STUDIES IN RADIATION CHEMISTRY

by

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We accept this thesis as conforming to the
required standard

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April 1971
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ABSTRACT

The experimental work presented in this dissertation consists of two separate parts. Firstly, a study of the reaction of hydrated electrons with molecular nitrogen is reported. Secondly, the results of an investigation of the effects of \( \gamma \)-radiation on the polar aprotic solvent, propylene carbonate; (a) in the glassy solid state at 77 °K, and (b) as a liquid at room temperature, are presented.

Hydrated electrons were generated by \( \gamma \)-radiolysis of aqueous solutions containing \( \text{H}_2 \) and \( \text{OH}^- \) and also containing \( \text{N}_2 \) at concentrations up to 0.1 M (200 atm pressure). Significant yields of ammonia were obtained, but by completely eliminating the gas space above the solution it was shown that the majority of the \( \text{NH}_3 \) arose through "direct action" of the radiation on dissolved \( \text{N}_2 \). Although the hydrated electron is one of the most powerful and reactive reducing agents, it is unable to cause reduction fixation of molecular nitrogen. An upper limit of \( k_1 < 18 \text{ M}^{-1}\text{s}^{-1} \) was estimated for the rate constant of the reduction reaction. Conversion of the hydrated electrons to \( \text{H} \) atoms in acid solution did not affect the ammonia yield, implying that \( \text{H} \) atoms are also unable to reduce nitrogen.

In the glassy solid state at 77 °K, \( \gamma \)-irradiation of propylene carbonate produced species identified as trapped electrons. They were characterised by a narrow \( (\Delta H_{\text{ms}} = 4.5 \text{ G}) \),
Gaussian shaped ESR line at $g = 2.0028$ and an optical absorption band with $\lambda_{\text{max}} \sim 370$ nm. The electrons were unstable at 77 °K and decayed via a non-homogeneous process believed to be reaction with positive ions. Also formed by the $\gamma$-radiation were four unidentified trapped radicals, all characterised by doublet ESR signals centered at $g = 2.0023$ and with hyperfine splittings of 42, 58, 83, and 124 G. Ultraviolet photolysis of the irradiated glasses at 77 °K produced new radicals identified as $\text{CO}_3^-$, $\text{HCO}$ and $\text{CH}_3$. The $\text{CO}_3^-$ radical gave a single ESR line at $g \sim 2.015$ and a broad visible optical absorption band with $\lambda_{\text{max}} \sim 600$ nm. $\text{HCO}$ was identified by its asymmetric doublet ESR signal with hyperfine splitting of about 130 G and a multi-line vibronic absorption spectrum in the 500 - 750 nm region. The methyl radicals were unstable in the matrix and were identified by their characteristic 1:3:3:1 quartet ESR spectrum with hyperfine splitting of about 21 G.

$\gamma$-radiolysis of liquid propylene carbonate at 25 °C produced $\text{H}_2$, CO and CO$_2$ as the major gaseous "molecular" products with yields: $G_{\text{H}_2} = 0.75 \pm 0.05$, $G_{\text{CO}} = 1.2 \pm 0.1$, and $G_{\text{CO}_2} = 3.2 \pm 0.3$. Methane was also produced via a secondary process involving methyl radicals with a yield: $G(\text{CH}_4) = 0.20 \pm 0.02$. Scavenger experiments with $\text{N}_2\text{O}$, $\text{I}_2$, methanol and acid indicated that an anionic reducing species was formed by the radiation with a yield of $G_X^- = 2.0 \pm 0.2$. This species was probably a solvated electron although the possibility of it being a reactive molecular anion could not
be excluded on the basis of the steady state radiolysis data. A transient optical absorption at 630 nm was observed on pulse radiolysis of propylene carbonate with 3 nsec pulses of 0.5 MeV electrons. However, either solvated electrons or the $\text{CO}_3^-$ radical ion could have been responsible for the absorbance.
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In loving memory of my father,

ERIC ALBERT KURT SHAEDE (1904 - 1969)

and a very dear friend,

WILLIAM LYLE MACKEN (1883 - 1967).
"Fundamental studies in radiation chemistry aim to identify the various SPECIES formed in particular systems and to understand the PHYSICAL PROCESSES by which they arise. The AMOUNTS formed for a given dose of radiation are measured. Then the CHEMISTRY of the species in their reactions with each other and other compounds present is studied. This involves investigations of reaction kinetics and mechanisms, and of intermediates through to the final, stable end products." \(^1\)

Thus the general scheme of radiation chemical investigations may be represented by Figure 1.

Figure 1. Scheme of reactions in radiation chemistry.
(after Figure 1.1, O'Donnell and Sangster, reference 2, page 2)
This thesis is concerned with several of the fundamental aspects of radiation chemistry outlined above. Specifically, the chemical reaction of the hydrated electron, an important primary species in the radiolysis of water, with molecular nitrogen was studied. In addition an investigation of the primary species formed by $^{60}$Co $\gamma$-radiation in a polar organic liquid (propylene carbonate) was conducted both directly, in the solid state, by electron spin resonance and optical spectroscopy; and indirectly, in the liquid phase, by competition kinetic studies involving scavengers and analysis of the final stable products of the radiolysis.

Understanding radiation chemical phenomena requires a basic knowledge of the processes by which radiation interacts with matter since the chemical effects are a direct consequence of the absorption of energy from the radiation.

A. INTERACTION OF HIGH ENERGY RADIATION WITH MATTER

Since the majority of investigations in radiation chemistry involve the use of high energy photons or electrons as the radiation source, the present discussion will be limited to the interactions of these radiations with matter. In general the physics and chemistry of the interactions of other types of radiation, namely neutrons and charged particles such as protons, alpha particles and fission fragments, are substantially different to that of electrons (and photons) and a complete discussion of all of the interactions is beyond the scope of this thesis.
1. **Electromagnetic Radiation (X or γ-rays)**

Electromagnetic radiation is absorbed by matter via four principal processes: (a) the photoelectric effect, (b) the Compton process, (c) pair production, and (d) photo-nuclear reactions. The importance of each of the four reactions depends primarily in the energy of the incident photon and depends to a lesser extent on the atomic number of the absorbing material.

Since X or γ-rays obey absorption laws common to other electromagnetic radiation (such as visible light), they are not completely absorbed by a finite thickness of absorber. Thus a beam of high energy photons of initial intensity, \( I_0 \), will have a final intensity, \( I \), after passing through a thickness, \( x \), of absorbing material as given by the equation (i),

\[
I = I_0 \cdot e^{-\mu x}
\]

where \( \mu \) is the total linear attenuation coefficient equal to the sum of the individual coefficients for each of the four interaction processes mentioned above. This equation is analagous to the Beer-Lambert law for the absorption of light. The range of electromagnetic radiation is often discussed in terms of the "half thickness" of an absorber, i.e. the thickness required to reduce the original intensity by one half. For 1 MeV photons the half thickness in water is about 10 cm.

The photoelectric effect is the interaction of electromagnetic radiation with an atom or molecule which results in the complete absorption of the photon and simultaneous ejection
of an electron with kinetic energy, \( E \), given by equation (ii),
\[
E = h\nu - \phi
\]
where \( h\nu \) is the photon energy and \( \phi \) is the "binding energy" of the electron.\(^2\) This process is important only for comparatively low photon energies (\( < 0.1 \text{ MeV} \)) and increases with increasing atomic number.

An elastic collision between a photon and a loosely bound or unbound electron, known as the Compton process, results in the transfer of some of the photon's energy to the electron. Conservation of momentum requires that the photon must change direction, i.e. is scattered, and the amount of energy transferred to the electron, \( E \), is given by the equation (iii),
\[
E = h\nu - h\nu'
\]
where \( h\nu \) and \( h\nu' \) are the incident and scattered photon energies respectively. The energy of the scattered photon, \( h\nu' \), is related to its original energy and the scattering angle, \( \theta \), by the relationship (iv),
\[
h\nu' = \frac{h\nu}{1 + \left(\frac{h\nu}{m_0c^2}\right)(1 - \cos \theta)}
\]
where \( m_0c^2 \) is the rest mass energy of the electron.\(^2\) The important aspects of Compton scattering which are evident from equation (iv) are: (a) the energy lost by a photon increases as the scattering angle \( \theta \) increases, (b) the energy loss for
a given scattering angle increases with increasing photon energy, and (c) the energy of a photon scattered at the maximum angle ($\theta=180^\circ$) approaches a limiting value of 0.256 MeV (i.e. $\frac{1}{2}m_0c^2$) as the initial photon energy increases. Since interaction with electrons is involved in the Compton process, its effectiveness increases with increasing "electron density" (i.e. ratio of atomic number, Z, to atomic mass, A) of the absorber. Photons with energy in the range 0.2 to 5 MeV are almost exclusively absorbed by the Compton process for low atomic number materials.

Pair production results when a high energy photon is annihilated in the region of an atomic nucleus with the concomitant production of an "electron" pair -- a positive and a negative electron. This process has a threshold energy of 1.02 MeV, the energy required to produce two electron rest masses, and therefore the net kinetic energy of the electrons, $E_p + E_e$, is given by equation (v),

$$E_p + E_e = h\nu - 2m_0c^2 = h\nu - 1.02 \text{ MeV} \quad (v)$$

where $h\nu$ is the photon energy. Pair production becomes an important absorbing process only for very high photon energies ($>10 \text{ MeV}$).

Photonuclear reactions also require very high photon energies in order to eject neutrons or protons from atomic nuclei. The photon energy must exceed the "binding" energy of a nuclear particle and typically is in the range of 6 to 18 MeV. However this process makes a negligible contribution
to the total linear attenuation coefficient for electromagnetic radiations normally used in radiation chemical studies.

In summary, the most important interaction for photons of moderate energy (e.g. $^{60}$Co $\gamma$-rays at 1.17 and 1.33 MeV) is the Compton process. Because this absorption essentially results in the conversion of high energy photons to high energy electrons, it is necessary to consider in detail the interaction of high energy electrons with matter since they are the species directly responsible for radiation chemical effects.

2. High Energy Electrons

Unlike electromagnetic radiation, electrons have a finite range in an absorbing material. They lose their energy via two important processes, namely radiation emission (Bremsstrahlung) and inelastic collisions with other electrons in the medium.

When a high energy electron passes close to an atomic nucleus it is decelerated by the electric field. According to classical physics this means that the electron must radiate electromagnetic radiation (Bremsstrahlung) in order that the system conserve both energy and momentum. The rate at which the electron loses energy, $-dE/dx$, is proportional to $e^2Z^2/m^2$ where $e$, $Z$ are the electronic and nuclear charges respectively and $m$ is the electron mass. Bremsstrahlung emission is negligible for energies below about 100 keV and becomes significant only above 1 MeV. Of course this electromagnetic radiation
will then be partially re-absorbed in the medium by the processes discussed in the previous section.

The predominant mechanism for energy loss by electrons with energy less than 1 MeV is through inelastic Coulombic interactions with the electrons of the absorbing material. Interactions of this type produce the ionization and excitation which leads to chemical change in the system.

The ratio of energy loss by radiation emission to that lost by collision is given approximately by the formula (vi),

$$\frac{(dE/dx)_{rad}}{(dE/dx)_{coll}} \approx \frac{EZ}{1600 \ m_0c^2}$$  \hspace{1cm} (vi)

where E is the electron energy and Z is the atomic number of the material.\(^3\)

A third process which affects the range of electrons in an absorber is their deflection by the Coulombic fields of the atomic nuclei. This results only in a change in direction and is greatest for low electron energies and high atomic number materials.

Thus electrons lose their energy and are deflected as they pass through a medium. The total initial energy and the rate of energy loss consequently determine the range or penetration distance of the electron. For monoenergetic electrons, a graph showing the number of electrons transmitted at a given distance within the bombarded material, as a function of distance, is nearly linear with a negative slope and finishing in
a small tail. The extrapolated or practical range, $R_p$, is found by extrapolating the linear portion of the curve. The maximum range, $R_o$, is the point where the tail of the curve merges with the background. For a beam of non-monoenergetic electrons (e.g. $\beta$-particles or Compton electrons) the curve does not have a linear region and only a maximum range, $R_o$, can be determined. The range of electrons has been empirically related to their energy for aluminum absorbers. For energies between 0.01 and 2.5 MeV the range of $\beta$-particles with maximum energy, $E$, or the extrapolated range of monoenergetic electrons of energy, $E$, is given by equation (vii),

$$\text{Range} = 412 \ E \ 1.265 - 0.0954 \ \ln \ E$$  \hspace{1cm} (vii)

where the range is given in mg cm$^{-2}$. \(^3\) This formula can also be applied to most other low atomic number materials since the range expressed in units of mg cm$^{-2}$ varies only slightly with atomic number. Thus the range of 1 MeV electrons as calculated from equation (vii) is 412 mg cm$^{-2}$ which corresponds to a thickness of 0.41 cm for water.

The net result of the passage of a high energy electron through a condensed medium is an irregular distribution of ionized and excited molecules. The path of the primary electron is referred to as its "track", which is generally near linear at high energy but deflections become more common as the electron slows down. Ionizations and excitations which occur at irregular intervals along the track are called "primary events". The primary ionizations will produce secondary electrons with sufficient energy to escape recombination with their positive
ion and they may be classified into two energy categories; the low energy secondary (<100 eV) and the high energy secondary electrons (>100 eV). The low energy secondary electrons will suffer large deflections and form a region of tertiary ionization and excitation called a "spur", which to a first approximation may be regarded as spherical in shape. Each spur will thus initially contain a number of excited molecules, positive ions and very low energy electrons with an average of somewhat less than 100 eV deposited in this area.

The more energetic secondary electrons have sufficient range to form short tracks of their own, called "δ-rays", and these electrons can be further classified into two sub-groups. The most energetic secondary δ-electrons will form a true track of their own along which there will be further ionization and the formation of spurs. Known as a "branch track", the average separation of spurs along its path will be sufficient so that there will be no overlapping. In contrast, the less energetic δ-electrons will have only enough energy to form a very short track and the spurs along it will overlap to form a kind of "super spur" which is sometimes referred to as a "blob". For a 1 MeV electron stopped in water about 67% of the energy is deposited in isolated spurs, 22% along the branch tracks, and 11% in blobs.¹

From the above discussions it is clear that the physical effect of radiation is to produce an inhomogeneous distribution of ionized and electronically excited molecules and very low
energy electrons in the medium as may be depicted by Figure 2.

Figure 2. Distribution of spurs and primary events along the track of a fast electron in a liquid. (after Figure 2-8, Henley and Johnson, reference 2, page 31)

The fate of these primary species governs the subsequent chemistry in the system.

B. CHEMICAL CONSEQUENCES OF THE ABSORPTION OF HIGH ENERGY RADIATION

"In general, most of the reactions which occur in radiation chemistry are ordinary thermal chemical reactions, although some involve rather unusual chemical species. In some cases regions of excess energy - "hot spots" - may be present, and these regions can provide activation energies greater than those available thermally. However, these reactions also obey chemical laws, and there is no need to treat radiation chemistry as a domain beyond the realms of chemistry because of the vast energies available." ¹

Following the absorption of high energy radiation, the excited molecules and ions formed by the physical processes described in the previous section undergo a variety of changes and reactions. The ions may recombine, the excited molecules may dissociate or luminesce and many other reactions may occur as the species diffuse and become homogeneously distributed
throughout the medium. A general outline of these chemical processes which occur following the physical stage of the radiolysis is schematically illustrated in Figure 3.

The time scales on which these events occur, and indeed whether they occur, depend to a large extent on the polarity of the medium and its physical state (i.e. solid, liquid, or gas). The following discussion will be restricted to the condensed phases, specifically liquid and frozen polar systems which will be treated separately.

1. Polar Liquids

An indication of the probable time scale for the radiation events in a typical dielectric liquid, water, is given in Table 1.

During the physiochemical stage of the radiolysis, which begins within $10^{-14}$ seconds after the incidence of the radiation; ion-molecule reactions occur, electronically excited molecules are involved in energy transfer processes or else dissociation, and radical diffusion begins. In addition the low energy electrons become thermalized, that is they have energy equivalent to $kT$ or $\sim 0.025$ eV, and may enter into ion-molecule reactions or else become solvated by causing a polarization of the solvent dipoles (dielectric relaxation). Solvated electrons and their properties will be discussed in detail in a later section.

