data in Figure IV-9 gives $k_7'/k_2 = 2.8 \times 10^{-3}$ Torr$^{-1}$. Therefore, at 1000 Torr total pressure, collisional detachment is 2.8 times as probable as autoionization. If we take $\tau_a(= k_{2^{-1}}) = 4 \times 10^{-13}$ sec, then $k_7' = 7.0 \times 10^9$ sec$^{-1}$ Torr$^{-1}$. The rate for collisional detachment is very high and is indicative of the importance of this mechanism in $C_2H_4$.

The analysis on electron attachment to $C_6H_6$ in $N_2$ was performed under the assumption that collisional detachment is unimportant in that system ($k_3 \gg k_7$). In view of the magnitude of $k_7'$ it might be necessary to revise those results taking collisional detachment into consideration.

However, the importance of such a process seems to be a function of the stabilizing body and also perhaps of the metastable ion itself since detachment was not observed to be significant in $O_2-N_2$ and in $O_2-C_2H_4$ mixtures (see Chapter III). Actually, in the case of $O_2^-, C_2H_4$ was found to be more efficient in stabilizing the negative ion than was $N_2$.

5. The Electron Affinity of $C_6H_6$

Many theoretical estimates have been made of the electron affinity, $E_{A_B}$, of benzene; these calculations justify the commonly accepted value of
Figure IV-9. \( \frac{(\alpha w)_{N_2}}{(\alpha w)_{\text{mix}}} \) vs. \( P_{C_2H_4} \) in a Mixture of \( C_6H_6, C_2H_4, \) and \( N_2 \) at a Total Pressure of 5000 Torr.

The \( C_6H_6 \) Pressure was kept Constant at 8 Torr.
-1.4 eV (see Table IV-2). Compton, Christophorou, and Huebner (1966) observed a compound negative ion resonance (CNIR) in $\text{C}_6\text{H}_6^-$ with an onset at $\sim 0.9$ eV and a maximum at $\sim 1.4$ eV. In view of these findings $E_{AB} \geq -0.9$ eV. Considering the present result which indicates that $\text{C}_6\text{H}_6^-$ exists in the gas phase, we must conclude that $E_{AB} > 0$ eV. We would expect $E_{AB}$ to be very small in light of the small lifetime estimated for $\text{C}_6\text{H}_5^-$ in section 2. The value of $-1.4$ eV may correspond to the vertical attachment energy. This quantity is defined [see Christophorou (1971a)] as the energy difference between the neutral molecule in its ground rotational, vibrational, and electronic states plus an electron at rest at infinity and the molecular negative ion formed without a change in internuclear separation. Since many of the theoretical estimates of $E_{AB}$ yield values close to the vertical attachment energy it would seem that their calculations neglected nuclear relaxation. In light of the finding that $E_{AB} > 0$ we must conclude that the potential energy surface of $\text{C}_6\text{H}_6^-$ lies below that of $\text{C}_6\text{H}_6$ with its minimum at considerably greater internuclear separations.
Table IV-2

Literature Values for the Electron Affinity of Benzene;
Threshold of Lowest CNIR State of Benzene

<table>
<thead>
<tr>
<th>Electron Affinity (eV)</th>
<th>Reference and Method</th>
<th>Threshold of Lowest CNIR State (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>-1.63</td>
<td>1^a</td>
<td>0.9 ± 0.3</td>
</tr>
<tr>
<td>-1.62</td>
<td>2^a</td>
<td>0.95</td>
</tr>
<tr>
<td>-1.59</td>
<td>3</td>
<td></td>
</tr>
<tr>
<td>-1.42</td>
<td>4^a</td>
<td></td>
</tr>
<tr>
<td>-1.4</td>
<td>5-7^a</td>
<td></td>
</tr>
<tr>
<td>-0.36</td>
<td>8^b</td>
<td></td>
</tr>
<tr>
<td>-0.06</td>
<td>9^a</td>
<td></td>
</tr>
</tbody>
</table>

^a Theory.
^b Kinetics of electrode processes.

Table IV -2 (continued)