The distinction between the physiochemical and the true
Figure 3. Primary processes in the action of radiation on matter.
### TABLE 1

**APPROXIMATE TIME SCALE FOR THE RADIOLYSIS OF LIQUID WATER**

(adapted from Table 8.3, reference 1, page 252-3)

<table>
<thead>
<tr>
<th>Time (sec)</th>
<th>Events</th>
<th>Reactions</th>
<th>Species Present</th>
</tr>
</thead>
<tbody>
<tr>
<td>$10^{-18}$</td>
<td>Electron of 1 MeV energy traverses molecule</td>
<td>$\text{H}_2\text{O} \rightarrow \text{H}_2\text{O}^+ + \text{e}^-$</td>
<td>$\text{H}_2\text{O}^+$</td>
</tr>
<tr>
<td>$10^{-15}$</td>
<td>Thermal electron (0.025 eV) traverses a molecule. Time between successive ionizations by a MeV electron. Time for &quot;vertical&quot; excitation to an electronic excited state.</td>
<td>$\text{H}_2\text{O} \rightarrow \text{H}_2\text{O}^*$</td>
<td>$\text{H}_2\text{O}^*$ (localized in spurs or track zone)</td>
</tr>
<tr>
<td>$10^{-14}$</td>
<td>Ion molecule reactions. Period of molecular vibration. Dissociation of molecules excited to repulsive states.</td>
<td>$\text{H}_2\text{O}^+ + \text{H}_2\text{O} \rightarrow \text{H}_3\text{O}^+ + \text{OH}^-$</td>
<td>$\text{OH}^-$</td>
</tr>
<tr>
<td>$10^{-12}$</td>
<td>Secondary electrons reduced to thermal energy. Electron capture. Internal conversion from higher to lowest electronic state.</td>
<td>$\text{H}_3\text{O}^+ + \text{e}^- \rightarrow \text{H}_2\text{O} + \text{H}^-$</td>
<td>$\text{H}^-$</td>
</tr>
<tr>
<td>$10^{-11}$</td>
<td>Radical moves one &quot;jump&quot; in diffusion.</td>
<td>$\text{e}^- \rightarrow \text{e}^-_{aq}$</td>
<td>$\text{H}^-, \text{OH}^-, \text{e}^-_{aq}$</td>
</tr>
<tr>
<td>$10^{-11}$</td>
<td>Relaxation time for the orientation of the water dipoles.</td>
<td>$\text{e}^- + \text{H}_2\text{O} \rightarrow \text{H}^+ + \text{OH}^-$</td>
<td>$\text{H}_2\text{O}^*$ (?)</td>
</tr>
</tbody>
</table>

(... continued on page 14)
<table>
<thead>
<tr>
<th>Time (sec)</th>
<th>Events</th>
<th>Reactions</th>
<th>Species Present</th>
</tr>
</thead>
<tbody>
<tr>
<td>$10^{-10}$</td>
<td>Minimum time for diffusion controlled reactions in the bulk of the liquid.</td>
<td>$H^+ + OH^- \rightarrow H_2O$</td>
<td>$H^+$, $OH^-$, $e_{aq}^-$</td>
</tr>
<tr>
<td>$10^{-9}$</td>
<td>Electron with initial energy of 1 MeV comes to &quot;rest&quot;.</td>
<td>$2 \text{OH}^- \rightarrow H_2O_2$, $2 \text{H}^+ \rightarrow \text{H}<em>2$, $2 e</em>{aq}^- \rightarrow H_2 + 2OH^-$</td>
<td>$H_2O_2^*(?), \text{H}_2$, $H_2O_2$ (all in or near spurs and track)</td>
</tr>
<tr>
<td>$10^{-8}$</td>
<td>Radiative lifetime of singlet excited states. Formation of molecular products complete in $\gamma$-ray spurs.</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$10^{-5}$</td>
<td>Reaction time for radicals with solutes in molar concentrations. Lifetime of the hydrated electron.</td>
<td>$R^+ + S \rightarrow \text{products}$</td>
<td></td>
</tr>
<tr>
<td>$10^{-4}$</td>
<td>Time required for a radical to diffuse the inter-spur distance in the track of an MeV energy electron.</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$10^{-3}$</td>
<td>Radiative lifetime of triplet excited states.</td>
<td></td>
<td></td>
</tr>
<tr>
<td>0</td>
<td>Chemical reactions complete.</td>
<td></td>
<td>$H_2$, $H_2O_2$ and products of radical react with solutes.</td>
</tr>
</tbody>
</table>
chemical stages of the radiolysis is generally drawn at about $10^{-9}$ seconds, which also happens to be the time required to slow a 1 MeV electron to thermal velocity. During the chemical stage, the radicals and ions formed in the spurs diffuse outward and those which escape recombination eventually become homogeneously distributed throughout the liquid. Reactions of these "primary" species with solute (scavengers) or solvent molecules can then occur to form stable "primary" radiolysis products. Those species which react within the spurs to form stable molecules, termed "molecular products", are generally not scavengeable at normal solute concentrations (i.e. $10^{-2}$ M), however if very high solute concentrations are used (i.e. 1 M) the precursors of these "molecular products" may be scavenged. When very large radiation doses are given, the "primary" products may become involved in reactions with the primary radical species to form different "secondary" species and products (e.g. in water, $H_2O_2$ a molecular product, eventually reaches sufficient concentration to react with $e^{-}_{aq}$, $OH^{-}$, and $H^{+}$ to form $OH^{-} + OH^{•}, H^{•} + H_2O$, and $OH^{•} + H_2O$ respectively).

2. Frozen Polar Systems

By freezing a liquid and lowering the temperature sufficiently, it is possible to slow down the chemical stages of radiolysis listed in Table 1. In many systems this simplifies the reactions which can occur and in some cases, allows direct observation of the primary species and intermediates involved.

Radicals formed either during the primary radiolysis
processes or from reactions of mobile primary species such as H atoms, become trapped in low temperature matrices. Ions may also become stabilized; the positive ions by transferring a proton to a neighbouring molecule with resulting formation of an additional radical, and the negative ions by becoming trapped in defects in the matrix where the solvent dipoles are suitably oriented to provide stabilization. In particular, electrons are often trapped in "pre-formed" positive "holes" in the medium. Alternatively, the ions may quickly induce electronic polarization of the surrounding molecules and stabilize themselves in this manner until dipole relaxation can occur to form a "deeper" trap. These trapped negative ions and radicals are often paramagnetic and therefore may be observed by electron spin resonance spectroscopy. Optical spectroscopy also may be used in identification of the species.

Kevan\(^4\) has summarized the basic objectives of research into the radiolysis of frozen systems in the following manner:

(a) Which species may be detected and how do their yields relate to the overall radiolysis mechanism?

(b) What reactions do trapped intermediates undergo and how do these reactions compare to those occurring in the liquid phase?

(c) What is the nature of the trapping sites of the various species?

(d) What is the spatial distribution of the intermediates and how does it affect the chemistry in the system?

(e) Are new types of species generated radiolytically in frozen systems due to matrix stabilization?
(f) Is energy stored in irradiated frozen systems? If so, how efficient is the process and can energy be selectively transferred from site to site?

Thus studies on frozen systems are often complimentary to liquid phase investigations and help in solving the overall radiolysis mechanism.

3. Radiation Chemical Units and Terms

The yield of a species or product formed by radiolysis is known as the "G value". It is defined as the number of molecules, ions, atoms or radicals which are formed (or disappear) for every 100 eV of energy deposited by the radiation in the system. For "primary" species or "molecular" products the notation \( G_x \) is generally used and \( G_x \) normally is in the range of 0-10. Yields of products which are not formed solely from a primary process are indicated by \( G(X) \). For secondary processes involving chain reactions it is not unusual for a \( G \) value to exceed 10.

In order to obtain an absolute measure of the \( G \) value of any species formed by radiation it is necessary to know the total amount of energy absorbed by the medium. This quantity is termed the "absorbed dose" and it is expressed in many different units, the most common of which is the "rad". One rad is defined as the deposition of 100 ergs g\(^{-1}\). This unit is sometimes converted to a more convenient quantity, i.e. eV g\(^{-1}\), by the factor \( 6.24 \times 10^{13} \) eV g\(^{-1}\)rad\(^{-1}\), since \( G \) value calculations require knowing the total dose in units of eV. There are
numerous methods used to determine dose (dosimetry). They vary from chemical reactions with accurately known yields (e.g. oxidation of Fe$^{+2}$ in 0.8N sulfuric acid solution has G(Fe$^{+3}$) = 15.5 for $^{60}$Co γ-rays) to electronic devices capable of measuring the number of charged particles or ions produced and calorimetric methods designed to measure the energy deposited when it is all converted to heat.\(^3\)

C. **STABILIZED ELECTRONS**\(^5\)

In the previous sections it has been shown that the interaction of ionizing radiation with matter produces high energy electrons which through a cascade of processes eventually give rise to numerous low energy electrons. (In fact a single 1 MeV electron may produce between $10^4$ and $10^5$ secondary electrons.) These low energy electrons ($\lessapprox 10$ eV) lose most of their remaining energy by excitation of electronic transitions and vibrational states of the medium. When their energy reaches or drops below $\sim 0.5$ eV, the "sub-excitation" electrons become thermalized, which means that their velocity decreases to $\sim 10^7$ cm s$^{-1}$ (at room temperature) and their energy is further reduced to $\sim 0.03$ eV. The separation distance between the cations and electrons increases during the latter stage of energy loss and the thermalized electron may leave its spur and possibly overcome the Coulombic field of the cations. Charge neutralization does eventually occur however if the electron is unable to escape the influence of its positive ion and this process is called "geminate recombination". The probability that the thermalized electrons will escape from the influence
of the Coulombic field depends on the polarity of the medium (its dielectric constant), its degree of order (liquid, crystalline or glassy amorphous state), and the temperature (viscosity).

If the thermal electrons do escape geminate recombination then they may be stabilized by the surrounding medium, either through a solvation process in polar liquids or by trapping in pre-formed "holes" in frozen systems. An alternative fate for these thermal electrons is of course to react with a solvent molecule and this reaction will depend on the electron affinity of the solvent.

1. **Electron Solvation Process**

During the early investigations of the radiation chemistry of water, by far the most thoroughly studied system to date, several theories were advanced to account for the observed chemistry, and particularly the production of hydrogen. Samuel and Magee\(^6\) proposed that the subexcitation electrons would be moderated to thermal energies within 10\(^{-13}\) seconds and while still in the Coulombic field of the parent ions. Since the dielectric relaxation time of water is 10\(^{-11}\) seconds, the dipoles would not be able to reorient themselves quickly enough to solvate the electron. Therefore geminate recombination would occur to produce an excited water molecule which would then dissociate to give an H atom and an OH radical with sufficient energy to escape the solvent cage. Thus the primary species in the Samuel-Magee theory are H and OH radicals formed in the immediate vicinity of the spur.
An alternative model of Lea\textsuperscript{7} and Gray\textsuperscript{8} suggested that the secondary electron would move about 150 Å from the parent positive ion and thus beyond the effect of its electrostatic field. Under these circumstances the electron and the positive ion would react independently with the solvent. It was postulated that the electron reacts to give an H atom and OH\textsuperscript{−}, while the positive ion produces an OH radical. Platzman\textsuperscript{9} essentially agreed with the Lea-Gray theory about the electron escaping the Coulombic field of H\textsubscript{2}O\textsuperscript{+}, however he pointed out that the reaction of thermal electrons with water is relatively slow. He concluded that the electron might not undergo this reaction but could survive to become solvated. The solvated electron would then react in a manner similar to the H atom.

Platzman's postulate was later proven to be correct when it was experimentally determined that an ionic reducing species with unit negative charge was involved in the radiolysis of water.\textsuperscript{10} This species was subsequently identified as the hydrated electron by its intense optical absorption in the red which was similar in characteristics to the optical absorption band of chemically produced solvated electrons in liquid ammonia.\textsuperscript{11} Since these "early" studies, numerous reports have been made on the formation of solvated electrons in a variety of liquids.\textsuperscript{5}

The exact details of the mechanism of the solvation process are still speculative since no one has yet been able to actually observe the formation of solvated electrons despite the fact that time resolution into the 10\textsuperscript{−11} second region has
been achieved. The most generally accepted qualitative picture of the solvation process involves the thermal electron initially (within $10^{-15}$ seconds) electronically polarizing the surrounding molecules. This electronic polarization is thought to effectively "immobilize" the electron while the slower atomic and dipolar polarizations can occur to solvate it. A schematic representation of these events for water and a comparatively non-polar liquid, n-hexane, is shown in Figure 4.

![Figure 4](image)

Figure 4. Qualitative representation of the potential energy of an electron as a function of time after localization in a liquid. (after Figure 4, Freeman, reference 12, page 23)

Solvated electrons are formed in both systems, however the much greater potential energy gain by the electron in water due to dipole orientation makes the hydrated electron a more "stable" species. In addition, because of the dielectric constant differences between n-hexane and water, the yield of electrons which escape geminate recombination will be much larger for water.

The essential difference between the "trapped" electron and the solvated one is simply that the dielectric has reached its equilibrium point in the case of the solvated electron,
whereas it has not completely relaxed in the "trapped" case. The solvated electron is in thermal equilibrium with the medium while the "trapped" state is not.

2. Electron Trapping in Frozen Systems

In the case of frozen systems, on the other hand, the thermalized electrons are thought to be stabilized by wholly or partially pre-formed traps which exist in the low temperature matrix. In glassy amorphous systems, the randomness of the molecular orientations of the liquid state is "frozen in" by quick cooling. Consequently there is a large concentration of pre-formed "traps" (i.e. dipole-oriented molecules forming an effective positive hole) available to compete with the parent ion's Coulombic attraction. This is in contrast to crystalline systems where short range order prevails. Thus for example, glassy alcohols trap electrons very efficiently ($G_{e-}^{tr} = 2.5$ for methanol) whereas the same material in a polycrystalline form does not. 4

The trapping process is thought to be similar to the solvation process discussed above, although the advantage of at least partial pre-orientation of the dipoles allows for a much greater trapping efficiency. Normally higher yields of trapped electrons are observed relative to the solvated electron yield in the same material. This is probably a direct consequence of the fact that the trapped electrons in polar media are stabilized within the immediate vicinity of the spur (i.e. they don't travel as far in the solid as in the liquid). Thus the spatial distribution of trapped electrons
is likely to be very different to that of solvated ones.

3. **Properties of Stabilized Electrons**

Stabilized electrons formed by radiolysis have properties very similar to those of solvated electrons formed by dissolution of alkali metals in ammonia and amines. They are very powerful reducing species, reacting often with diffusion controlled rate constants in solution, and consequently have relatively short lifetimes in irradiated liquid systems (i.e. $10^{-5}$ seconds or less).

Solvent-stabilized electrons are characterized by broad intense optical absorption spectra in the visible or near infrared regions. This is their most important property as far as detection and kinetic studies are concerned. The species are also paramagnetic and therefore electron spin resonance (ESR) is extensively used to study the long lived trapped electrons in frozen systems. Recent advances in ESR techniques have also enabled the short lived solvated electrons produced by pulse radiolysis of liquids to be studied.\textsuperscript{13}

Stabilized electrons are now known to exist in a whole variety of media from the non-polar liquified noble gases to highly polar solvents such as water and alcohols.\textsuperscript{5} Table 2 contains some of the spectral data for electrons stabilized in a few of the more extensively studied systems.

4. **Yields of Stabilized Electrons**

It has been reasonably well established that the yield
### TABLE 2

**SELECTED PROPERTIES OF STABILIZED ELECTRONS FORMED BY RADIOLYSIS**

<table>
<thead>
<tr>
<th>Medium</th>
<th>Ds</th>
<th>T (°K)</th>
<th>Optical Data</th>
<th>ESR Data</th>
<th>Yield</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>λmax (nm)</td>
<td>ε (M⁻¹cm⁻¹)</td>
<td>q-factor</td>
</tr>
<tr>
<td>7N NaOH glass</td>
<td>-</td>
<td>77</td>
<td>580</td>
<td>19,000</td>
<td>2.0006</td>
</tr>
<tr>
<td>Water</td>
<td>78.2</td>
<td>293</td>
<td>720</td>
<td>17,000</td>
<td>2.0002</td>
</tr>
<tr>
<td></td>
<td>77</td>
<td>77</td>
<td>640</td>
<td>17,000</td>
<td>2.0009</td>
</tr>
<tr>
<td>Heavy water</td>
<td>78.5</td>
<td>293</td>
<td>700</td>
<td>20,200</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>77</td>
<td>77</td>
<td>630</td>
<td>20,200</td>
<td>2.0007</td>
</tr>
<tr>
<td>Methanol</td>
<td>32.6</td>
<td>293</td>
<td>630</td>
<td>17,000</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>77</td>
<td>77</td>
<td>526</td>
<td>11,000</td>
<td>2.0018</td>
</tr>
<tr>
<td>Isopropanol</td>
<td>18.6</td>
<td>293</td>
<td>820</td>
<td>13,000</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>77</td>
<td>77</td>
<td>615</td>
<td>15,300</td>
<td>2.0018</td>
</tr>
<tr>
<td>Methyl tetra-</td>
<td>4.6</td>
<td>293</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>hydrofuran</td>
<td>77</td>
<td>77</td>
<td>1250</td>
<td>16,800</td>
<td>2.0011</td>
</tr>
<tr>
<td>Ethylene Glycol</td>
<td>38.7</td>
<td>293</td>
<td>580</td>
<td>14,000</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>77</td>
<td>77</td>
<td>513</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>

**Footnotes:**
- a. Data from references 4, 5d, and 5e.
- b. Static dielectric constant at room temperature.
- c. Line width between points of maximum slope.
- d. Polycrystalline solid.
- e. Glassy amorphous solid.
of solvated electrons correlates with the static dielectric constant of the liquid. This empirical correlation is illustrated graphically in Figure 5 which contains data from several sources and obtained by a variety of techniques. For some of the solvents, conclusive proof that the ionic reducing entity is in fact a solvated electron does not exist. Indeed, in a few cases the species could well be a radical anion formed by an ion-molecule reaction of either the thermal electron or a very short lived solvated one with the solvent. For this reason the term "free ion yield", \( G_{f1} \), is used in Figure 5 because it is more universally applicable and in essence it represents the number of thermal electrons which escape geminate recombination.

The yields of trapped electrons in frozen systems, however, do not seem to correlate well with any particular physical property of the matrix, other than its degree of order. In most glassy solids the yields of trapped electrons are high, and in many cases higher than the yield of solvated electrons in the liquid material. This is likely to be the result of the fact that one or more of the following factors may be operating in the glassy state to lower the probability of prompt geminate recombination:  

17. (a) "sub-ionization" electrons may have a lower cross-section for energy loss per collision in the solid matrix than in the liquid because of fewer vibrational and rotational states to which energy can be transferred, (b) the trap depth resulting from either self trapping by suitably oriented dipoles or from imperfections in the matrix may be sufficient to compete with the Coulombic
Figure 5. Yield of radiolytically generated free ions ($G_{fi}$) as a function of the static dielectric constant ($D_s$) of the liquid.

- $\bullet$ = Alcohols and waters; reference 5e.
- $\bigcirc$ = Nitriles, ketones, ethers, amides, pyridine, dimethyl sulfoxide, propylene carbonate, hydrocarbons; reference 14.
- $\bigtriangledown$ = Formamide; reference 15.
- $\square$ = Ammonia; reference 16.
force of the positive ion, and (c) as the trapped charge concentration increases with dose, the presence of competing electric fields from several positive ions weakens the directional effect on the trapped electron. Thus for example, the yield of trapped electrons in glassy methanol at 77\(^\circ\)K is \(G_{e_{tr}} = 2.5\) whereas the yield of solvated electrons in the same material at room temperature is only \(G_{e_s} = 1.1\).
CHAPTER II

AN ATTEMPT AT NITROGEN FIXATION UTILIZING HYDRATED ELECTRONS

A. INTRODUCTION

1. Background to the Problem

Nitrogen fixation* has always been of particular interest to scientists because of its importance to the evolution of life on the earth. In current biological systems, nitrogen is taken from the atmosphere and incorporated with the aid of micro-organisms, via ammonia, into organic nitrogen compounds under very mild conditions. In contrast to this, temperatures of 300-600 °C and several hundred atmospheres pressure of nitrogen are required in the industrial Haber-Bosch process to overcome the inertness of the molecule and convert nitrogen to ammonia. Thus a crucial question to understanding evolution is how nitrogen was reduced in prebiological times when only the basic ingredients; nitrogen, hydrogen, and methane existed in a relatively mild environment.

Although the problem of biological nitrogen fixation has been, and currently is, one of the major areas of research in biology and biochemistry; it was only recently that the chemists' interest in non-enzymatic nitrogen fixation was rekindled by Allen and Senoff's discovery of a transition metal.

*footnote 1. Nitrogen fixation is used here in its broadest sense to include any process which converts molecular nitrogen to some other molecule.
complex of molecular nitrogen. This discovery and subsequent rapid growth in the field of nitrogen complex chemistry, with the additional discovery that the nitrogen ligands could be reduced in certain systems, stimulated interest in this laboratory in the possibility of radiation chemical fixation of molecular nitrogen.

The hydrated electron, a primary species formed in the radiolysis of water, is known to be an extremely powerful reducing agent with a standard electrode potential of \(-2.7\) V. This makes it comparable in reducing strength to metallic sodium in water. In addition, it is the ideal nucleophile for simple electron transfer reactions and it shows extremely high rate constants for reactions with a wide variety of compounds, some of which had previously been regarded as non-reducible. Furthermore, almost all of these reactions proceed with virtually no energy of activation, although in some cases the reaction rate is diminished by a small pre-exponential factor. Thus the aim of this investigation was to determine whether reaction (1) occurs with an observable rate.

\[
e_{aq} + N_2 \rightarrow [N_2^-]_{aq} \rightarrow NH_3 \text{ (or } N_2H_4 \text{ or } NH_2OH) \quad (1)
\]

2. Literature Survey

Non-enzymatic nitrogen fixation has been achieved in a variety of ways in addition to those involving transition metal complexes. In addition to the Haber-Bosch process for the catalytic conversion of $N_2/H_2$ mixtures to ammonia, gas phase oxidative and/or reductive nitrogen fixation has been
accomplished by: (a) radiolysis of $N_2/O_2$ or $N_2/H_2$ gas mixtures, 
(b) sonolysis of air, (c) gas discharge methods, and (d) 
heterogeneous reaction of molecular nitrogen with some group I 
and II metals to give ionic nitrides which can be hydrolysed to 
give ammonia. The electrolytic reduction of molecular nitrogen
in an aprotic solvent using an alkali metal or the napthalene
anion radical in conjunction with a transition metal ion has
been reported and the radiation chemical fixation of molecular
nitrogen in $\gamma$-irradiated organic compounds has been claimed.

In aqueous solution, the oxidation of nitrogen by excited
singlet oxygen molecules was reported and a process for hetero-
geous catalytic fixation of nitrogen or air in an aqueous
solution utilizing high energy radiation has been patented.

In addition to the literature mentioned above, and
particularly relevant to the present study, are a number of
publications concerned with the radiolysis of aqueous solutions
of nitrogen and air. Dmitriev and Pshezhetskii reported that the $\gamma$-radiolysis of neutral aqueous solutions containing
either pure nitrogen or nitrogen-oxygen mixtures produced fixed
nitrogen in the form of nitrite, nitrate, and ammonia. The
yields of these products increased with increasing gas pressure
above the solution and the presence of oxygen apparently had
little effect on the yields. A value of $G(NH_3) \sim 0.1$ was quoted
for a pressure of one atmosphere of either pure nitrogen or an
80/20 mixture of nitrogen and oxygen, with this rising to
$G(NH_3) \sim 0.7$ at 150 atmospheres. An attempt was made to explain
these results on the basis of reactions of H, OH and $HO_2$. 

radicals with nitrogen; however, on the basis of the now known reaction rate constants of $H_\text{aq}$ ($e^-$) and OH with oxygen, it is very difficult to understand how nitrogen at $10^{-4}$ M (1 atm) would be able to efficiently compete with any oxygen or impurities present and give ammonia. Hammar et al. obtained very contrary results for nitrogen-hydrogen mixtures in neutral water using a reactor radiation source and taking care to eliminate the gas space above the liquid. Their results of $G_{N_2}(NH_3) = 2.6 \pm 1.3$ for 75% $N_2$ - 25% $H_2$ are at least four orders of magnitude lower than those of Dmitriev and Pshezhetskii since the $G_{N_2}(NH_3)$ notation refers to the yield calculated on the basis of the energy absorbed directly by the dissolved nitrogen. At one atmosphere less than $1/10,000$ of the energy deposited in the solution would be absorbed directly by the dissolved nitrogen. Sato and Steinberg essentially agreed with the results of Hammar et al. They studied the $\gamma$-radiolysis of air in aqueous solution and found that $G_{\text{air}}(NH_3) = 2.3$ at neutral pH, with $G_{\text{air}}(NH_3)$ varying significantly with pH and flow rate of air through their apparatus.

3. The Chemical System

The experiments reported in this dissertation were designed to study in detail just one aspect of the radiation chemistry of aqueous nitrogen; namely the reaction of the hydrated electron with dissolved nitrogen. For this reason the experimental conditions were chosen to optimize the chances of observing the reaction since it certainly would not be expected to be very fast.
In alkaline solutions containing hydrogen, the primary radiolysis species other than $e^-_{aq}$ are converted to hydrated electrons via the series of reactions (2), (3), and (4).\(^{22}\)

$$\text{OH} + \text{H}_2 \rightarrow \text{H} + \text{H}_2\text{O} \quad (2) \quad k_2 = 4 \times 10^7 \text{ M}^{-1}\text{s}^{-1}$$

$$\text{H} + \text{OH}^- \rightarrow e^-_{aq} + \text{H}_2\text{O} \quad (3) \quad k_3 = 2 \times 10^7 \text{ M}^{-1}\text{s}^{-1}$$

$$\text{H}_2\text{O}_2 + e^-_{aq} \rightarrow \text{OH}^- + \text{OH}^- \quad (4) \quad k_4 = 1.2 \times 10^{10} \text{ M}^{-1}\text{s}^{-1}$$

Furthermore, trace quantities of oxygen are also eliminated quickly by reaction (5). Thus the H\(_2\)/OH\(^-\) system produces a very "clean" source of hydrated electrons with a substantial yield $G(e^-_{aq}) \sim 6$. Although the bimolecular reaction of the hydrated electron (6) has a high rate constant, at the low dose rates used, the steady state concentration of hydrated electrons will be so low that this reaction may be disregarded.

$$\text{O}_2 + e^-_{aq} \rightarrow \text{O}_2^- + \text{H}_2\text{O}_2 \quad (5) \quad k_5 = 1.9 \times 10^{10} \text{ M}^{-1}\text{s}^{-1}$$

$$e^-_{aq} + e^-_{aq} \rightarrow \text{H}_2 + 2\text{OH}^- \quad (6) \quad k_6 = 5 \times 10^9 \text{ M}^{-1}\text{s}^{-1}$$

Nominally then, in the H\(_2\)/OH\(^-\) system containing dissolved nitrogen, reaction (1) will be in competition only with reactions of the hydrated electrons with impurities or hydrogen peroxide generated via the "molecular" process ($G_{\text{H}_2\text{O}_2} = 0.8$).\(^2\)

A second advantage of the presence of molecular hydrogen was to supply the stoichiometric $\text{H}$ necessary for the ultimate reduction of $\text{N}_2$ to $\text{NH}_3$. It seemed reasonable to assume that once the barrier to reduction had been overcome in the formation of $\text{N}_2^-$ or $\text{N}_2\text{H}$, then its eventual conversion to ammonia (or at least hydrazine or hydroxylamine) would be inevitable in the reducing environment. Indeed both $\text{N}_2^-$ and $\text{N}_2\text{H}$ have been proposed as feasible intermediates on the basis of theoretical
electron affinity studies.  

A number of preliminary experiments were performed in this laboratory by Walker and Edwards in an attempt to test the system and reaction (1). They used a stainless steel high pressure cell which contained a glass vessel of variable volume to hold the aqueous solution. By pressurizing the cell to several hundred atmospheres a significant dissolved nitrogen concentration (~0.1 M) could be achieved. Ammonia analysis was performed on the solution after γ-radiolysis using the Nessler spectrophotometric technique. Although substantial yields of ammonia were observed, the results were not reproducible. In addition, it was virtually impossible to determine from their data how much, if any, of the ammonia was produced via reaction (1) since at all times a significant radiation dose was absorbed by the N₂/H₂ gas mixture above the solution and the ammonia produced by gas phase radiolysis was also being measured. To alleviate this problem, a technique was developed in which complete isolation of the nitrogen saturated liquid was possible.

B. EXPERIMENTAL

1. Reagents

All chemicals used were analytical grade or better. Solutions of various pH were made using "Analar" sulfuric acid and sodium hydroxide. Hydrogen and nitrogen were Matheson prepurified grade. Further oxygen removal from the hydrogen-nitrogen mixtures was achieved by incorporation of a "Deoxo"
palladium catalyst in the gas train. Compositions of the gas mixtures used were determined using a Varian Aerograph A90-P-2 gas chromatograph with a 20 foot 13X molecular sieve column and WX thermal conductivity detectors.

Water was purified by three consecutive distillations; the first from tap water, the second from acidified dichromate, after which it was $\gamma$-irradiated with a 0.5 Mrad dose to remove trace organic impurities. Finally it was placed under continuous cyclic reflux distillation from alkaline permanganate until used. The water was shown to contain less than $5 \times 10^{-7}$ M ammonium ions by the analysis procedure to be discussed later and it probably contained much less than $10^{-6}$ M reactive organic impurities.

2. **Radiation Source**

A $^{60}$Co Gammacell 220 radiation source was used which had an activity of 6170 Curies when loaded in June, 1967. The dose rate was determined by the Fricke ferrous sulfate procedure which is discussed in detail in Appendix 1. The dose rate inside the high pressure cell was determined to be 2500 rads min$^{-1}$ ($1.6 \times 10^{17}$ ev g$^{-1}$min$^{-1}$) and the day to day variation in dose rate caused by decay of the source was corrected for using a computer program also discussed in Appendix 1.

3. **Apparatus and Techniques**

A syringe technique by which the solution containing a high concentration of dissolved nitrogen could be effectively
isolated to prevent gas phase radiolysis was developed. 50 ml all-glass syringes (Becton, Dickinson and Co.) were modified by cutting off the flared end of the barrel and grinding the tapered glass tip to fit a modified B7 socket (the flared ends of the B7 sockets were also cut off). The plungers of the syringes were also cut leaving a section about 1\(\frac{1}{2}\) inches long to fit inside the modified syringe barrel. A B14 socket was sealed in place "inside" the plunger section to facilitate operation of the syringe by inserting a section of glass tubing with a B14 cone on the end. In addition a modified B7 socket "cap" was ground to fit each syringe tip in order to provide a liquid tight seal. A photograph of the modified syringe and attachments appears in Figure 6.

The modified syringes were designed to fit snugly inside the stainless steel high pressure apparatus which is shown in Figure 7. This cell was manufactured from a single piece of #304 stainless steel and its dimensions were 88 mm O.D. by 172 mm long with the bore for the syringe being 35 x 145 mm. The top, 25 mm thick, was held down by eight 3/8 inch by 1\(\frac{1}{2}\) inch cap screws and the pressure seal was made by a rubber "O" ring. 1/8 inch thick circular rubber pads were placed on the inside of the cell to protect the syringes during operation. High pressure nitrogen was fed into the cell via 1/4 inch stainless steel high pressure tubing and valve which were fitted to the side of the cell by a standard high pressure coupling. A schematic of the pressure system is shown in Figure 8. Before use, the apparatus was pressure tested to
Figure 6. Photograph of the modified 50 ml all-glass syringes and attachments.
Figure 7. Photograph of the stainless steel high pressure cell used to pressurize the syringes.
Figure 8. Schematic diagram of the high pressure system.
10,000 psig which was more than twice the normal operating pressure.

The syringes were filled with a nitrogen-hydrogen gas mixture and aqueous solution using the apparatus illustrated in Figure 9. The syringe was attached via the B7 socket and lubricated with the solution. By tilting the apparatus in the appropriate directions; first the gas sample could be admitted to the syringe and this followed by the gas saturated aqueous solution. Then after quickly removing the syringe from the B7 socket, while flushing a portion of the liquid out, a B7 cap was placed over the end. Using this procedure it was possible to fill the syringes without any appreciable atmospheric oxygen contamination. When the syringe was then pressurized, the gas inside was compressed and the plunger was pushed down to contact the liquid surface since most of the gas present dissolved in the solution at the high pressure. A small glass plate was used as a mixer in the syringes and the solutions were made homogeneous by inverting the high pressure cell during equilibration.

In a typical experimental series, all of the glass apparatus would first be scrupulously cleaned by initially soaking in permanganic acid (KMnO₄ in 95% H₂SO₄), followed by rinsing with distilled water, soaking in a nitric acid solution of hydrogen peroxide to remove traces of MnO₂, and finally rinsing well with singly, doubly and triply distilled water successively. The apparatus was then dried in a special organic free oven at 100 °C and then assembled. Corning silicone
Figure 9. Diagram of the apparatus used to fill the syringes with gas and liquid samples, shown with a syringe attached.
grease was used on the stopcocks which controlled the gas flow; all other joints were lubricated with the experimental solution. With the syringe disconnected and a B7 plug substituted, the solution was deoxygenated by bubbling high purity hydrogen through the apparatus for about one hour. Then, with the stopcocks closed, the solution was "pre-irradiated" for 30 minutes (~2 x 10^5 rads) under the hydrogen atmosphere. This pre-irradiation was intended to remove any traces of reducible organic or inorganic contaminants in the solutions. Following the pre-irradiation, a weighed syringe was attached to the apparatus and lubricated with a bit of the solution. After flushing the entire system with the N_2/H_2 mixture for about 2-3 hours, the syringe was filled with ~30 ml of gas and ~20 ml of liquid, then removed and capped using the procedure described above. The syringe was then weighed to obtain the weight of solution and pressurized in the high pressure cell using pure nitrogen at 3000 psig (200 atm). At this pressure virtually all of the gas would dissolve in the solution and to ensure that this occurred, the pressurized sample was left to equilibrate for about one hour, during which time it was occasionally inverted to cause the mixing plate to "stir" the solution. The equilibrated sample was then irradiated in the Gammanacell for various times ranging from 60 - 12,000 minutes. After the irradiation, the cell was slowly depressurized (fast depressurization invariably led to a shattered syringe caused by the plunger becoming jammed) and the syringe was removed and the solution analysed. It was noted that when the syringes were removed (about 5 minutes after depressurization) only
about 10 - 15 ml of gas was observed above the solution which was evolving gas continuously. By shaking the syringe and allowing sufficient time, the gas volume soon increased to its original value. These observations indicated that during the pressurization stage no leakage of the syringe occurred and also that most of the gas had dissolved in the liquid under pressure.

4. **Analytical Procedures**

The irradiated solutions were analysed for ammonia using the very sensitive "indophenol blue" method. The procedure used was similar to the one developed by Tetlow and Wilson\(^{37}\) and complete details of the technique and calibration data are given in Appendix 2. Basically, the procedure involved converting the ammonia to the indophenol blue dye using phenol and sodium hypochlorite in very alkaline solution. The concentration of ammonia was related to the absorbance of the dye at 630 nm. The sensitivity of the test was about \(5 \times 10^{-7}\) M ammonium ions, however interference of hydrogen peroxide as discussed in the Appendix limited the working sensitivity to about \(5 \times 10^{-6}\) M. In analysis of a typical experiment, the irradiated solution was divided into two parts; one of which was analysed in the normal manner and to the other portion a known quantity of \(\text{NH}_4^+\) solution was added as an "internal" standard to check on any possible effects of other radiolysis products (such as hydrogen peroxide).