CHAPTER V

ATTACHMENT OF LOW ENERGY ELECTRONS TO $\text{C}_2\text{H}_5\text{Br}$

IN HIGH DENSITIES OF $\text{N}_2$ AND $\text{Ar}$

I. INTRODUCTION

Continuing our effort to link together knowledge on electron attachment in dilute gases and in condensed media we investigated low energy (< 3 eV) electron attachment to bromoethane ($\text{C}_2\text{H}_5\text{Br}$) in mixtures with $\text{N}_2$ for $P_{\text{N}_2} \leq 25,000$ Torr (~ 33 atm) and in mixtures with argon for $P_{\text{Ar}} \leq 42,500$ Torr (~ 56 atm). Dissociative electron attachment to $\text{C}_2\text{H}_5\text{Br}$ has been investigated previously by Christodoulides and Christophorou (1971) using swarm techniques at relatively low total pressures (~ 1.3 atm) and by Collins, Christophorou and Carter (1970) using a time-of-flight mass spectrometer. These results were discussed within the framework of the resonance-scattering theory of dissociative electron attachment to diatomic molecules [see Bardsley, Herzenberg and Mandl (1964, 1966), Bardsley and Mandl (1968), and O'Malley (1966)] and provided evidence that dissociative electron attachment proceeds via a short-lived compound negative ion state. Since $\text{Br}^-$ was the only ion observed in the mass spectrometer, it was reasonable to consider $\text{C}_2\text{H}_5\text{Br}$ as a diatomic-like molecule $\text{R-Br}$ as far as dissociative attachment is concerned.
In the present study \( C_2H_5Br \) has been found to capture slow (< 3 eV) electrons in high densities of \( N_2 \) and \( Ar \) with a cross section which increases with increasing carrier gas density. The dependence of the attachment rate on carrier gas density has been studied in detail and a model is presented which accounts for the experimental results. In addition, certain differences between the present study and the previous ones [Christodoulides et al. (1971), and Collins et al. (1970)] will be presented and discussed.

II. EXPERIMENTAL RESULTS

The bromoethane used in this study was purchased from Matheson, Coleman and Bell, Inc. and was of a quoted purity of 99.9%. The ratio of the nitrogen carrier gas pressure, \( P_{N_2} \), to the sample gas pressure, \( P_{C_2H_5Br} \), was in the range \( 1 \times 10^{-5} \leq \frac{P_{N_2}}{P_{C_2H_5Br}} \leq 5 \times 10^{-6} \). The ratio of the argon carrier gas pressure, \( P_{Ar} \), to the sample gas pressure was in the range \( 1 \times 10^{-5} \leq \frac{P_{Ar}}{P_{C_2H_5Br}} \leq 1 \times 10^{-7} \). All measurements were made at room temperature (298°K). Neither argon nor nitrogen pressures were corrected for compressibility because the correction is small even at the highest pressures used.

The dependence of the attachment rate, \( (\alpha w)_0 \), on the pressure-reduced electric field, \( E/P_{298} \), and the mean electron energy, \( \langle \epsilon \rangle \), is shown in Figure V-1 for the indicated \( N_2 \) pressures. The values of the drift velocity, \( w \), and the mean electron energy, \( \langle \epsilon \rangle \), were taken from Christophorou (1971a). As in earlier studies, \( (\alpha w)_0 \) designates the value of
Figure V-1. Attachment Rate, \((aw)_0\), as a Function of \(E/P_{298}\) and \(\langle \epsilon \rangle\) for \(\text{C}_2\text{H}_5\text{Br}\) in \(\text{N}_2\) for the Indicated \(\text{N}_2\) Pressures.
\( \alpha w \) as \( P_{C_2H_5Br} \to 0 \). However, in the experiments with \( N_2 \), there was no observable partial pressure dependence to \( \alpha w \). In Figure V-2 we show \( (\alpha w)_o \) as a function of both \( E/P_{298} \) and \( \langle \epsilon \rangle \) for argon as a carrier gas. Care was taken to keep the sample pressure low (\( \leq 20 \mu \)) so that the argon distribution functions are not disturbed appreciably. Figure V-3 presents the partial pressure dependence of the rate at a total pressure of 500 Torr. This case was selected because it shows the most drastic partial pressure dependence for low \( \langle \epsilon \rangle \). For high \( P_{Ar} \) and for \( \langle \epsilon \rangle \geq 1 \text{ eV} \), \( \alpha w \) is independent of \( P_{C_2H_5Br} \), but at low \( \langle \epsilon \rangle \) and low \( P_{Ar} \), there is a significant partial pressure dependence. The rates presented in this chapter for each \( P_{Ar} \) are those extrapolated to \( P_{C_2H_5Br} = 0 \text{ Torr} \).

The data for electron attachment to \( C_2H_5Br \) in \( N_2 \) and \( Ar \) media indicate that the attachment rates increase with increasing carrier gas pressure. In Figures V-4 and V-5 \( (\alpha w)_o \) is presented as a function of \( P_{N_2} \) and \( P_{Ar} \), respectively, for a number of \( \langle \epsilon \rangle \). It is seen that, initially, \( (\alpha w)_o \) increases linearly with \( P_x (x = N_2, Ar) \), but as \( P_x \) increases further, \( (\alpha w)_o \) shows a less than linear dependence on \( P_x \). At the highest values of \( P_x \), \( (\alpha w)_o \) is seen to be virtually pressure independent. These results will be discussed further in section III where a model will be proposed to account for the observed rates.

In Figure V-6, the attachment rates extrapolated to zero total pressure for both the present work and the earlier study [Christodoulides and Christophorou (1971)] are shown. From these data, it is evident that
Figure V-2. Attachment Rate, \((\omega_0)\), as a Function of \(E/P_{298}\) and \(\langle \epsilon \rangle\) for \(\text{C}_2\text{H}_5\text{Br}\) in Ar.
Figure V-3. The Partial Pressure Dependence of $(\alpha \omega)_0$ for C$_2$H$_5$Br in Ar at $P_{Ar} = 500$ Torr.
Figure V-4. The Attachment Rate, $(\omega w)_0$, for C$_2$H$_5$Br in N$_2$ as a Function of PN$_2$ for Several $\langle \epsilon \rangle$. 
Figure V-5. The Attachment Rate, \((aw)_o\), for \(C_2H_5Br\) in \(Ar\) as a Function of \(P_{Ar}\) for Several \(\langle \epsilon \rangle\).
Figure V-6. The Attachment Rates Extrapolated to Zero Total Pressure for the Present Work and the Work of Christodoulides and Christophorou.

(*) - Present Data for N₂; (O) - Present Data for Ar; (▲) - Previous Data for N₂; (△) - Previous Data for Ar.
there is a considerable discrepancy between the two experiments. The magnitude of $\omega$ agrees rather well (within 14\% at the peak), but the shape (and hence the cross section) is quite different. Efforts to resolve these differences have failed and for this reason, both sets of data are shown for purposes of comparison. In Figure V-6, the solid circles are the present data using N$_2$ and the open circles are the present data using argon. The solid triangles represent the N$_2$ data and the open triangles represent the argon data of Christodoulides and Christophorou (1971).

The swarm unfolding technique (see Chapter II) has been applied to the present data in Figure V-6 to obtain absolute attachment cross sections, $\sigma_a(e)$, as a function of electron energy $e$. These functions [for N$_2$ data (•) alone, for Ar data (▲) alone, and for N$_2$-Ar data (○)] are presented in Figure V-7 and are seen to be very consistent in both magnitude and shape. A calculation of $\sigma_a(e)$ by Christodoulides and Christophorou (1970) [using the swarm-beam technique (see Chapter II)] is also presented in Figure V-7 for purposes of comparison. A comparison of the results of the two calculations shows that there is a discrepancy both in the position of the peak of $\sigma_a(e)$ [$e_{\text{max}} = 1.1 \text{ eV for the present study}; e_{\text{max}} = 0.76 \text{ eV for the work of Christodoulides and Christophorou (1970)}$] and in the magnitude of the cross section [$\sigma_{\text{max}} \sim 1 \times 10^{-17} \text{ cm}^2$ for the present work; $\sigma_{\text{max}} \sim 0.4 \times 10^{-17} \text{ cm}^2$ for the previous study]. The full-width at half maximum (FWHM) for the data of Christodoulides and Christophorou is seen to be much wider (FWHM $\sim 0.5 \text{ eV}$) than that in the present study (FWHM $\sim 0.15 \text{ eV}$). The swarm-beam
Figure V-7. \( \sigma(\epsilon) \) Calculated Using the Data of Figure V-6 for the Present Work and the Previous One by Christodoulides et al.

- (○) - \( \text{N}_2 \) Data; (●) - \( \text{Ar} \) Data; (▲) - \( \text{N}_2, \text{Ar} \) Data; (△) - Swarm Unfolding of Christodoulides' Data.
calculation assumes that the negative ion yield $I(\epsilon)$ is proportional to the
attachment cross section, thereby giving a relative cross section spectrum.
The resulting $\sigma_a(\epsilon)$ calculated in this way has the same shape and width as $I(\epsilon)$.
In the swarm unfolding technique, both the magnitude and the shape of $\sigma_a(\epsilon)$
are allowed to change during the calculation. These differences in the
assumptions made in the calculation of $\sigma_a(\epsilon)$ contribute to part of the
discrepancy between the two cross section functions. An unfolding calculation
of $\sigma_a(\epsilon)$ using the data of Christodoulides and Christophorou (1970) shows very
high residuals with most of the discrepancy being in the argon data. From
this analysis, it appears that the argon rates of Christodoulides and
Christophorou (1970) fall off too rapidly since the calculated rates ($R_{cal}$ in
Chapter II) are considerably higher than the experimental ones. However,
the swarm unfolding procedure is quite sensitive to the shape and the
magnitude of $\omega$ and often, small changes in $\omega$ will give rise to large
changes in $\sigma_a(\epsilon)$. Because of the substantial improvements made in the
electronics system, we feel that the measurement techniques used in this
work are somewhat more precise than those used previously and we
therefore place greater confidence in the present rates.