Qualitative spot checks for the presence of hydrazine and hydroxylamine were performed using trinitro-benzene-sulfonic acid as described by LaPue\(^{38}\).
C. RESULTS

The pertinent data from the "successful" experiments are listed in Table 3. (Several experiments were unsuccessful because of shattered syringes.) The two methods used to calculate the yields of ammonia, $G_W(NH_3)$ and $G^N_2(NH_3)$, are based on the dose absorbed by the water and directly by the nitrogen molecules, respectively. Experiment A-4 was done to tie in with the preliminary experiments of Walker and Edwards$^{35}$. In this experiment the plunger was removed from the syringe so that the solution was in contact with a large gas volume and gas phase radiolysis could occur.

In all cases the spot tests for hydrazine and hydroxylamine were negative indicating that these "intermediates" were not present in significant yields at the time of analysis.

The overall results of these experiments may be summarized as follows: the yield of ammonia from an isolated solution of nitrogen at 0.1 M was $G_W(NH_3) \sim 0.002$ and this yield was independent of the pH of the sample.

D. DISCUSSION

The fact that the yield of ammonia based on the dose absorbed by the water was $G_W(NH_3) \sim 0.002$ means that despite the favourable conditions for reaction of hydrated electrons with nitrogen, it does not occur to a significant extent. The value of $G^N_2(NH_3) = 0.7$ for the neutral solution of nitrogen is in reasonable agreement with that measured by Hammar et al.
### TABLE 3

**SUMMARY OF NITROGEN FIXATION EXPERIMENTS**

<table>
<thead>
<tr>
<th>Exp</th>
<th>pH</th>
<th>Dissolved Gas $^{\text{a}}$ (Mx10$^{2}$)</th>
<th>Dose (eVx10$^{-20}$)</th>
<th>$[^{\text{NH}_4}]$</th>
<th>$G^{W}(\text{NH}_3)^{\text{b}}$</th>
<th>$G^{N_2}(\text{NH}_3)^{\text{c}}$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>$[\text{N}_2]$</td>
<td>$[\text{H}_2]$</td>
<td>$[\text{O}_2]$</td>
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<tr>
<td>A-1</td>
<td>11</td>
<td>1.8</td>
<td>0.38</td>
<td>&lt;0.001</td>
<td>1.6</td>
<td>0.0036</td>
</tr>
<tr>
<td>2</td>
<td>11</td>
<td>8.9</td>
<td>1.6</td>
<td>&lt;0.001</td>
<td>1.5</td>
<td>0.0036</td>
</tr>
<tr>
<td>3</td>
<td>11</td>
<td>8.9</td>
<td>1.6</td>
<td>&lt;0.001</td>
<td>23</td>
<td>0.060</td>
</tr>
<tr>
<td>4$^{e}$</td>
<td>11</td>
<td>13</td>
<td>0.27</td>
<td>&lt;0.001</td>
<td>1.5</td>
<td>1.9</td>
</tr>
<tr>
<td>B-1</td>
<td>7</td>
<td>7.5</td>
<td>&lt;0.001</td>
<td>2.2</td>
<td>2.5</td>
<td>0.0052</td>
</tr>
<tr>
<td>2</td>
<td>7</td>
<td>9.2</td>
<td>&lt;0.001</td>
<td>&lt;0.001</td>
<td>2.6</td>
<td>0.0067</td>
</tr>
<tr>
<td>3</td>
<td>7</td>
<td>7.1</td>
<td>0.79</td>
<td>&lt;0.001</td>
<td>2.6</td>
<td>0.0052</td>
</tr>
<tr>
<td>C-1</td>
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<td>8.0</td>
<td>&lt;0.001</td>
<td>2.4</td>
<td>23</td>
<td>0.051</td>
</tr>
<tr>
<td>2</td>
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<td>&lt;0.001</td>
<td>&lt;0.001</td>
<td>24</td>
<td>0.062</td>
</tr>
<tr>
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<td>7</td>
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<td>1.2</td>
<td>&lt;0.001</td>
<td>26</td>
<td>0.056</td>
</tr>
<tr>
<td>4</td>
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<td>0.72</td>
<td>&lt;0.001</td>
<td>280</td>
<td>0.64</td>
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<tr>
<td>D-1$^{g}$</td>
<td>7</td>
<td>7.9</td>
<td>0.79</td>
<td>&lt;0.001</td>
<td>25</td>
<td>0.056</td>
</tr>
<tr>
<td>2</td>
<td>2</td>
<td>7.1</td>
<td>0.79</td>
<td>&lt;0.001</td>
<td>25</td>
<td>0.050</td>
</tr>
</tbody>
</table>

**Footnotes:**

a. The concentrations of dissolved gases were calculated from the solubility data - ref.39.  
b. $G^{W}(\text{NH}_3)$ is the yield of ammonia based on the energy absorbed by the water.  
c. $G^{N_2}(\text{NH}_3)$ is the yield of ammonia based on the energy absorbed directly by nitrogen.  
d. Ammonia concentrations given as an upper limit because of the very small absorbance ($\sim 0.03$) which could have been caused by peroxide.  
e. Plunger removed from the syringe, large gas volume above the solution.  
f. Severe hydrogen peroxide interference due to presence of oxygen.  
g. About 4 g of stainless steel chips added to the solution.
(\(G_{N_2}^{\text{NH}_3} = 1.8 \pm 0.9\)) \(^{33c}\) and by Sato and Steinberg \((G_{\text{air}}^{\text{NH}_3} = 2.3\)) \(^{33d}\). This ammonia is very likely produced by the direct action of the \(\gamma\)-radiation on the dissolved nitrogen molecules to give \(N_2^+\) or \(N_2^*\) which then react with the solvent or dissolved hydrogen to eventually give ammonia. This process apparently proceeds with a similar efficiency to the gas phase reaction since \(G_{N_2}^{\text{NH}_3} = 0.7\) was obtained by Cheek and Linnenbom for the gas phase radiolysis of nitrogen-hydrogen mixtures. \(^{25e}\) A further significance of the \(G_{N_2}^{\text{NH}_3}\) value is that once the reduction process has been initiated, the end product is ammonia. This agrees with the results of the qualitative tests for hydrazine and hydroxylamine which indicated that these intermediates were not formed in a significant amount. (The limit of detection of the test was about \(10^{-5}\) M for hydrazine and about \(10^{-3}\) M for hydroxylamine which gives corresponding upper limits of \(G_{W}(N_2H_4) \leq 0.005\) and \(G_{W}(\text{NH}_2\text{OH}) \leq 0.5\)).

The fact that some, if not all, of the ammonia formed in these experiments arises from direct action of radiation on the dissolved nitrogen means that an upper limit of \(G_{W}(\text{NH}_3) \leq 10^{-3}\) can be placed on the yield of ammonia produced through the reaction of nitrogen with hydrated electrons. This allows a calculation of an upper limit for the rate constant of reaction (1). Assuming the alternative fate of the hydrated electrons is reaction with unspecified impurity, \(X\), at the diffusion controlled rate of \(10^{10} \text{ M}^{-1}\text{s}^{-1}\), then an estimate of the concentration of \(X\) will allow calculation of \(k_1\). Purification of the water and its deoxygenation probably reduced the impurity
level to about $10^{-6}$ M. Since large radiation doses were used in the presence of molecular hydrogen, most of this initial impurity would be eliminated within the first few minutes of the irradiation. In addition, hydrogen peroxide produced by the "molecular" processes would be destroyed by $e_{aq}^-$ almost as fast as it was being produced and it would reach a "steady state" concentration of very much less than $10^{-6}$ M. Therefore a very conservative estimate of the steady state reactive impurity concentration, $[X]$, would be $10^{-6}$ M. Applying the steady state kinetic treatment to $e_{aq}^-$:

$$\text{rate of production of } e_{aq}^- = G(e_{aq}^-) \cdot I$$
$$\text{rate of loss of } e_{aq}^- = k_x [X]_{ss} [e_{aq}^-]_{ss}$$

where $I$ is the radiation intensity, implies:

$$[e_{aq}^-]_{ss} = \frac{G(e_{aq}^-) \cdot I}{k_x [X]_{ss}}$$

The rate of ammonia production is given by:

$$\text{rate of production of NH}_3 = k_1 [N_2] [e_{aq}^-]_{ss}$$
$$= G^W(NH_3) \cdot I$$

Since $G(e_{aq}^-) = G_{e_{aq}^-}^H + G_{g_{aq}^-}^H + G_{G_{aq}^-}^H = 5.7$ at high pH then for a nitrogen concentration of 0.1 M it follows that:

$$k_1 = \frac{G^W(NH_3) \cdot I}{[N_2] [e_{aq}^-]_{ss}} = \frac{G^W(NH_3) \cdot I}{[N_2] \cdot \frac{G(e_{aq}^-) \cdot I}{k_x [X]_{ss}}}$$
Thus a conservative upper limit for the reaction rate constant for production of ammonia from hydrated electrons reacting with nitrogen is $k_1 \leq 18 \text{ M}^{-1}\text{s}^{-1}$. This is one of the slowest rate constants estimated for hydrated electrons. (If reaction (1) gave hydroxylamine instead of ammonia, the upper limit on the rate constant would be about $5 \times 10^3 \text{ M}^{-1}\text{s}^{-1}$, however because of the insensitivity of the test this calculation is considerably less certain than that for ammonia.)

The significance of the experiment at pH 2 (D-2) is that the hydrogen atom reaction with nitrogen is also extremely slow. At pH 2, all of the hydrated electrons would be converted to H atoms via reaction (7).

$$e_{aq}^- + H_{aq}^+ \rightarrow H + H_2O \quad (7) \quad k_7 = 2 \times 10^{10} \text{ M}^{-1}\text{s}^{-1}$$

This result is not particularly surprising since hydrogen atoms are much less powerful reducing agents than hydrated electrons and their reaction rates are generally slower.

Experiment D-1 in which the solution contained stainless steel chips indicated that no catalytic enhancement of the reaction could be achieved by its presence.

In conclusion, these experiments have reiterated that the nitrogen molecule is extremely stable towards reduction, either by hydrated electrons or hydrogen atoms. It therefore seems unlikely that the fixation of nitrogen in nature (even
in the pre-biotic times) could ever arise through "indirect action" of high energy radiation.

E. SUGGESTIONS FOR FURTHER STUDY

Since the hydrated electron is unable to reduce "free" molecular nitrogen, an interesting question is whether it can fix molecular nitrogen in a bound form. As was discussed in the introduction to this study, it has been reported that some of the transition metal complexes apparently can be reduced in organic solvents to give ammonia. Thus it might be expected that the hydrated electron would be able to initiate reduction of coordinated nitrogen.

Unfortunately most of the known transition metal complexes of nitrogen are unstable in aqueous solution. One of the osmium compounds, however, was thought to be stable and in conjunction with Professor B. R. James and Dr. E. Ochiai an experiment was performed to see if Os^{II}(NH_3)_5N_2Cl_2 could be reduced. This experiment proved to be a failure since the complex was fairly rapidly hydrolysed in the alkaline solution and some of the ammonia ligands were apparently replaced by OH^- ones.

In light of the above remarks, a suggestion for further studies of the reducing power of the hydrated electron towards nitrogen would be to examine the aqueous radiation chemistry of suitable nitrogen complexes when compounds which are not hydrolysed have been synthesized. This area of research could
have commercial potential if a suitable system were found
where a transition metal ion would first coordinate the nitrogen
and then after the initiation of reduction, complex another
nitrogen molecule. A continuous cyclic process can be envisaged
wherein the transition metal ion acts essentially as a homo­
geneous catalyst, with nitrogen and hydrogen flowing through an
alkaline solution under radiolysis, and thus producing ammonia.
CHAPTER III

ASPECTS OF THE RADIATION CHEMISTRY OF PROPYLENE CARBONATE

Propylene carbonate (4-methyl-2-dioxolone, which may be abbreviated as PC in the following discussions) is a very polar aprotic solvent with some extraordinary physical and chemical properties. Illustrated in Figure 10, propylene carbonate is a five membered heterocyclic ring system which has two stereoisomers. Among its unusual features are:

(a) a very large liquid range from less than -70 °C to +240 °C,
(b) a moderately high dielectric constant of 65 at room temperature which is very temperature dependent, rising to greater than 90 below -60 °C,
(c) a corresponding very large permanent dipole moment of 4.94 x 10^-18 esu cm although this does not appear to cause strong intermolecular association in the solvent as evidenced by a Kirkwood correlation factor of near unity and NMR and IR data, (d) ultraviolet transparency above 225 nm which indicates that the C=0 is not an "organic" carbonyl but rather that the electron system is delocalized as in the CO_3^{2-} ion, and (e) chemical stability; PC does not react with strong reducing agents such as the
alkali metals,40,41 (or dissolve them), nor is it easily oxidized by strong oxidants such as permanganate.41 In addition, PC is readily purified by simple vacuum distillation and it is not toxic or hygroscopic.42 The major disadvantage of PC is that it is hydrolysed by acids and bases, although its neutral aqueous solutions are stable.40a

In light of the particularly interesting and unusual aspects of propylene carbonate, the present investigation was initiated to examine some of the facets of the radiation chemistry of PC. In particular, it was of interest to determine whether electrons could be stabilized in the system, since this laboratory has been particularly involved with solvated electrons, both in water and in polar aprotic solvents of high dielectric constant, such as formamide43a and dimethyl sulfoxide.15 A general investigation of the radiolysis of PC would also provide original information about a class of compounds whose radiation chemistry is essentially unexplored. A thorough survey of the literature revealed that although the electrochemistry of PC had been studied to a limited extent, its radiation chemistry has never been investigated.* Of the other cyclic organic carbonates (literally dozens of variations of the basic five membered ring system could be synthesized) only ethylene carbonate and its tetraphenyl derivative have been briefly examined.44

*footnote 2. After this study was begun, Hayon reported the free ion yield for PC as obtained by pulse radiolysis of its anthracene solution.
During the initial stages of this investigation, it was discovered that propylene carbonate formed an excellent glassy solid when cooled quickly in liquid nitrogen. Subsequent γ-irradiation of these glasses at 77 °K and examination by electron spin resonance revealed some very unusual radical spectra. Because of this, the emphasis of the initially proposed radiation chemical investigation was shifted from the liquid phase to the glassy solid state. Thus the majority of the results presented here will be concerned with the radiolysis of the low temperature glasses. Although a significant amount of data was obtained from the liquid phase experiments, this study was not as extensive as was originally planned.
PART I - RADIOLYSIS OF PROPYLENE CARBONATE IN THE SOLID STATE

A. INTRODUCTION

Studies of the radiolysis of frozen polar systems have been mainly concerned with water, its solutions and the alcohols\(^4\), although ketones and esters have been examined\(^45\) and comprehensive investigations of the very polar acetonitrile compounds have been published\(^46\). The weakly-polar frozen systems which have been the most extensively studied are the glassy ethers, such as methyl-tetrahydrofuran\(^47\).

In virtually every compound which forms a glassy solid (amorphous state in which the random orientation of the liquid phase is thought to be "frozen in") radiolytically generated species identified as trapped electrons have been discovered\(^5\). These entities are characterised by intense, near-infrared or visible optical absorption spectra and single narrow, Gaussian shaped, electron spin resonance lines near the free spin g-value of 2.0023. The ESR line is normally quite easily power saturated. This saturation does not cause the usual line broadening but rather is an "inhomogeneous" type of saturation where the line shape does not change while its intensity decreases uniformly. Photobleaching of the trapped electrons with light in the region corresponding to their optical absorption spectrum also occurs. The species may also be eliminated by added solutes of high electron affinity, i.e. electron scavengers, such as napthalene. Though normally stable for long periods of time in very polar glasses at 77 °K,
trapped electrons in weakly polar systems (such as methyl-
tetrahydrofuran) are not stable and they decay via processes
at least partially attributable to "geminate recombination"
with their parent positive ions

Trapped radicals produced by radiolysis are however,
not so easily identified. Since high energy radiation is not
very discriminating in its primary excitation, there is seldom
specific decomposition, but rather numerous different radicals
are generally formed in a single system. The combination of
proton hyperfine splitting of the individual radical ESR
spectra and anisotropy of the signals, together with the
overlapping of the lines usually prevents positive identifi­
cation of the species in all but the very simplest systems,
such as water and methanol. A brief discussion of the basic
theory of ESR and its applications to amorphous solids is
given in Appendix 3. Optical absorption spectroscopy is
also of only limited value in identifying organic radicals
since most absorb in the ultraviolet and the spectra are again
usually broad and overlapping. Variable temperature studies,
scavenger techniques, photobleaching experiments, and ESR
r.f. power saturation effects sometimes help to unravel the
complexity of irradiated organic systems. In most cases
however, the radical species defy positive identification
unless they can be generated in an unambiguous manner, such
as OH radicals by the photolysis of $H_2O_2$.

Since propylene carbonate is a very polar compound and
because glassy polar systems are known to trap electrons very
efficiently the present investigation was begun. Its aim
was to determine whether electrons could be stabilized in
glassy PC, and if so, to study their properties both by ESR
and optical techniques. Any information obtained with regard
to the radical species produced would be considered an added
benefit of the investigation.