The swarm unfolding technique has also been applied to obtain attach-
ment cross sections at higher pressures. Figure V-8 shows an example of this
calculation for $P_x = 5000$ Torr and 10,000 Torr. Similar cross section
functions were obtained for pressures between these two values.
Figure V-8. $\sigma_a(\epsilon)$ Calculated Using Attachment Data at $P_x = 5000$ Torr and 10,000 Torr.
III. DISCUSSION

1. Reaction Scheme for Electron Attachment to

\[ \text{C}_2\text{H}_5\text{Br} \text{ in High Densities of N}_2 \text{ and Ar} \]

The data in Figures V-1, V-2, V-4, and V-5, pages 78, 80, 82, and 83, respectively, will be analyzed on the basis of the following reaction scheme:

\[ \text{e} + \text{C}_2\text{H}_5\text{Br} \xrightarrow{k_1} \text{C}_2\text{H}_5\text{Br}^{-*} \] (V-1)

\[ \text{C}_2\text{H}_5\text{Br}^{-*} \xrightarrow{k_2} \text{C}_2\text{H}_5 + \text{Br}^{-} \] (V-2)

\[ \text{C}_2\text{H}_5\text{Br}^{-*} \xrightarrow{k_3} \text{C}_2\text{H}_5\text{Br} + \text{e} \] (V-3)

\[ \text{X} + \text{C}_2\text{H}_5\text{Br}^{-*} \xrightarrow{k_{4x}} \text{C}_2\text{H}_5\text{Br}^{-} + \text{X} + \text{energy} \] (V-4)

where \( X = \text{N}_2 \) or Ar. Analysis of Equations (V-1) to (V-4) gives

\[ (\alpha w)_o = \frac{k_1 \{k_2 + k_3 n_x\}}{k_2 + k_3 + k_{4x} n_x} \] (V-5)

where \( n_x \) is the number density of \( x \), proportional to \( P_x \). Equation (V-5) can be written as

\[ (\alpha w)_o = \frac{k_1 k_2 + k_1 k_{4x} P_x}{k_2 + k_3 + k_{4x} P_x} \] (V-6)

In the limit where \( P_x \to 0 \), Equation (V-6) reduces to
which is the usual expression for a pure dissociative process requiring no stabilization. These rates were presented earlier in Figure V-6, page 84, as a function of the mean electron energy $\langle \epsilon \rangle$. The "stabilization rate," $\alpha w_{st} = (\alpha w)_o - (\alpha w)_{P \to 0}$, is shown in Figure V-9 for two pressures ($P_x = 2,500$ Torr and $10,000$ Torr). In Figure V-10, a comparison is presented between $(\alpha w)_o$ and $(\alpha w)_{st}$ at $P_x = 10,000$ Torr. In this figure, $(\alpha w)_{st}$ has been normalized to $(\alpha w)_o$ at the peak energy $\langle \epsilon \rangle = 0.75$ eV. The two curves are seen to be similar for $\langle \epsilon \rangle < 0.9$ eV; they differ at higher energies because $(\alpha w)_o$ is pressure independent (and hence $\alpha w_{st} \to 0$) for $\langle \epsilon \rangle \geq 1.1$ eV. The similarity of these two curves lends support to the hypothesis that there is just one compound negative ion state involved in the reaction scheme (V-1) to (V-4).

The dissociation rate, Equation (V-7), can be subtracted from Equation (V-6) to give

\[
(\alpha w)_{st} = \frac{k_1 k_2}{k_2 + k_3} \frac{k_4 x P_x}{x}
\]

which can be rewritten as
Figure V-9. The Stabilization Rate, $(\alpha w)_st$, as a Function of $\langle \epsilon \rangle$ for $P_x = 2500$ Torr and 10,000 Torr.

(●) - $N_2$ Data; (o) - Ar Data.
Figure V-10. A Comparison Between \((\omega w)_o\) and \((\omega w)_{st}\) at \(P_X = 10,000\) Torr.

\((\omega w)_{st}\) has been Normalized to \((\omega w)_o\) at the Peak Energy \(\langle \epsilon \rangle = 0.75\) eV.

\((o) = (\omega w)_o\); \((\bullet) = (\omega w)_{st}\).
\[
\frac{1}{(aw)}_{\text{st}} = A + \frac{B}{P_x}
\]  

(V-9)

where \( A = \frac{k_2 + k_3}{k_1 k_3} \) and \( B = \frac{(k_2 + k_3)}{k_1 k_3 k_4} \). The experimental data on \((aw)_0\) vs. \(P_x\) are plotted in the manner suggested by Equation (V-9) in Figure V-11 for several mean energies and they are seen to be consistent with Equation (V-9) for \(P_x \leq 25,000\) Torr. Beyond this point \((1/P_x = 0.4 \times 10^{-4}\) Torr\(^{-1}\)) the data diverge from the model. From a linear least squares fit to the data in Figure V-11, the constants \(A\) and \(B\) can be obtained. These are presented in Table V-1.

2. Determination of the Three Body Coefficients

The three body coefficients for the reaction

\[
e + C_2H_5Br + X \xrightarrow{k_{3b}} C_2H_5Br^- + X + \text{energy} \quad (V-10)
\]

\((X = N_2\) or \(Ar\)) have been determined by a least squares fit to the data in Figure V-4, page 82, and Figure V-5, page 83, for \(P_x \leq 5,000\) Torr. In this region \((aw)_0\) varies linearly with \(P_x (k_2 + k_3) \gg k_4 P_x\) and \(k_{3b}\) is found to be equal to \(k_1 k_4 P_x / (k_2 + k_3)\). These rate constants are small and depend strongly on the electron energy as is shown in Figure V-12.

3. Rate Constant Analysis

From the previous analysis we have determined \((aw)_{P_x \rightarrow 0} = k_1 k_2 / (k_2 + k_3)\) and \(k_{3b} = k_1 k_4 P_x / (k_2 + k_3)\). Dividing the dissociation rate,
Figure V-11. $1/(\alpha w)_{st}$ vs. $1/P_x$ for $\text{C}_2\text{H}_5\text{Br}$ in $\text{N}_2$ and $\text{Ar}$. 
Table V-1

Values of A and B

<table>
<thead>
<tr>
<th>( \langle \epsilon \rangle )</th>
<th>A</th>
<th>B</th>
</tr>
</thead>
<tbody>
<tr>
<td>(eV)</td>
<td>(sec Torr)</td>
<td>(sec Torr^2)</td>
</tr>
<tr>
<td>( x 10^{-6} )</td>
<td>( x 10^{-2} )</td>
<td></td>
</tr>
<tr>
<td>0.23</td>
<td>1.40</td>
<td>1.55</td>
</tr>
<tr>
<td>0.33</td>
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</tr>
<tr>
<td>0.49</td>
<td>0.73</td>
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<td>0.55</td>
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<td>0.43</td>
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<td>0.65</td>
<td>0.60</td>
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<tr>
<td>0.75</td>
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<tr>
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<td>0.56</td>
<td>0.40</td>
</tr>
<tr>
<td>0.93</td>
<td>1.00</td>
<td>0.42</td>
</tr>
<tr>
<td>1.012</td>
<td>1.40</td>
<td>0.48</td>
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</table>
Figure V-12. Three-body Rate Coefficients for the Reaction
\( e + C_2H_5Br + X \rightarrow C_2H_5Br^- + X + \text{energy} \) (\( X = N_2 \) or Ar).
(\omega)_p \rightarrow 0' by \( k_{3b} \) gives \( k_3/k_{4x} \) as a function of \( \langle \epsilon \rangle \). This ratio is plotted in Figure V-13 (closed circles are \( N_2 \) data; open circles are \( Ar \) data) and is seen to increase with increasing \( \langle \epsilon \rangle \). From the \( (\omega)_p \rightarrow 0 \) plot and the inverse plot (Figure V-11, page 94) we can determine \( k_2/k_3 = (\omega)_p \rightarrow 0 \times A \) and therefore the ratio \( k_2/(k_2 + k_3) \). \( k_2/(k_2 + k_3) \) is the probability that \( C_2H_5Br^- \) will dissociate as compared to the competing process of autoionization. The quantities \( k_2/k_3 \) and \( k_2/(k_2 + k_3) \) are plotted in Figure V-14 as a function of \( \langle \epsilon \rangle \) and also are listed in Table V-2. It can be seen from Figure V-14 that, as the electron energy increases, dissociation becomes much more probable than autoionization (at \( \langle \epsilon \rangle = 1.087 \text{ eV}, k_2 = 4.23 \) \( k_3 \) and \( k_2/k_2 + k_3 = 0.81 \)). The ratio \( k_3/k_{4x} \) can also be determined from \( (k_2/k_{4x})/(k_2/k_3) \). This quantity is plotted in Figure V-15 as a function of mean energy \( \langle \epsilon \rangle \).

The absolute rate of electron attachment, \( k_1 \), for \( P_x \rightarrow \infty \) can be determined from the ratio \( (\omega)_p \rightarrow 0/k_2/(k_2 + k_3) \). This quantity is plotted in Figure V-16 as a function of \( \langle \epsilon \rangle \). The open circles are values calculated in the manner above; the dark circles represent values of \( (\omega)_p \rightarrow 0 \) for \( \langle \epsilon \rangle \geq 1.1 \text{ eV} \). As can be seen from Figure V-5, page 83, \( (\omega)_p \rightarrow 0 \) is pressure independent for \( \langle \epsilon \rangle \geq 1.1 \text{ eV} \). The pressure independence of \( (\omega)_p \rightarrow 0 \) for \( \langle \epsilon \rangle \geq 1.1 \text{ eV} \) can be attributed to the fact that, in this range

\( k_2/k_{4x} \rightarrow \infty \) (see Figure 13) and that \( k_2/k_3 \rightarrow \infty \) (see Figure V-14). Under these conditions we have
Figure V-13. $\frac{k_2}{k_4}$ as a Function of $\langle \epsilon \rangle$.

Closed Circles are N₂ Data; Open Circles are Ar Data.
Figure V-14. $k_2/k_3$ and $k_2/(k_2 + k_3)$ as a Function of $\langle \varepsilon \rangle$.