B. EXPERIMENTAL

1. Reagents

Eastman Kodak practical grade propylene carbonate was
purified by fractional distillation under vacuum as described
in Appendix 4. The purified solvent was stored under dry
helium in a dispensing apparatus which is also discussed in
Appendix 4 along with the physical analyses.

All other chemicals used were analytical reagent grade
or equivalent.

Helium used for deoxygenation was supplied by Canadian
Liquid Air and it was dried by passing through a long copper
coil immersed in liquid nitrogen.

2. Radiation Source

A $^{60}$Co Gammacell 220 was used for the irradiations.
The source activity was 6170 Curies when loaded in June 1967.
An approximate dose rate of 4000 rads min$^{-1}$ (2.5 x $10^{17}$ eV g$^{-1}$
min$^{-1}$) was estimated from ferrous sulfate dosimetry done for
other experimental apparatus. Total doses ranged from
2 x $10^4$ to 1 x $10^6$ rads (1 x $10^{18}$ to 8 x $10^{19}$ eV g$^{-1}$).
3. **Sample Preparation and Irradiation**

Electron spin resonance measurements were made on glassy "balls" of PC, 2-3 mm in diameter, prepared by dropping the deoxygenated PC into a dewar of liquid nitrogen as described by Alger \(^{48}\). The samples prepared in this way were nearly perfect spheres, completely transparent, free from bubbles and cracks, and mechanically sound. Attempts to prepare a glass in small diameter quartz tubing always gave a polycrystalline sample.

For the optical studies, the sample of PC was sealed in a 1 cm square "spectrosil" quartz spectrophotometer cell after thorough degassing by multiple freeze-pump-thaw cycles. When immersed in liquid nitrogen, these sample usually became polycrystalline. On occasion, however, a reasonably transparent "glass" was formed with relatively few cracks and these samples were used. It was noted that the addition of even very small quantities of water to the PC did not improve the quality of the glass. In fact, addition of only 0.1% water caused the samples to become cloudy and virtually opaque.

All glassware used in handling the propylene carbonate samples, i.e. beakers, pipettes, spectro-cells etc., was always scrupulously cleaned using the routine permanganic acid-peroxide-distilled water treatment.

The sample balls of PC for the ESR studies were irradiated in a small pyrex dewar containing liquid nitrogen. In some cases, when kinetic studies and yield measurements were made, the samples were placed in a small beaker lined with
aluminum foil to prevent possible bleaching by the blue fluorescence which pyrex emits under radiolysis at liquid nitrogen temperature. Similar precautions were taken with the samples for the optical studies.

4. **Electron Spin Resonance Measurements**

All electron spin resonance spectra were measured using a Varian Associates E-3 spectrometer which operated at 9.3 GHz (X-band) and with 100 kHz field modulation. The spectra at 77 °K were recorded with the samples contained in a quartz dewar filled with liquid nitrogen. For measurements above 77 °K, the custom-made quartz dewar shown in Figure 11 was used. The sample ball was supported in the center of this dewar on the end of the thin evacuated quartz tube which also contained the thermocouple. Cooling was achieved using nitrogen flowing through a long copper coil immersed in a large dewar of liquid nitrogen. In practice, the dewar was first cooled to the minimum possible temperature (85-90 °K) and the gas flow was then momentarily interrupted while a sample ball was quickly transferred from a liquid nitrogen bath and dropped into the top of the dewar. Continuous monitoring of the temperature with a chart recorder indicated that during the transfer process the samples probably warmed to about 95 °K before the gas flow was restarted. The temperature was varied simply by altering the flow rate of cold nitrogen through the dewar. A given temperature could be maintained to ± 2 °K by this method which proved to be adequate for the purposes of the experiments reported here.
Figure 11. Variable temperature ESR dewar
The magnetic field strength and field scan linearity were calibrated with a proton-probe gaussmeter and the microwave frequency was checked with a Hewlett-Packard model 5255A digital frequency counter. The microwave power levels were not calibrated and the values quoted are those read directly from the power control dial of the instrument.

Spectroscopic splitting factors, \( g \)-values, were determined using a finely powdered sample of DPPH (diphenyl picrylhydrazyl) sealed in a thin quartz tube which was placed in the dewar along with the sample. \( g_{\text{DPPH}} = 2.0036 \) was used and the unknown \( g \)-values were calculated using the formula (viii)

\[
g_r = 2.0036 \left(1 - \frac{\Delta H}{H_r}\right)
\]

where \( \Delta H \) is the difference in the magnetic field between the center of the unknown resonance and that of the DPPH and \( H_r \) is the absolute magnetic field of the "r" resonance.\(^{48}\)

Radiation yields (G values) were estimated using irradiated methanol as a standard. Both the PC sample and methanol were prepared under identical conditions; i.e. the samples were made as close to the same size as possible and both were irradiated simultaneously in the same dewar to provide identical absorbed doses (about 1.2 Mrad). The trapped electrons in methanol were photo-converted to the \( \text{CH}_2\text{OH} \) radical to avoid the power saturation problems of this species and \( G(\text{CH}_2\text{OH}) = 6.7 \) was used for the total yield of \( \text{CH}_2\text{OH} \) radicals\(^4\). The ESR spectra of both PC and methanol were recorded for a single ball in identical positions in the cavity and under identical spectrometer conditions. The areas under the absorption curves
were estimated by double integration (see ref. 63, page 442) and the relative G values were calculated using the ratio of the areas. These G values were subject to considerable error due to the uncertainty in the relative diameters of the sample balls, in the integration technique and in $G(CH\_2OH)$.

All the ESR spectra reproduced in this thesis were recorded directly onto the drawing paper by the E-3 spectrometer using reduced gain and increased field sweep.

5. Optical Absorption Measurements

Optical absorption spectra were recorded using a Cary model 14 spectrophotometer. The sample cell was maintained at 77 °K in a quartz dewar with optical windows. Liquid nitrogen bubbling in the dewar caused some "noise" problems but by using a slow scan rate and maximum pen damping, a reasonable signal-to-noise ratio was obtained. A sample of un-irradiated PC in a 1 cm cell at room temperature was used in the reference compartment and the instrument was "balanced" using neutral density filters in the reference beam. This was required because the partial crystallinity of the sample caused appreciable scattering of the sample beam. Black cardboard baffles were used to block out most of the scattered light.

For measurements in the infrared region the sample was protected from bleaching by the visible light of the tungsten IR source lamp by placing a thick UV-visible cutoff filter (Corning # 2-61) between the source and the sample. (When
the Cary 14 is operating in the IR mode, the entire emission
of a tungsten lamp passes through the sample before reaching
the monochromator and detector.)

6. Light Sources for Photobleaching Experiments

An unfiltered low pressure mercury vapour lamp (Hanovia
# 687A45) was generally used for the ultraviolet photolysis
experiments. This lamp had a "Vycor" envelope and therefore
transmitted only wavelengths above 220 nm. In the ESR
experiments, the samples were either bleached directly in the
cavity by shining the light through the grill of the cavity
or else the dewar containing the sample balls was placed
directly against the lamp envelope and both were surrounded
with aluminum foil. When photolysed in the cavity, the
light intensity was rather low but changes in the spectra
could be followed directly; whereas irradiation outside the
cavity was considerably more intense and caused rapid changes.

An ordinary 100 watt tungsten lamp was used for the
visible photolysis experiments and the samples were usually
bleached directly in the cavity. Isolation of various wave-
length regions was achieved by using Corning glass filters.
In each case these were checked to ensure that an undesirable
UV or IR "window" was not present.
C. **RESULTS AND DISCUSSION**

1. **The Trapped Electron**

(a) **Electron spin resonance observations**

γ-irradiation of glassy propylene carbonate at liquid nitrogen temperature with a 1 Mrad dose imparted only a very pale greenish colour to the samples. (This is in contrast to most other glassy materials which become intensely coloured when irradiated at low temperature.)

The ESR derivative spectrum obtained using the lowest operable microwave power (about 0.5 mW) immediately following the irradiation is shown in Figure 12. This spectrum consists of nine principal lines spread over a region some 130 G wide and centered at the "free-spin" $g$-value. The most striking feature of this group is the narrow central single line, labeled "A". (The other eight lines in Figure 12 will be examined in detail in Part 2 of this section which will deal with radicals other than $e^-_{tr}$.) As the microwave power level was increased above 0.5 mW the intensity of line "A" began to slowly decrease at first until it was virtually completely saturated at about 10 mW as indicated in Figure 13. This saturation effect was of the "inhomogeneous" type where the line width remained essentially constant with only the peak amplitude decreasing uniformly. A higher resolution trace of line "A" appears in Figure 14. The line was determined to be at $g = 2.0028 \pm 0.0002$ when measured relative to DPPH (this value compares favourably with $g = 2.0030$ calculated from the measured field and frequency). The line-width as measured between points of
Figure 12. ESR spectrum of $\gamma$-irradiated glassy PC immediately following the irradiation using the lowest operable microwave power (about 0.5 mW). (Dose $\sim$ 0.8 Mrad)
Figure 13. ESR spectrum of the same sample as Figure 12 only at about 10 mW microwave power.
Figure 14. High resolution ESR scan of line "A" of Figure 12. This line is attributed to trapped electrons in PC.
maximum slope, i.e. "peak-to-peak" on the derivative, was found to be $\Delta H_{ms} = 4.5 \pm 0.1$ G. Analysis of the line-shape, both by the method of slopes and the normalization method$^{48}$, indicated it to be very nearly Gaussian which is in agreement with the observed saturation characteristics. The normalization technique of line-shape analysis is applied to line "A" in Figure 15 where both the Gaussian and Lorentzian line-shapes are illustrated. On the basis of the Gaussian line-shape, the "free-spin" $g$-value and the power saturation characteristics, all of which are very similar to those of trapped electrons in other media$^{4,5}$, this single line, "A", was assigned to trapped electrons in PC.

The much narrower line of $e_{tr}^{-}$ in PC as compared to other polar glasses (e.g. alcohols and ices where $\Delta H_{ms} = 10 - 15$ G) can be explained by the absence of hydroxylic hydrogen atoms in PC. In the alcohols and ices, line broadening is thought to be caused by hyperfine interactions of the OH protons surrounding the trapping sites. Therefore in this regard, PC should be compared to the glassy ethers where ESR line-widths of $3 - 4$ G are observed for trapped electrons.$^5$

The initial yield of trapped electrons in glassy PC samples was estimated using glassy methanol as the standard as described in the experimental section. Comparison of the area under the absorption curve of line "A" with the total area under the CH$_2$OH triplet gave $G_{e_{tr}}^{-} = 0.3 \pm 0.2$ using $G_{e_{tr}}(\text{CH}_2\text{OH}) = 6.7$. (The error indicated here for $G_{e_{tr}}^{-}$ only includes the uncertainties in $G($CH$_2$OH), in the relative sample sizes and in the integration technique.) This yield is
Figure 15. High resolution ESR scan of the trapped electron line showing the normalization method of line shape analysis. • = Gaussian, x = Lorentzian.
somewhat lower than was expected on the basis of the polarity of the solvent and the "visual quality" of the glass. For example, in most glassy alcohols and ices $G_{etr} = 2 - 3$ and even in the relatively non-polar methyl-tetrahydrofuran glass $G_{e}\simeq 2.6$. In addition, the room temperature liquid phase radiolysis results to be discussed later in this thesis and those of Hayon $^{14}$ indicate that the yield of solvated electrons (or free ions) is $G \approx 2$, which would predict a yield of trapped electrons greater than 2 for the low temperature glass, since in most other systems $G_{etr} \geq G_{e}$ (e.g. in methanol $G_{etr} = 2.7$ as compared with $G_{e} = 1.1$). A probable explanation of this discrepancy is that at the microwave power level used a substantial degree of saturation was occurring to give a misleading result. In any event, yield measurements by ESR are subject to so many uncertainties that their absolute values are not particularly reliable. The relative values obtained are, however, significant and in this case the value of $G_{etr} \approx 0.3$ means that electrons are trapped reasonably efficiently in the glassy PC. Determination of the exact degree of trapping efficiency will require a much more accurate G value obtained by some method other than ESR. A spectrophotometric technique whereby the electrons are converted to a strongly absorbing species with a known molar absorptivity, such as the naphthalene anion, together with absolute dosimetry, would give a "good" G value.

Attempts to scavenge the trapped electrons in glassy PC with silver nitrate, carbon monoxide and carbon dioxide were unsuccessful. This was likely due to their limited
solubility in PC, which was less than $10^{-2}$ M; whereas much larger solute concentrations are normally required to scavenge electrons in glassy solids. Addition of water and aqueous solutions of hydrogen peroxide or formaldehyde gave cloudy polycrystalline samples which were not studied. However, iodine at 0.02 M did completely remove the trapped electron ESR line as well as modify the radical spectrum somewhat as shown in Figure 16. This is in accord with the known efficiency of iodine as an electron scavenger, which for example reacts with the hydrated electron at $k_2 = 5 \times 10^{10} \text{ M}^{-1}\text{s}^{-1}$. Iodine has also been reported to be a trapped electron scavenger in glassy ethanol. The absence of ESR signals for the expected product $I_2^-$ ion probably can be explained on the basis of dissociation of $I_2^-$ to form $I^-$ and $I^\cdot$, with the $I^\cdot$ radical then undergoing secondary reactions which result in the observed modification of the ESR spectrum of the other radicals. Napthalene, at 0.1 M, also removed the trapped electron ESR signal, replacing it with an incompletely resolved multi-line signal as shown in Figure 17. This new paramagnetic species was most probably the napthalene anion, an assignment which is supported by the observation that these samples were green in colour which is characteristic of the napthalene anion. Napthalene has been used as an electron scavenger in the glassy alcohols although the species formed was believed to be the protonated anion in these systems.

The observation that the trapped electrons were not stable in the irradiated PC glasses at 77 °K was perhaps the most puzzling discovery of this study. The fairly rapid
Figure 16. ESR spectrum of γ-irradiated glassy PC at 77 °K containing 0.02M iodine.
Figure 17. ESR spectrum of $\gamma$-irradiated glassy PC at 77 $^\circ$K containing 0.1 M napthalene.
spontaneous decay of the ESR line was first noticed in a sample that had stood in the dark for several hours following the irradiation. The intensity of line "A" relative to the radical spectrum was found to be greatly reduced. This natural decay did not appear to produce any new paramagnetic species nor was there any noticeable change in the intensity of the other radical spectra. (It would however be difficult to detect an overall change in the broad radical spectrum since the change in area would only be about 10%.) In subsequent experiments, the natural decay of $e_{tr}^-$ was followed directly by ESR for several hours after the irradiation. These studies revealed the decay characteristics illustrated in Figure 18, where data obtained for three different total doses is given. The peak-to-peak height of the ESR derivative signal is plotted as a function of time. Since the peak width, $\Delta H_{ms}$, did not change substantially during the interval over which the decay was monitored, the derivative peak height is proportional to the total number of spins present. (In actual fact, a very slow, smooth decrease in $\Delta H_{ms}$ of about 8% occurred over an interval of 350 minutes. This was not considered to be significant however, since when a correction was made for this decrease it did not alter the results of the kinetic analyses.) Because data for the very early stages of the decay (first 10 minutes) could not be experimentally obtained, the curves plotted in Figure 18 were normalized using an extrapolated "zero time" peak height. This was obtained from the second order kinetic plots by extrapolation of the initial linear region (see Figure 20).
Figure 18. Isothermal spontaneous decay of trapped electrons in $\gamma$-irradiated glassy PC at 77 °K as followed by ESR. (Data are arbitrarily normalized at "0" time.)
Figure 19 shows the first order kinetic analyses of decay data in which the logarithm of the peak heights are plotted versus time. All three sets of data give smooth curves which indicates that the decay mechanism does not follow simple first order kinetics. First order decay would be expected if the electrons were simply reacting with one of the solvent molecules constituting their traps.

Second order analysis of the data is given in Figure 20 where the inverse of the normalized peak heights are plotted versus time. These graphs all have two linear regions; an initial "faster" decay whose duration depends on the length of the irradiation, followed by a "slower" decay which is followed for at least one "half-life". Data not shown in these Figures was obtained at 500 and 1500 minutes after a 300 minute irradiation and these points fit the extrapolated second order plot in Figure 20 within the experimental error involved in removing the dewar from the ESR cavity. This indicated that the "slower" decay process was followed for at least two "half-lives". This apparent second order decay is not consistent with a homogeneous reaction of the electrons with positive ions (these species would be present in equal concentration) because the slopes of the second order kinetic plots are apparently different, implying a dose-dependent rate constant. The difference in the slopes is partially due to the normalization factors used, although the un-normalized data also gave different slopes. It should be noted however, that the data were obtained using different spectrometer conditions (gain and sample size) and thus absolute spin concentrations could not be measured.
Figure 19. First order kinetic analyses of the trapped electron decay data from Figure 18.
Figure 20. Second order kinetic analyses of the trapped electron decay data from Figure 18.
It is therefore possible that the differences in slope of the lines in Figure 20 may be a consequence of the experimental methods used. In any event, if the reaction process involved a homogeneous distribution of electrons, then the initial transient deviation would have to be attributed to a non-homogeneity of the system during the early stages following the irradiation. On this basis, the lowest dose experiment should have taken the longest time to become homogeneous because the spur separation distance would be greatest. In addition, Figure 18 shows that the overall decay is fastest for the lowest dose, but this may arise from the fact that a much larger proportion of the species observed after the long irradiation are "long-lived" ones. It is also difficult to envisage either species being sufficiently mobile to diffuse rapidly through the highly polar low temperature matrix and become homogeneously distributed. Their initial distribution would certainly not be homogeneous. Simple homogeneous second order decay would therefore seem to be ruled out unless some very unusual process for charge migration exists in this system.

A third possibility for the spontaneous decay mechanism is that the electrons are "pre-destined" to react with a particular positive ion. In this case the kinetics may not follow any simple reaction order but rather the decay would depend on the separation-distance distributions of the electrons and cations. This type of decay is thought to occur in 3-methyl pentane and methyl-tetrahydrofuran glasses. The initial decay rates of the trapped electrons in these systems were found to be directly proportional to dose and by normalization
of the data the decay curves were found to be superimposable for at least the first 50% of the decay and over a considerable variation in dose. In these systems the decay of each electron is apparently by a process which is independent of the total number of positive charges in the matrix. It is not easy to see if this is the case for $e_{tr}^{-}$ in PC glasses because the irradiation times and the decay "half-lives" are comparable.

The electron decay kinetics in PC as shown by Figure 18 most probably represent the species reacting with positive ions via a totally non-homogeneous process. The results of the 5 minute irradiation experiment indicate that 50% of the electrons produced are lost within 15 minutes after the end of the irradiation. Therefore a large fraction of those produced during the early stages of the 30 and 300 minute irradiations have decayed before the irradiation was finished. The initial transient features indicated in the second order plots (Figure 20) are therefore due to decay of the "short-lived" species formed during the last few minutes of the irradiation. These species may be those trapped close enough to their parent positive ion that they are already effectively "captured" and thus have no choice but to react. The remainder of the electrons are those which are sufficiently distant from a positive ion that the trap energy is comparable to or greater than the Coulombic forces and therefore they have a relatively long lifetime governed primarily by diffusion. Interpretation of the kinetics of this system will be a complex mathematical problem. A general theoretical treatment of
bimolecular reactions in solid and liquid systems where diffusion is the rate controlling factor has been made by Waite. Solutions of the problem are however easily obtained only if the distribution of the reacting species is assumed to be random and if no long-range forces are involved. These assumptions would not be expected to be valid in the case of ionic radicals produced in irradiated low temperature solids since Coulombic interactions may be involved in addition to a non-random distribution. Although Waite's general treatment has provisions for extension to include non-random distributions and inter-ionic forces, solutions are extremely complex and not easily applied to the experimental data. In addition, because the initial distribution of the species is most often unknown, this would require a successive approximation method to fit the theory to the experimental data using various assumed distributions.

One important implication of the decay studies is that the yield of trapped electrons estimated by comparison with methanol is obviously low. Since the experiment involved a long irradiation time (300 minutes) in order to obtain a reasonable signal level, the electrons measured were clearly only the "long-lived" ones. Most of the short-lived species would have already decayed during the irradiation. Thus the value of $G_{e_{tr}} = 0.3$ is undoubtedly low (perhaps by as much as a factor of 10). It must therefore reflect only a lower limit for the primary yield of trapped electrons in glassy propylene carbonate.
As would be expected, the trapped electrons were thermally unstable above liquid nitrogen temperature. When a sample was warmed above 90 °K, the ESR line disappeared almost immediately. A broad signal showing unresolved hyperfine structure replaced the $e_{tr}^-$ signal but this new species was believed to originate from the decay of one of the other radical species and not from the electron. The electron's fate on warming was most likely the same as its fate at liquid nitrogen temperature, only the reaction rate increasing with temperature.

Photobleaching experiments using a tungsten lamp and various optical filters were performed on a sample in the ESR cavity. The most significant result of these experiments was that the natural decay of the trapped electrons was not affected by light with $\lambda > 500$ nm but it was substantially accelerated by light in the 300 - 500 nm region. As will be discussed in the next section, this result supports the assignment of an absorption band in the violet region to the trapped electrons. It is also in agreement with the visual observation of only a pale green colour indicating that there are no broad absorption bands in the visible or near infrared regions. As in the natural decay at 77 °K, photolysis did not produce any new paramagnetic species as shown by the "photobleached" spectrum in Figure 21. The signals remaining near the center of this spectrum (in addition to a small amount of trapped electrons remaining) were most likely there initially, only obscured by the more intense $e_{tr}^-$ line. Again the fate of the trapped electrons on photolysis is probably the same as the
Figure 21. ESR spectrum of γ-irradiated glassy PC after visible photolysis to remove most of the trapped electrons.
natural decay, i.e. reaction with a positive ion, the process merely being accelerated by the energy input of the light, probably via a photoionization process.

(b) Optical absorption spectrum

As mentioned at the beginning of the previous section, irradiated glassy PC balls became pale green in colour. This effect was more easily seen for the samples in the 1 cm spectrophotometer cells, which were a dark green following irradiation with a 1 Mrad dose.

The optical absorption spectrum recorded immediately after the irradiation is represented by curve 1 of Figure 22. There was a strong absorption band in the UV with a maximum below 280 nm. This was probably due to radicals or radiolysis products having an organic carbonyl group since PC does not absorb above 225 nm. The more interesting parts of this spectrum are the shoulder on the UV band in the 300 - 500 nm region and the complex band showing "vibrational" structure between 500 and 750 nm. As will be discussed in a later section the 500 - 750 nm absorption can be attributed to a small initial yield of $\text{CO}_3^-$ and $\text{HCO}$ radicals both of which absorb in this region. A search of the near infrared region revealed no absorption beyond 750 nm out to 1300 nm for a sample irradiated with a 1 Mrad dose.

When the irradiated PC was stored in the dark at 77 °K for 24 hours, the shoulder of the UV band was greatly reduced in intensity as indicated by curve 2 of Figure 22 and the
Figure 22. Optical absorption spectra of $\gamma$-irradiated PC at 77 °K (sample partially crystalline) in a 1 cm cell. Curve 1 was obtained immediately after the irradiation, curve 2 was obtained 24 hours later. (Dose $\approx 1.3$ Mrad)
sample appeared pale blue in colour due to the remaining absorption in the red region. Since the natural decay of the trapped electrons was accelerated by photolysis with blue light and since about 90% of the trapped electrons would have decayed naturally in the 24 hour period (as implied from the ESR studies), a logical assignment of the shoulder of the UV band is to $e_{tr}^{-}$.

The spectrum constructed by subtracting curve 2 from curve 1 of Figure 22 is a broad band with a $\lambda_{\text{max}} \approx 370$ nm (3.4 eV) as shown in Figure 23. The width of this band at half maximum, $W_{1/2}$, is approximately 0.9 eV, which is of the same order of magnitude as that of trapped electrons in other media. The lack of any asymmetry on the high energy side of the absorption band, which is normally characteristic of trapped and solvated electron spectra, is probably due to the method used to construct the spectrum. In the 300 - 350 nm region differences between two large absorbances $>1$ were involved and therefore there is a considerable uncertainty in the net absorbance due to $e_{tr}^{-}$. It is also possible, if not probable, that the natural decay of the trapped electrons does not involve a uniform loss of electrons from the different depth traps, i.e. the electrons in the lowest energy traps may be lost preferentially. Since the absorption spectra of trapped electrons are believed to represent a population distribution of the different trap depths, the above method for constructing the spectrum would then give a false picture of the absorption band shape and its $\lambda_{\text{max}}$. Obviously Figure 23 may not represent the true absorption band, however it does give a
Figure 23. Absorption spectrum attributed to trapped electrons in PC at 77 °K as constructed by subtraction of curve 2 from curve 1 of Figure 22.
qualitative picture of the spectrum.

The assignment of this band to trapped electrons is consistent with the high dielectric constant of PC. Ekstrom\(^{5d}\) presented some "unpublished" data for trapped electrons in a formamide + 15% water glass at 77 °K where an absorption with \(\lambda_{\text{max}} \sim 400\) nm was apparently observed. (Pure formamide has a dielectric constant of 109 and the presence of 15% water would probably reduce the effective dielectric constant considerably.) In addition if the correlation between the room temperature dielectric constant and the absorption maxima for electrons trapped in various glassy media at 77 °K is extended, then a \(\lambda_{\text{max}}\) in the region of 400 nm may be expected for trapped electrons in PC with its dielectric constant of 65.

Further evidence supporting the above assignment is an approximate calculation of the molar absorptivity, \(\epsilon_{\text{max}}\), for the absorption band. Assuming that the yield of electrons in PC is \(G_{\epsilon_{\text{tr}}} = 0.3\) (i.e. that measured by ESR), then \(\epsilon_{\text{max}}\) is calculated to be \(9 \times 10^3\) M\(^{-1}\)cm\(^{-1}\). This is only slightly lower than the \(\epsilon_{\text{max}}\) observed for trapped electrons in other media where \(\epsilon_{\text{max}}\) ranges from \(8 \times 10^3\) to \(2 \times 10^4\) M\(^{-1}\)cm\(^{-1}\).

The yield measured by ESR is undoubtedly not accurate as discussed above. In addition the samples used for the optical studies were not "good" glasses but rather partially crystalline and thus the trapped electron yield in these samples could have been considerably lower than that for the glasses used in the ESR measurements. Consequently a more meaningful quantity to calculate is \(G_{\epsilon_{\text{tr}}} \times \epsilon_{\text{max}}\) and this has a value
of about $3 \times 10^3 \text{M}^{-1}\text{cm}^{-1}$ (electrons/100 eV).

(c) **Summary**

In summary, the above data presents a strong case for the existence of trapped electrons in glassy propylene carbonate. Their properties, as listed in Table 4, are in accord with the properties of trapped electrons in other media (see Table 2 and references 4,5), with the exception of the mysterious instability of the species. This instability is particularly difficult to rationalize on the basis of the assignment of the absorption band with $\lambda_{\text{max}} = 370$ nm to the species. If this assignment is correct, it means that the average trap depth for the electrons is about 3.5 eV. This indicates that the electron is very strongly bound in its trap as would be expected from the very large dipole moment of PC ($4.9 \times 10^{-18}$ esu cm). Consequently to try to explain the natural decay on the basis of "thermal diffusion" of the electrons from trap to trap is not possible. In addition, the high dielectric constant of the medium should weaken the interionic forces between the cations and the electrons unless the electrons are trapped immediately adjacent to a positive ion.
TABLE 4

CHARACTERISTICS OF ELECTRONS TRAPPED IN PROPYLENE CARBONATE GLASSES AT 77 °K

ESR

<table>
<thead>
<tr>
<th>Characteristic</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>g-factor</td>
<td>2.0028 ± 0.0002</td>
</tr>
<tr>
<td>$\Delta H_{ms}$</td>
<td>4.5 ± 0.1 G</td>
</tr>
<tr>
<td>line-shape</td>
<td>Gaussian</td>
</tr>
</tbody>
</table>

OPTICAL

<table>
<thead>
<tr>
<th>Characteristic</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\lambda_{max}$</td>
<td>~370 nm (3.4 eV)</td>
</tr>
<tr>
<td>$W_{1/2}$</td>
<td>~0.9 eV</td>
</tr>
</tbody>
</table>

YIELD

<table>
<thead>
<tr>
<th>Characteristic</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>$G_{e-tr}$</td>
<td>&gt;0.3 electrons/100 eV</td>
</tr>
</tbody>
</table>

STABILITY

Not stable at 77 °K; spontaneous decay via a non-homogeneous process believed to be reaction with positive ions. Approximate first "half-life" for 1 Mrad dose is about 4 hours; with the apparent "half-life" decreasing with dose at a given dose rate (0.3 Mrad/hr).
2. **Trapped Radicals in Irradiated PC**

   (a) **Radicals formed during radiolysis at 77 °K**

   The radicals formed during the initial radiolysis of glassy PC at 77 °K gave an ESR spectrum which consisted of eight principal lines centered at essentially the free-spin g-value and spread over a region some 130 G wide as shown in Figure 12. No indication of any signals with a splitting of 500 G attributable to H atoms was found. One pair of the lines shown in Figure 12, labeled "C", was easily power saturated as the microwave intensity was increased as indicated in Figure 13. This broad doublet, with a splitting of 58 ± 3 G, was thermally unstable above about 90 °K and at about 110 °K it decayed rapidly to completely reveal the underlying six lines, "B", "D", "E", as illustrated in Figure 24. A new paramagnetic species with incompletely resolved small hyperfine splitting "grew" in at the center of the spectrum as the broad doublet decayed. The radical responsible for the broad doublet "C" could not be conclusively identified although a speculative guess would be the radical:

   ![Radical Structure](image)

   which might be expected to give a very broad ESR doublet with a large proton hyperfine splitting.

   The other six lines were just as elusive in their identification as doublet "C". However, with the aid of photobleaching, isothermal decay and scavenger experiments, it was possible to show that the six lines were really three sets of
Figure 24. ESR spectrum of \( \gamma \)-irradiated glassy PC at \( \sim 110 \) °K after thermal decay of the trapped electrons and other radicals.
doublets with hyperfine splitting of $42 \pm 2$, $83 \pm 3$, and $124 \pm 4$ G respectively. All three doublets were centered at $g = 2.0023 \pm 0.0003$. When a sample was first warmed to about 110 °K to remove the broad doublet "C" (which obscured the resolution of lines "B" and "D") and then photolysed with the unfiltered mercury lamp, the middle doublet "D" was observed to decrease in intensity fairly rapidly with a concomitant production of a new intense line, "F", at the center of the spectrum. Line "F" appeared superimposed on the existing central multicomponent signal. This is illustrated in Figure 25 where it is clear that doublet "D" has decreased markedly in intensity after only a few minutes of UV irradiation. Doublet "E" was also slightly reduced in intensity following photolysis but the relatively smaller decrease suggested that this was a separate radical. In addition, if a filter was used to eliminate the UV light below 240 nm, doublet "E" was not significantly affected by photolysis but doublet "D" still decayed although at a reduced rate. Doublet "B" did not seem to be influenced at all by the ultraviolet light. Further evidence to support the individuality of doublet "B" was obtained by allowing a sample to stand in the dark for several hundred hours at liquid nitrogen temperature. During this time the relative intensity of doublet "B" was substantially reduced as shown in Figure 26. In addition, Figure 16 indicated that iodine scavenged this radical as well as the electrons, since doublet "B" is conspicuously absent from this spectrum. This scavenging could have occurred by a secondary process involving the I atoms formed from $I_2^-$ decomposition. Alternatively, it
Figure 25. ESR spectrum of $\gamma$-irradiated glassy PC at $\sim110$ °K after partial UV photolysis of the radical responsible for doublet "D".
Figure 26. ESR spectrum of $\gamma$-irradiated glassy PC at 77 °K after standing for 200 hours in the dark.
may have involved a direct reaction with the iodine molecule since I₂ is known to be a good radical scavenger as well as electron scavenger. All of the radicals formed by the radiolysis decayed very rapidly if the temperature of the sample was raised above 150 °K, although they were relatively stable at about 110 °K (except for the doublet "C" radical) and were indefinitely stable at 77 °K (except for the doublet "B" radical).

Thus the radiolysis of glassy PC at 77 °K appears to give rise to four major radical species. These are all characterised by very large doublet hyperfine splitting which clearly must result from coupling of the unpaired electron with α protons. The total radical yield as estimated from the comparison with irradiated methanol was $G_r = 4 \pm 2$.

None of these primary species can be conclusively identified because of their unusual ESR spectra, specifically the very large proton hyperfine splitting and the isotropic appearance of the lines which would not be expected from very simple radicals such as HCO, HCO₂, OH, etc. A very speculative assignment of the radical formed on UV photolysis of the radical "D" is to the CO₂⁻ radical ion. CO₂⁻ is known to give a narrow ESR line very near the free-spin $g_{av} = 2.001^{53,54}$ and line "F" is essentially in this position. If this assignment is correct, then a possible candidate for the radical "D" would be the HCO₂ radical (i.e. this may be photodissociated to give H⁺ and CO₂⁻). This speculation is supported to some extent by the liquid phase radiolysis results to be discussed in a later section, where a large yield of "molecular" CO₂
was found. CO$_2$ might be expected to originate from a radical such as HCO$_2$ or to produce HCO$_2$ by scavenging reactions. However Nazhat et al. have reported observing the radical HCO$_2$ in irradiated frozen sodium formate solutions. They attributed a single line to it at $g = 2.0121$ indicating that the unpaired electron is localized on the oxygen atoms.