($\bullet, \triangle$) $N_2$ Data; (o, •) Ar Data.
Table V-2

Values of $k_2/k_3$ and $k_2/k_2 + k_3$

<table>
<thead>
<tr>
<th>$\langle \epsilon \rangle$ (eV)</th>
<th>$k_2/k_3$</th>
<th>$k_2/k_2 + k_3$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.23</td>
<td>0.14</td>
<td>0.12</td>
</tr>
<tr>
<td>0.33</td>
<td>0.19</td>
<td>0.16</td>
</tr>
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<td>0.42</td>
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<td>0.53</td>
<td>0.35</td>
</tr>
<tr>
<td>0.55</td>
<td>0.60</td>
<td>0.37</td>
</tr>
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<td>0.68</td>
<td>1.08</td>
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</tr>
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<td>1.11</td>
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<td>0.85</td>
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<td>0.58</td>
</tr>
<tr>
<td>0.94</td>
<td>2.42</td>
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</tr>
<tr>
<td>1.012</td>
<td>3.26</td>
<td>0.76</td>
</tr>
<tr>
<td>1.095</td>
<td>4.23</td>
<td>0.81</td>
</tr>
</tbody>
</table>
Figure V-15. $k_3/k_4x$ as a Function of $\langle \epsilon \rangle$.

Closed Circles are $N_2$ Data; Open Circles are Ar Data.
Figure V-16. The Absolute Rate of Electron Attachment, $k_1$, as a Function of $\langle \epsilon \rangle$.

$(\Delta)$ - N$_2$ Data; (o) - Ar Data; (e) - $(\alpha \omega)_0$ for $\langle \epsilon \rangle \geq 1.1$ eV.
These inequalities also show that $k_{3b} \to 0$ for $\langle \epsilon \rangle \geq 1.1 \text{ eV}$.

4. Autodetachment Lifetime of $\text{C}_2\text{H}_5\text{Br}^-$

Previously, Christodoulides and Christophorou (1971) attributed
the values of $(\alpha\omega)_0$ to a dissociative electron attachment process involving a
short-lived ($\leq 10^{-13} \text{ sec}$) compound negative ion state of $\text{C}_2\text{H}_5\text{Br}^-$ and a
pressure-dependent process, involving a longer-lived state, which could be
either dissociative or nondissociative. In the notation used in this chapter,
the short-lived dissociative process corresponds to the rate
$$(\alpha\omega)_P \to 0^* = k_1 k_2 / (k_2 + k_3)$$
and the longer-lived pressure dependent process corresponds
to $$(\alpha\omega)_{st} = (\alpha\omega)_0 - (\alpha\omega)_P \to 0^*$$
Although two states may be involved,
considering the similarity between $(\alpha\omega)_0$ and $(\alpha\omega)_{st}$ as evidenced in
Figure V-10, page 92, one may postulate the existence of just one compound
negative ion state which has several modes of decay. These decay channels
include dissociation (rate = $k_2$), autoionization (rate = $k_3$) and collisional
stabilization (rate = $k_4 x P_x$). The reaction scheme (V-1) to (V-4) was derived
under this assumption and the experimental data support the model.

In Chapter III, a method was presented for finding the critical
pressure, $P_c^*$, for which the rate of autoionization of the negative ion $M^-^*$
was equal to the rate of stabilization of $M^{-*}$ by a third body $X$. Assuming that the pressure dependent process is just the stabilization channel, the lifetime of this channel ($k_3^{-1}$) can be determined using the methods of Chapter III. There is obviously competition between the processes of dissociation and autoionization which is equivalent to having the probability of stabilization, $p$, less than unity. Such a determination using Equation (III-16) [see also Equation (IV-7)] will yield a lower limit to $k_3^{-1}$. The results of such a calculation show that $k_3^{-1} \approx 5.6 \times 10^{-12}$ sec using

$$P_c = \frac{k_3}{k_{4x}}.$$  

The results obtained above can be used to determine a lower limit to the lifetime ($k_2^{-1}$) of the dissociative channel. We have $k_2^{-1} = k_3^{-1}(k_3/k_2)$ and, since the last factor is known as a function of $\langle \epsilon \rangle$, we can determine a lower limit to $k_2^{-1}$ as a function of $\langle \epsilon \rangle$. The results of this calculation are shown in Figure V-17. It is evident that $k_2^{-1} < k_3^{-1}$ over the range where $k_2 > k_3$ and $k_2^{-1} > k_3^{-1}$ over the range where $k_2 < k_3$.

The calculations above have yielded values of $k_2^{-1}$ and $k_3^{-1}$ which are lower limits to the lifetimes of the processes of dissociation and autoionization, respectively. The lifetime of the compound negative ion state would be expected to be somewhat shorter than $k_2^{-1}$ and $k_3^{-1}$ because if a given quantum mechanical state has decay channels $k_i$ ($i = 1, \ldots, N$), then the total rate $k = \sum k_i$ and the lifetime is $\tau_a = k^{-1} = (\sum k_i)^{-1}$. However, it is difficult to place a lower limit to $\tau_a$ in this case because the values of $k_2^{-1}$
Figure V-17. $k_2^{-1}$ as a Function of $\langle \epsilon \rangle$. 
and $k_3^{-1}$ are only lower limits. Because of this fact, we will not attempt to calculate the lifetime of $C_2H_5Br^*$ further.