In summary, the most unusual feature of the radical species formed by the primary action of radiation on glassy PC is the apparent absence of "normal" radicals with small $\alpha,\beta$ proton coupling such as is observed in most other irradiated organic systems. For example, one might have expected H atom abstraction to occur in this system to give radicals such as:

![Radical Structure](image)

but this apparently does not occur with a significant yield, at least not during the primary radiolysis. (Radicals of this type could account for the multiline spectrum in the center of Figure 24 caused by thermal reaction of some of the primary radicals with the solvent.) Instead of this type of radical; at least four different species, all apparently with only $\alpha$ protons, were formed. It is hoped that further studies of PC, including its deuterated forms, will help to reveal the identity of the paramagnetic species generated by the radiolysis.
(b) **Radicals formed by UV photolysis of the irradiated PC glasses at 77 °K**

Ultraviolet photolysis of the \(\gamma\)-irradiated glasses at liquid nitrogen temperature produced radicals which could be positively identified. Figure 27 shows the ESR spectrum of an irradiated PC sample after a very short exposure to the full intensity of the mercury lamp. The samples underwent a very dramatic colour change and became a deep blue. As shown in Figure 27, a new intense asymmetric line, labeled "G", appeared down-field from the free-spin \(g\)-value and a value of \(g_{av} \approx 2.015\) was measured from the center of this line relative to DPPH. By following the changes in the ESR spectrum using low intensity UV illumination of the sample directly in the ESR cavity, it was concluded that at least part of the blue colouration was due to the new paramagnetic species associated with line "G". In addition, this radical was apparently generated by the photolysis of the species responsible for the broad doublet "C" of Figure 12. This observation was supported by the fact that neither the blue colour nor the narrow ESR line "G" could be produced by UV photolysis of the samples at 110 °K after the broad doublet had decayed thermally. The blue colour was due to a very large increase in the 500 - 750 nm absorption band that was shown in Figure 22. UV photolysis of the samples used for the optical studies produced the same blue colour and the intensity of the 500 - 750 nm band was greatly increased. Figure 28 shows this band in more detail, particularly what appears to be vibrational
Figure 27. ESR spectrum of $\gamma$-irradiated glassy PC at 77 °K after brief UV photolysis. Samples were dark blue in colour.
Figure 28. Absorption spectrum in the 500 - 750 nm region for γ-irradiated PC after brief UV photolysis. Spectrum attributed to a combination of the HCO and CO₃⁻ bands.
fine structure. On the basis of the blue colour and the single ESR line at \( g \approx 2.015 \), this new radical can be assigned to the \( \text{CO}_3^- \) radical anion. \( \text{CO}_3^- \) has been observed spectroscopically in aqueous solution where a broad asymmetric absorption with \( \lambda_{\text{max}} \approx 600 \) nm was detected on flash photolysis and pulse radiolysis of aqueous carbonate solutions. \(^{55}\) Ershov \textit{et al.} \(^{56}\) reported essentially the same optical spectrum for \( \text{CO}_3^- \) in frozen aqueous carbonate glasses irradiated at 77 °K. They also attributed an asymmetric ESR line at \( g_{\text{av}} = 2.011 \) to the species. It is therefore evident that what appears to be vibrational fine structure on the 500 - 750 nm band is really absorption bands due to another species superimposed on the broad structureless band of \( \text{CO}_3^- \).

The only likely species which could give a multiple line vibronic spectrum in this system is \( \text{HCO} \). \( \text{HCO} \) is known to show at least seven narrow absorption bands in the region between 500 and 750 nm when trapped in a carbon monoxide matrix at 20 °K. \(^{57}\) Although the positions of the bands observed in PC at 77 °K (\( \sim 690, \sim 650, \sim 630, \sim 610, \sim 590, \) and \( \sim 575 \) nm) do not agree precisely with those observed in the CO matrix at 20 °K (670, 635, 605, 579, 555, 533, and 510 nm) the differences are probably caused by the overlapping of the \( \text{CO}_3^- \) spectrum and rather poor resolution. The presence of \( \text{HCO} \) was definitely established by its ESR spectrum \(^{58}\) which is the asymmetric doublet, labeled "H", in Figure 27. (A large isotropic hyperfine splitting factor of 137 G is responsible for the doublet; while \( g_{xx} = 2.0041, g_{yy} = 2.0027 \) and \( g_{zz} = 1.9960 \) together with the anisotropic part of the hyperfine tensor,
\[ B_{xx} = -4.2 \, \text{G}, \; B_{yy} = -0.8 \, \text{G}, \; B_{yz} = 5.8 \, \text{G} \; \text{and} \; B_{zz} = 5 \, \text{G}, \; \text{give rise to the complex line shape.}^{58b} \] These signals are in essentially the same position as doublet "E" but these species are apparently different radicals. On following the photolysis at low light intensity, doublet "E" was observed to first decrease in intensity and then slowly change shape and increase in intensity as the new species "grew" in. Positive identification was made by comparison with HCO generated by UV photolysis of irradiated methanol.\(^4\),\(^59\)

Also evident in Figure 27 are signals due to other paramagnetic species which increased in intensity as the UV photolysis was prolonged. After about 20 minutes of intense photolysis, the samples became nearly colourless with complete loss of the \( \text{CO}_3^- \) signal at \( g \sim 2.015 \). The HCO radical was also bleached to some degree by the ultraviolet light. (Both the \( \text{CO}_3^- \) and HCO signals could also be bleached by red light from a helium neon laser.) The ESR spectrum recorded after the intense UV illumination is shown in Figure 29 where it is clear that several new paramagnetic species are present. Remaining portions of radicals "B" and "D" are indicated appropriately. In addition to these and an unidentified signal "I", four narrow lines are evident as marked by the arrows. At first it was thought that they were unrelated but when the sample was UV irradiated for a further 30 minutes, all four signals increased equally as shown in Figure 30 indicating that they were indeed related. Since the splitting of the quartet was \( 21 \pm 2 \, \text{G} \) and since they were centered at essentially the free-spin \( g \)-value with an intensity ratio of 1:3:3:1, this
Figure 29. ESR spectrum of $\gamma$-irradiated glassy PC at 77 °K after 20 minutes of intense UV photolysis. Samples virtually colourless. Arrows indicate the methyl radical. (compare with Figure 27)
Figure 30. ESR spectrum of $\gamma$-irradiated glassy PC at 77 °K after 50 minutes of intense UV photolysis. Arrows indicate the methyl radical.
species is undoubtedly the methyl radical. This assignment is confirmed by the relative instability of the radical as detected by the slow decrease in signal intensity as the sample stood for several hours following the photolysis. (A half-life of about 2 hours was estimated from a qualitative decay study.) The decay produced an increase in the intensity of the broad asymmetric signal "I" at the center of the spectrum as indicated in Figure 31. This species is probably a radical with only \( \gamma \) protons and thus very small hyperfine splitting, formed by H atom abstraction by the reactive methyl radicals.

In summary, UV photolysis of irradiated PC glasses at 77 °K produced radicals identified as \( \text{CO}_3^- \), HCO and \( \text{CH}_3 \); the latter being unstable in the matrix at liquid nitrogen temperature.
Figure 31. ESR spectrum of UV photolysed, γ-irradiated PC samples at 77 oK; about four hours after the photolysis. Showing the decay of the methyl radicals (arrows). (compare with Figure 30)
PART II - RADIOLYSIS OF PROPYLENE CARBONATE IN THE LIQUID PHASE

A. INTRODUCTION

This section requires little introduction in addition to that given in Chapter I and in the general remarks made at the beginning of the current Chapter.

Propylene carbonate as a "saturated" organic compound would be expected to be relatively unreactive with thermal electrons generated by radiolysis. Its inertness towards reaction with the alkali metals tends to support this prediction. The high dielectric constant of the medium (65) should allow a large fraction of the thermal electrons to escape geminate recombination. The large permanent dipole moment of PC (4.9 x 10^{-18} esu cm) would be sufficient to provide ample solvation energy if the thermal electrons survive long enough to become solvated. Thus on the basis of its known physical and chemical properties, one might predict that solvated electrons would be generated in a relatively large yield in this system. Indeed, Hayon recently published a determination of this yield by an indirect method which gave $G_{e^-} = 2.25$. However, by his technique of measuring the yield of anthracene anions generated in the pulse irradiated liquid, it is not possible to say conclusively whether the reducing species measured was a solvated electron. A reactive solvent anion could conceivably also undergo a fast charge transfer reaction with anthracene to give the anthracene anion.
Support for this alternate mechanism was recently obtained by a colleague in this laboratory for the radiolysis of dimethyl sulfoxide\textsuperscript{43b}, where the reducing species does appear to be a solvent anion formed in a yield equal to that expected for solvated electrons and measured as such by Hayon\textsuperscript{14}. Experience in this laboratory with another high dielectric solvent, formamide\textsuperscript{15}, also indicated that solvent anions could well be the reactive reducing species, although competition kinetic studies for reduction reactions with electron scavengers such as \( \text{N}_2\text{O}, \text{H}^+, \text{and Ag}^+ \) gave rate constant ratios very similar to those known for solvated electrons in water.

It can be inferred from the above discussion that scavenger studies in irradiated systems can produce valuable information about the free ion yield in a solvent. However, they cannot always be relied upon to identify the species unambiguously. Only by direct observation, using ESR or optical techniques in conjunction with pulse radiolysis (or flash photolysis), can solvated electrons be positively identified in a medium.

With the above thoughts in mind, the basic objective of the current study was to investigate the radiolysis of liquid propylene carbonate, both pure and with added solutes. By determining the radiolytically generated product yields and observing the effects of the added scavengers on these yields and the yields of products from scavenger reactions, it was hoped that the yield of reducing species could be deduced.
B. EXPERIMENTAL

1. Reagents

Eastman Kodak practical grade propylene carbonate (PC) was purified by first drying over Linde 4A molecular sieves and then double vacuum fractionation as described in Appendix 4. The dry purified solvent was stored under dry helium in a glass dispensing apparatus which is also discussed in Appendix 4, along with the physical analyses of the solvent.

Nitrous oxide, used as an electron scavenger, was obtained from Matheson and purified by "trap-to-trap" distillation in a high vacuum system, where it was subsequently stored in a five litre flask until required.

All other chemicals used as scavengers were analytical reagent grade or equivalent and were used as received. Water was purified as described in Chapter II.

Helium used for deoxygenation of the samples and for chromatography was supplied by Canadian Liquid Air. It was dried by passing through a long copper coil immersed in a liquid nitrogen bath.

2. Radiation Source

The $^{60}$Co Gammacell 220 was used for the irradiations. Ferrous sulfate dosimetry done in the sample cell used in the current study, as detailed in Appendix 1, indicated that the dose rate for the ferrous sulfate solution was 4500 rads min$^{-1}$ ($2.84 \times 10^{17}$ eV g$^{-1}$ min$^{-1}$) on August 1, 1970. Corrections for
the "electron density" difference between PC and the dosimeter solution and for the natural decay of the source activity were made as described in Appendix 1.

3. Apparatus and Techniques

(a) Sample cell and sample preparation

The pyrex glass sample cell and experimental techniques used in this study were similar to those originally used by Head\textsuperscript{60}. The sample cell is shown in Figure 32. A PC sample was inserted into this apparatus via the B7 socket opening using a pipette with a fine, drawn out, tip which would fit through the capillary tubing above the sample section of the cell. The B7 cone and socket joint was greased sparingly with Apiezon N high vacuum grease and held together with two stainless steel springs. The four-way stopcock was also greased with Apiezon N and held in place with an aluminum stopcock retainer as shown in the photograph of Figure 32. (The stopcock retainer and the springs were required because the cell was pressurized to 20 - 30 psig during the analysis procedure.) The sample cell was connected either to the external sample "loop" of the gas chromatography system or to the vacuum line via S13 ball joints on the other two arms of the four-way stopcock. By turning the stopcock in a suitable direction, the PC sample in the cell could either be isolated or exposed to the vacuum line or GC loop. The fritted disk at the bottom of the sample section provided a fine stream of gas bubbles through the liquid for deoxygenation or flushing the volatile radiolysis products into the GC.
Figure 32. Photograph of the sample cell used for the liquid phase radiolysis of PC.
The sample cell and assorted auxiliary glassware (i.e. beakers, pipettes, etc.) were routinely cleaned after each experiment (or series) using a standard procedure. The sample cell was first degreased using hexane and then was thoroughly flushed with hexane and then distilled water, using a water aspirator to suck the solvents through the cell. Following this initial washing, the cell was either annealed in the glassblowers' oven or baked in a 300 °C lab oven to remove the brown colouration produced by the radiation in the glass. After annealing, the cell and other glassware were soaked for at least 12 hours in permanganic acid, then rinsed with distilled water and soaked for several hours in a concentrated hydrogen peroxide - nitric acid solution to remove traces of MnO₂. Following this, the apparatus was thoroughly rinsed, first with singly distilled water and then with triply distilled water. Finally the glassware was dried in a "clean" oven at 250 °C for several hours before use.

In a typical experimental series, the pre-weighed clean cell was filled with a sample of purified PC which had been dispensed from the glass storage flask into a small beaker. The same filling pipette was used for all experiments and it delivered 17.9 ml of the solvent into the cell. The weight of each PC sample was however determined accurately by weighing the cell on a beam balance to the nearest 1/100th of a gram. This sample weight was then used in subsequent dose calculations. Following weighing and greasing of the cell, the PC sample was deoxygenated by flushing with dry helium for about 30 minutes, after which the cell stopcock was turned about 45° and the
sample was thereby sealed in the cell under a helium atmosphere. (The stopcock was only turned 45° so that the sample would remain above the fritted glass disk. If it was turned 90°, the sample tended to flow through the disk and fill the opposite side of the cell. The latter was not desireable since the dosimetry had been done with the ferrous sulfate solution above the disk.) After deoxygenation, the cell was either irradiated or else attached to the vacuum system for addition of nitrous oxide to the sample prior to irradiation. Solid and liquid scavengers were always added directly to the PC in a small beaker before the sample was put in the cell.

In all cases, irradiations were performed with the sample cell maintained at 25 °C in a circulating alcohol bath which fit inside the Gammacell cavity.

(b) **Gaseous product analysis**

Following irradiation the sample cell was attached to the external loop of the gas chromatograph. In the majority of the experiments, a specially modified Varian Aerograph A-90-P2 GC was used for analysis of the gaseous radiolysis products (N\(_2\), CH\(_4\), CO and CO\(_2\)). Details of this system are given in Appendix 5 along with operating and calibration data. Briefly, the chromatograph was equipped with dual columns connected in series with the detectors. The carrier gas, after flushing through the sample cell, passed through a 2 foot by 1/8th inch Porapak Q "pre-column" vapour trap whose purpose was to prevent PC vapour from entering the GC system. (This pre-column was back-flushed after each experiment to
remove the PC vapour.) The carrier gas then flowed through a 1 foot by 1/4 inch copper coil immersed in a liquid nitrogen bath where the condensable gases, i.e. $\text{CO}_2$ and $\text{N}_2\text{O}$, were trapped out. Following this, the helium passed through an 8 foot by 1/8th inch Porapak Q column at 0 °C before reaching the "sample" side of the thermal conductivity detectors with WX filaments. The permanent gases ($\text{N}_2$, CO and $\text{CH}_4$) were not separated by this column and all eluted at the same time to give a single peak on the recorder. The gas then flowed into a 20 foot by 1/4 inch 13X molecular sieve column at 100 °C where the $\text{N}_2$, CO and $\text{CH}_4$ were separated before entering the "reference" side of the detectors. The sample cell was continuously flushed by the carrier gas until after the elution of methane (about 15 minutes from initial exposure at 60 ml/min flow rate); at this point, the sample loop was bypassed to prevent overloading of the pre-column vapour trap. About five minutes after the sample loop was closed CO eluted and was measured. Subsequently, $\text{CO}_2$ was determined by warming the trap and vapourizing the gas condensed there. The 8 foot Porapak Q column at 0 °C held the $\text{CO}_2$ back for several minutes and thus allowed the "pressure peak", caused by warming the trap, to pass through the detectors. If nitrous oxide was present both $\text{CO}_2$ and $\text{N}_2\text{O}$ eluted nearly simultaneously and this prevented measurement of $\text{CO}_2$ in the presence of $\text{N}_2\text{O}$.

It was found that with a 60 ml/min flow rate, tailing of the $\text{N}_2$, $\text{CH}_4$ and CO peaks was not serious. Since $\text{CO}_2$ was trapped out, it gave a very narrow peak with no tailing. In addition, "double flush" experiments on the same irradiated
sample showed that during the 15 minute exposure to the carrier gas, greater than 99% of the permanent gases were removed from the cell and about 98% of the CO₂ was removed.

A typical chromatogram and sensitivity data are also presented in Appendix 5. The sensitivity was determined by injecting known amounts of the various gases with an "in-line" sample loop of calibrated volume. Peak areas were measured by manual triangulation. The linearity of detector response was checked by injecting known quantities of the gases with a second sample loop filled on a vacuum line to various pressures. The day-to-day variation in sensitivity was monitored by injecting a nitrogen "standard" with the "in-line" sample loop before each experiment. Since the variation in these nitrogen standard peak areas was always less than ± 5% of the mean, no corrections were made to the experimental data. The 5% deviation could be accounted for on the basis of changes in atmospheric pressure and temperature as well as uncertainty introduced by the manual integration technique.

Because the hydrogen response of the A-90-P2 system with helium as the carrier gas was insufficient to detect the quantities of hydrogen formed during the radiolysis, this product was measured using a Varian Aerograph 1720 GC with argon as the carrier gas. This chromatograph was equipped with 13X molecular sieve columns and WX thermal conductivity detectors. The same external sample loop system was used, the essential operating differences being a different flow rate and column temperature. Only H₂ (and N₂ for a nitrous
oxide series) was measured because of the excessively long retention times for CH₄ and CO.