5. Deviation of the Experimental Results from the Proposed Model

Figures V-4, V-5, and V-11, pages 82, 83, and 94, indicate that the experimental rates are in agreement with the proposed model for $P_{Ar} < 20,000$ Torr, but for $P_{Ar} > 20,000$ Torr, the rates are higher than predicted by Equations (V-1) to (V-4). Because of the many experimental difficulties at the higher pressures, it was feasible to take data for only a few $E/P$'s. The results for $(\epsilon) = 0.935, 1.012,$ and $1.087$ eV in Figures V-4, page 82, and V-5, page 83, show the small magnitude of this deviation. Figure V-18 shows a log plot of the residual attachment rate

$$\alpha_{w_{\text{res}}} = (\alpha_{w_{0}}) - (\alpha_{w_{\text{model}}})$$

as a function of pressure. $(\alpha_{w_{\text{model}}})$ is the attachment rate that would be measured had the reaction scheme (V-1) to (V-4) been the only one responsible for electron attachment. These values were then subtracted from the experimental rates at each $P_{Ar}$ and the rates $(\alpha_{w_{res}})$ were obtained which could not be accounted for on the basis of the assumed reaction scheme. From a straight-line least squares fit to the data in Figure V-18, we obtained a slope of 5.08. On the basis of this analysis, the measured rates in $C_2H_5Br$-Ar mixtures could be accounted for by a mechanism such as the one suggested at the beginning of this chapter and by another mechanism which depends more strongly on $P_{Ar}$. The nature of this latter reaction is not clear at the present time.
Figure V-18. The Residual Attachment Rate, \((\alpha w)_{res}\), as a Function of \(P_{Ar}\).
6. **Extrapolation of High Pressure Rates to the Liquid Phase**

Any coherent picture of radiation interaction with matter must be able to relate the abundant knowledge on isolated molecules to that in the condensed phase. The ultrahigh pressure swarm experiment has been shown to be an excellent method for relating gas phase information to "liquid state" behavior. From the previous analysis, the rate $k_1$, interpreted as the absolute attachment rate as $P_{Ar} \to \infty$, can be found as a function of $\langle \epsilon \rangle$. Under the assumptions of the model presented earlier, we have $k_1 \approx [(\alpha w)_0]_{\text{liquid}}$. On the basis of the data presented in Figure V-18, it is obvious that the model breaks down for $P_{Ar} \gtrsim 20,000$ Torr and that $(\alpha w)_0$ increases faster than predicted. We therefore see that $k_1$ is a lower limit to $(\alpha w)_0_{\text{liquid}}$. The apparent breakdown of the model was not observed in the data using $N_2$ as a carrier gas. However, very few $E/P$'s could be examined in the range $P_{N_2} \gtrsim 20,000$ Torr and the data that were taken were for low $\langle \epsilon \rangle$.

Another way of predicting liquid state attachment rates is to calculate

$$
(\alpha w)_0_{\text{liquid}} = k_{1 \text{max}} + (\alpha w)_{\text{res}, P_1} \quad \text{where} \quad (\alpha w)_{\text{res}, P_1} = 1.5 \times 10^7 \sec^{-1} \text{Torr}^{-1}
$$

is the residual attachment rate in Figure V-18 extrapolated to the density of liquid argon and $k_{1 \text{max}}$ is the maximum value of $k_1$ in Figure V-16, page 102. The residual attachment rate is found to be roughly independent of energy over the limited range that was covered experimentally ($0.7 \leq \langle \epsilon \rangle \leq 1.0$ eV). This analysis gives $(\alpha w)_0_{\text{liquid}} \approx$
$2 \times 10^7 \text{ sec}^{-1} \text{Torr}^{-1} = 0.37 \times 10^{12} \text{ M}^{-1} \text{ sec}^{-1}$. Attachment rates have not been measured for $\text{C}_2\text{H}_5\text{Br}$ in liquid argon, but the value above compares favorably with $0.34 \times 10^{12} \text{ M}^{-1} \text{ sec}^{-1}$ determined by Allen and Holroyd (1973) for $\text{C}_2\text{H}_5\text{Br}$ in neopentane. These investigators have found a range of values of the attachment rate which depends on the solvent used; these are $1.5 \times 10^{12} \text{ M}^{-1} \text{ sec}^{-1}$, $1.6 \times 10^{12} \text{ M}^{-1} \text{ sec}^{-1}$, $6.3 \times 10^{13} \text{ M}^{-1} \text{ sec}^{-1}$, and $0.042 \times 10^{12} \text{ M}^{-1} \text{ sec}^{-1}$ for $\text{C}_2\text{H}_5\text{Br}$ in n-hexane, n-pentane, 1,2,4 trimethylpentane, and tetramethylsilane, respectively. The values of $(\alpha w)_{\text{liquid}}$ obtained in this experiment agree well with the liquid values of Allen and Holroyd considering the crudeness of the model. The model presented earlier is definitely deficient in the prediction of liquid state values because it is not possible to take solvation effects into account. Solvation would certainly shift the $k_1(\langle \epsilon \rangle)$ curve toward thermal energies as is expected to be characteristic of electrons in liquids.
CHAPTER VI

SUMMARY

In this study, electron capture mechanisms and reaction schemes have been developed for electron attachment to various molecules embedded in dense gaseous media (for $N_2$, $P_{N_2} \leq 27,500$ Torr; for Ar, $P_{Ar} \leq 42,000$ Torr; for $C_2H_4$, $P_{C_2H_4} \leq 17,000$ Torr; for $C_2H_6$, $P_{C_2H_6} \leq 17,500$ Torr). As the density of each medium increases, each affects the attachment rate in a different manner, indicating the profound effect and importance of the environment on the electron attachment process.

The results of a study of the capture of slow ($< 1$ eV) electrons by $O_2$ embedded in dense $N_2$, $C_2H_4$ and $C_2H_6$ environments was presented and discussed. Large changes were observed in both the magnitude and energy dependence of the attachment rate with increasing density of these three media. Reaction schemes were also presented to account for the pressure dependence of the attachment rate. From this analysis, an autoionization lifetime of $2 \times 10^{-12}$ sec was estimated for $O_2$. An extrapolation of the high pressure rates to liquid densities gave electron attachment rates of $0.74 \times 10^{10}$ sec$^{-1}$ Torr$^{-1}$ and $3.3 \times 10^{11}$ sec$^{-1}$ M$^{-1}$ for $O_2$ in liquid $N_2$ and liquid $C_2H_4$, respectively. Although electron attachment to $O_2$ has not been measured in liquid $N_2$ and $C_2H_4$, the above values are in good agreement with those measured for $O_2$ in various solvents.
Benzene was found to capture slow (< 0.3 eV) electrons in high densities of N₂ and Ar with a rate which increased with increasing density. The dependence of the rate on carrier-gas density was studied and a model was presented which accounted for the experimental results. The lifetime of C₆H₆⁻ has been estimated on the basis of this model and found to vary from 1.0 x 10⁻¹² sec at 0.04 eV to ~ 0.2 x 10⁻¹² sec at 0.18 eV. The high pressure attachment rate data were extrapolated to liquid N₂ densities and a liquid rate of ~ 1 x 10⁹ sec⁻¹ M⁻¹ was obtained which is in good agreement with that estimated by other investigators. The finding that C₆H₆ captures electrons in the gas phase forced the conclusion that C₆H₆⁻ has a positive electron affinity in contrast to the accepted view that (EA)₆ < 0 eV.

Bromoethane (C₂H₅Br⁻) has also been found to capture electrons in high densities of N₂ and Ar with a rate which increases with increasing density. C₂H₅Br⁻ can decay through dissociation, autoionization, and stabilization channels and a model is presented which predicts the relative magnitude of each of these rates as a function of ⟨ε⟩. In general, dissociation is the most probable mode of decay for ⟨ε⟩ ≥ 1 eV. The high pressure rates have also been extrapolated to liquid Ar densities and a liquid rate of 0.37 x 10¹² sec⁻¹ M⁻¹ was found. Although attachment to C₂H₅Br has not been measured in liquid N₂ and Ar, this rate is in reasonable agreement with those obtained for C₂H₅Br in various solvents such as neopentane.
The work presented in this thesis shows that it is possible to predict electron attachment rates in liquid media from experiments performed in the high pressure gas phase. The high pressure swarm experiment is unique in that it bridges the gap between low pressure studies, where much is known about kinetic mechanisms, and studies in the condensed phase where relatively little is known about electron attachment mechanisms.
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VITA

Ronald Earl Goans was born in Clinton, Tennessee on August 12, 1946. He attended elementary schools in that city and was graduated from Clinton High School in 1964. He entered the University of Tennessee in June, 1964 and in June, 1968, he received a Bachelor of Science degree in Engineering Physics. In the fall of 1968 he accepted a graduate assistantship at the University of Tennessee and began study toward a Master's degree. He received this degree in December, 1969. In September, 1969 he accepted an Atomic Energy Commission Special Fellowship in Health Physics and began work toward a Doctor of Philosophy degree with a major in Physics. In September, 1972, he accepted an Oak Ridge Associated Universities Laboratory Participantship. The Doctor of Philosophy degree was awarded in June, 1974. He is a member of Tau Beta Pi and Sigma Pi Sigma.

He is married to the former Judy Winegar of Knoxville, Tennessee.