(c) **Vacuum techniques and determination of the solubility of nitrous oxide**

Deoxygenated PC samples were vacuum degassed by attaching the cell to the vacuum system illustrated in Figure 33. The S13 ball joints of the cell were connected to the two S13 sockets, each of which was isolated from the vacuum line by a small stopcock, S₁ and S₂. A third stopcock, S₃, further separated the external connections from the main vacuum manifold. Initially, with the four-way stopcock of the cell turned so as to isolate the sample from the vacuum, stopcocks S₁, S₂ and S₃ were opened and the line up to and including the "bore" of the four-way stopcock was pumped to a good vacuum (10⁻⁶ mm of Hg) using a three stage mercury diffusion pump backed by a rotary oil pump. Then with the stopcock S₂ closed, the four-way stopcock was slowly rotated 90° until the gas inside the cell started to "bubble" out via S₁. This part of the procedure required considerable care. If the cell was opened too quickly, the sample would bubble excessively and splash into the vacuum line. Once most of the helium was pumped out of the cell via S₁, S₂ was cautiously opened and the traces of gas remaining on that side of the sintered disk were removed. The cell and sample were finally pumped down to a good vacuum, after which, S₁, S₂ and S₃ were closed.

Nitrous oxide, which had previously been trapped out in trap T₁ (using a liquid nitrogen bath) and well degassed,
Figure 33. Schematic diagram of the vacuum system used to add nitrous oxide to the PC samples in the "bubbler" cell.
was then vapourized into the evacuated line that was isolated from the vacuum pumps by stopcock $S_4$. The initial $N_2O$ pressure was read on the mercury manometer and from the known volume of the line between $S_3$ and $S_4$, the initial amount of $N_2O$ was calculated using the ideal gas law; $PV = nRT$. Then $S_3$ was opened, followed by $S_2$ which was slowly opened to allow the $N_2O$ to bubble through the PC sample. $S_1$ remained closed at this stage. Again it was necessary to use great care in opening $S_2$, otherwise the sample would splash into the line. The $N_2O$ was allowed to bubble slowly through the sample until equilibrium was reached (about 30 minutes). Then $S_1$ was opened, the four-way stopcock closed by turning $45^\circ$ and the final pressure was read from the manometer. From the calibrated total volume of the system, the final amount of gaseous $N_2O$ was calculated. (A suitable correction was made for the manometer volume change.) The difference between the initial and final amounts of gaseous nitrous oxide gave the quantity which had dissolved in the PC sample. Using the known volume of PC the concentration of $N_2O$ was calculated. The variation of nitrous oxide concentration with equilibrated pressure is plotted in Figure 34. From the slope of the line through these data, the solubility of $N_2O$ in PC at room temperature (20-25 °C) was estimated to be $1.5 \times 10^{-4} \text{ M mm}^{-1}$. The slight scatter in the data most probably is a result of temperature variations from experiment to experiment. The "non-zero" intercept is believed to be due to the presence of the sintered disk in the apparatus.
Figure 34. Concentration of dissolved nitrous oxide in PC at room temperature (20 - 25 °C) as a function of the nitrous oxide pressure in the "bubbler" cell.
C. RESULTS

1. Pure PC - Gaseous Radiolysis Products

The four gaseous products formed with significant yield in PC irradiated at 25 °C were \( \text{H}_2 \), \( \text{CH}_4 \), CO and \( \text{CO}_2 \). Their yield was found to be independent of dose up to at least 0.3 Mrad \((1.9 \times 10^{19} \text{ eV g}^{-1})\) for \( \text{H}_2 \) and at least 1.4 Mrad \((8.6 \times 10^{19} \text{ eV g}^{-1})\) for \( \text{CH}_4 \), CO and \( \text{CO}_2 \). (Yields for larger doses than these were not measured.) Some of these data are plotted in Figure 35, where from the slopes of the lines the \( G \) values were calculated to be:

\[
\begin{align*}
G(\text{H}_2) &= 0.75 \pm 0.05 \\
G(\text{CH}_4) &= 0.20 \pm 0.02 \\
G(\text{CO}) &= 1.2 \pm 0.1 \\
G(\text{CO}_2) &= 3.3 \pm 0.2
\end{align*}
\]

No oxygen was produced by the radiolysis and non-gaseous products were not measured.

2. Scavenger Experiments

Several series of experiments were performed with nitrous oxide present as a scavenger. The yield of nitrogen produced by scavenging reactions at a fixed nitrous oxide concentration was found to be dependent on dose as illustrated in Figure 36. For a nitrous oxide concentration of 0.05 M, the initial \( G(\text{N}_2) = 1.8 \) decreased to \( G(\text{N}_2) = 0.9 \) after the sample had absorbed a total of about 0.8 Mrads \((5 \times 10^{19} \text{ eV g}^{-1})\). This decrease in \( G(\text{N}_2) \) was believed to be caused by a non-volatile product building up in the system and competing
Figure 35. Yields of gaseous radiolysis products from PC \( \gamma \)-irradiated at 25 °C, as a function of dose.
Figure 36. Nitrogen yield as a function of accumulated sample dose for a constant nitrous oxide concentration (0.05 M).
with nitrous oxide for the reducing species. This conclusion is based on the observation that the nitrogen yield measured for a small dose given to a sample previously irradiated with a large dose, but flushed to remove the volatile products, was much smaller than that obtained for a small dose given to a fresh sample. Because of this dependence of $G(N_2)$ on dose, all other experiments involving nitrous oxide were done on a new sample using the smallest practical dose of about $0.08 \text{ Mrad} \ (5 \times 10^{18} \text{ eV g}^{-1})$ for which a reasonably accurate $G(N_2)$ could be determined.

Nitrous oxide did not affect the hydrogen or carbon monoxide yields or significantly lower the methane yield. At the low doses used in most experiments, accurate methane determination was not possible because of its low yield and "tailing" of the nitrogen peak. However, the yield calculated for large dose experiments with $N_2O$ were in agreement with $G(\text{CH}_4)$ obtained for pure PC and the yields measured at low doses were never less than $G(\text{CH}_4) = 0.1$. Carbon dioxide could not be measured with nitrous oxide present because of the interference mentioned in the experimental section.

The yield of nitrogen, $G(N_2)$, for constant dose experiments, plotted as a function of nitrous oxide concentration is shown in Figure 37. $G(N_2)$ increased rapidly between 0 and 0.01 M nitrous oxide and then increased more slowly, eventually reaching a near plateau value of $G(N_2) = 2.0$ above 0.07 M. (The maximum experimentally obtainable nitrous oxide concentration was 0.1 M, which corresponded to 750 mm pressure.)
Figure 37. \( G(N_2) \) as a function of nitrous oxide concentration at constant dose (about \( 5 \times 10^{18} \text{ eV g}^{-1} \)).
Several experiments were performed with second scavengers present in addition to nitrous oxide. These data are listed in Table 5, along with data for the effects of the second scavengers alone. Iodine, a very efficient electron and radical scavenger, did not affect the carbon monoxide or carbon dioxide yields. It did, however, reduce the methane yield by a factor of at least 10. In the presence of 0.077 M nitrous oxide, iodine at 0.001 M competed effectively for the precursor of nitrogen and reduced $G(N_2)$ by a factor of 2. As the iodine concentration was increased 70 fold to 0.068 M it only decreased $G(N_2)$ by a further factor of 2, contrary to that expected on the basis of simple competition kinetics. Water at 0.22 M did not affect the nitrogen yield or that of any of the other gaseous products. Methanol at 0.18 M also did not affect $G(N_2)$ or $G(CH_4)$ and $G(CO)$. Several experiments were performed with sulfuric acid although it was known to cause hydrolysis of the propylene carbonate; producing $CO_2$, propylene oxide and propionaldehyde among other products. At 0.33 M $H^+$ the nitrogen yield was reduced by more than a factor of 2 with nitrous oxide at 0.075 M. It did not appear to significantly affect the hydrogen yield although if 0.2 M methanol was added, the hydrogen yield did increase slightly to $G(H_2) = 0.95$.

D. DISCUSSION

Since the hydrogen, carbon monoxide and carbon dioxide yields were not affected by the presence of the electron and
### TABLE 5

**SUMMARY OF SECOND SCAVENGER EXPERIMENTAL RESULTS**

<table>
<thead>
<tr>
<th>Second Scavenger</th>
<th>$S_2$ (M)</th>
<th>$N_2O$ (M)</th>
<th>$G(H_2)$</th>
<th>$G(N_2)$</th>
<th>$G(CH_4)$</th>
<th>$G(CO)$</th>
<th>$G(CO_2)$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nil</td>
<td>Nil</td>
<td>Nil</td>
<td>0.75</td>
<td>Nil</td>
<td>0.20</td>
<td>1.2</td>
<td>3.3</td>
</tr>
<tr>
<td>Nil</td>
<td>Nil</td>
<td>0.094</td>
<td>0.76</td>
<td>2.0</td>
<td>a</td>
<td>a</td>
<td>a</td>
</tr>
<tr>
<td>Nil</td>
<td>Nil</td>
<td>0.077</td>
<td>a</td>
<td>2.0</td>
<td>0.15</td>
<td>1.1</td>
<td>a</td>
</tr>
<tr>
<td>Iodine</td>
<td>0.053</td>
<td>Nil</td>
<td>a</td>
<td>Nil</td>
<td>0.02</td>
<td>1.1</td>
<td>3.4</td>
</tr>
<tr>
<td>&quot;</td>
<td>0.0010</td>
<td>0.077</td>
<td>a</td>
<td>1.1</td>
<td>0.03</td>
<td>1.1</td>
<td>a</td>
</tr>
<tr>
<td>&quot;</td>
<td>0.0046</td>
<td>0.077</td>
<td>a</td>
<td>0.86</td>
<td>0.01</td>
<td>1.1</td>
<td>a</td>
</tr>
<tr>
<td>&quot;</td>
<td>0.012</td>
<td>0.077</td>
<td>a</td>
<td>0.75</td>
<td>0.01</td>
<td>1.2</td>
<td>a</td>
</tr>
<tr>
<td>&quot;</td>
<td>0.022</td>
<td>0.077</td>
<td>a</td>
<td>0.65</td>
<td>0.03</td>
<td>1.1</td>
<td>a</td>
</tr>
<tr>
<td>&quot;</td>
<td>0.068</td>
<td>0.077</td>
<td>a</td>
<td>0.55</td>
<td>0.02</td>
<td>1.1</td>
<td>a</td>
</tr>
<tr>
<td>Water</td>
<td>0.22</td>
<td>Nil</td>
<td>0.77</td>
<td>Nil</td>
<td>0.17</td>
<td>1.2</td>
<td>3.5</td>
</tr>
<tr>
<td>&quot;</td>
<td>0.22</td>
<td>0.077</td>
<td>0.77</td>
<td>1.9</td>
<td>a</td>
<td>a</td>
<td>a</td>
</tr>
<tr>
<td>Methanol</td>
<td>0.18</td>
<td>0.051</td>
<td>a</td>
<td>1.7</td>
<td>0.14</td>
<td>1.2</td>
<td>a</td>
</tr>
<tr>
<td>$H^+ (H_2SO_4)$</td>
<td>0.33</td>
<td>0.075</td>
<td>a</td>
<td>0.60</td>
<td>0.14</td>
<td>1.1</td>
<td>a</td>
</tr>
<tr>
<td>&quot;</td>
<td>0.29</td>
<td>Nil</td>
<td>0.78</td>
<td>Nil</td>
<td>a</td>
<td>a</td>
<td>a</td>
</tr>
<tr>
<td>&quot;</td>
<td>0.29c</td>
<td>Nil</td>
<td>0.95</td>
<td>Nil</td>
<td>a</td>
<td>a</td>
<td>a</td>
</tr>
</tbody>
</table>

Footnotes:  
- a. Not determined.  
- b. Acid caused slow hydrolysis of the PC producing CO$_2$ among other products. This may have influenced the results.  
- c. 0.2 M methanol added in addition to the acid.
radical scavengers, nitrous oxide and iodine at greater than $10^{-2}$ M, these products are most likely formed via molecular processes. A probable mechanism for the formation of CO and CO$_2$ is through "spontaneous" dissociation of electronically excited propylene carbonate molecules, although rapid decomposition of positive ions could also produce these products. Indeed, the mass spectrum of PC (see Appendix 4) indicates the PC positive ion is very unstable in the gas phase and it does appear to lose CO and CO$_2$ very readily. The molecular hydrogen, on the other hand, is believed to result from fast H atom abstraction reactions.

The precursor of methane was readily scavenged by iodine, even at $10^{-3}$ M, which indicates the methane arises from relatively long-lived methyl radicals formed in the radiolytic decomposition processes of propylene carbonate. The fact that nitrous oxide did not significantly lower $G(\text{CH}_4)$ as compared with iodine, most probably reflects the much slower reaction rate constants for radical reactions of N$_2$O as compared with iodine. Iodine, for example, reacts $4 \times 10^5$ times faster with H atoms in aqueous solution.$^{22}$

The significance of the water experiments is to indicate that either water does not scavenge the precursors of the molecular products, H$_2$, CO, CO$_2$ and CH$_4$, or the precursor of nitrogen, or else the PC samples already contained sufficient water so that the additional amount added in these experiments would not have any increased effect. Water would be expected to act as an efficient positive ion scavenger, accepting a proton to form H$_3$O$^+$. 
In addition to the independence of the hydrogen yield on the presence of nitrous oxide, the failure of methanol at 0.2 M to affect the nitrogen yield for a nitrous oxide concentration of 0.05 M, also rules out the possibility of H atoms being the reducing species. Methanol is known to be a good hydrogen atom scavenger in aqueous solutions, with the ratio of the rate constants for H atom reactions with methanol and nitrous oxide being 20.\textsuperscript{22}

Thus the major reducing species in irradiated PC would appear to be a negative ion, either a solvated electron or a molecular anion. This species, $X^-$, which is readily scavenged by nitrous oxide to give nitrogen, apparently has a yield of $G(X^-) \sim 2$ as indicated by the "plateau" value of $G(N_2)$. If the alternative fate of species $X^-$ is assumed to be reaction with unspecified impurity or solvent "S", then analysis of the nitrogen yield dependence on nitrous oxide concentration may be made on the basis of simple competition kinetics. The two reactions occurring are (8) and (9).

\[
\begin{align*}
X^- + S & \xrightarrow{\text{k}_S} \text{products} \quad (8) \\
X^- + N_2O & \xrightarrow{\text{k}_{N_2O}} N_2 + \text{products} \quad (9)
\end{align*}
\]

Steady state treatment of this reaction mechanism for species $X^-$ gives the kinetic expression (ix).

\[
\frac{1}{G(N_2)} = \frac{1}{G(X^-)} \left[ 1 + \frac{\text{k}_S [S]}{\text{k}_{N_2O} [N_2O]} \right] \quad (ix)
\]

Thus a plot of $1/G(N_2)$ versus $1/[N_2O]$ should be a straight line with slope equal to $\text{k}_S \frac{[S]}{\text{k}_{N_2O} G(X^-)}$ and the intercept
equal to $1/G(X^-)$ if the simple competition holds. Such a plot for the data of Figure 37 is given in Figure 38. The relatively good linearity of the experimental data supports the simple competition mechanism and the intercept of 0.45 implies that $G(X^-) = 2.2$, a value in good agreement with the value of $G(N_2) = 2.0$ at 0.1 M nitrous oxide. Another implication of the simple competition mechanism is that apparently only one reducing species is reacting with nitrous oxide to give nitrogen.

The assignment of the reducing species to a negative ion and the measured yield of $X^-\rangle$ are in good agreement with the work recently published by Hayon$^{14}$ on the free negative ion yield in propylene carbonate. He determined $G(X^-) = 2.25$ by measuring the yield of anthracene anions formed on pulse radiolysis of the liquid.

The competition experiments between nitrous oxide and iodine for species $X^-\rangle$ gave some interesting results. At the fixed nitrous oxide concentration of 0.077 M, which was sufficient to scavenge at least 90% of the $X^-\rangle$, iodine at only $10^{-3}$ M reduced the nitrogen yield by almost a factor of two. However, as the iodine concentration was increased to 0.068 M, the nitrogen yield did not decrease as rapidly as would be expected on the basis of a simple competition mechanism. Indeed if the simple competition kinetic expression (ix) given above is modified so that the alternate fate of species $X^-\rangle$ is reaction with $I_2$, then the expression (x) should hold.
Figure 38. Data from Figure 37 plotted as $1/G(N_2)$ versus $1/[N_2O]$.
A plot of $1/G(N_2)$ versus $[I_2]/[N_2O]$ should then be linear with slope equal to the ratio $k_{I_2}/k_{N_2O} G(X^-)$ and the intercept equal to $1/G(X^-)$. This graph for the data in Table 5 is shown in Figure 39. The fact that it is far from linear means that a secondary reaction must be occurring between the product of the iodine scavenging reaction and nitrous oxide to give nitrogen. This result is not particularly surprising since the product of the reaction of $X^-$ with iodine is probably an iodine atom formed via the intermediate $I_2^-$. The iodine atom could then react with the nitrous oxide to give nitrogen and the following reaction scheme might prevail:

$$X^- + N_2O \rightarrow N_2 + \text{products} \quad (9)$$

$$X^- + I_2 \rightarrow I + I^- + \text{products} \quad (10)$$

$$I + N_2O \rightarrow N_2 + \text{products} \quad (11)$$

$$I + S \rightarrow \text{products} \quad (12)$$

where reaction (12) represents the alternate fate of the iodine atoms. Unfortunately kinetic analysis of reactions (9) - (12) gives a complex expression for the dependence of $G(N_2)$ on the $[I_2]$ and $[N_2O]$ and therefore the mechanism cannot be easily checked against the experimental data. However, the data shown in Figure 39 do indicate that iodine reacts much more rapidly with species $X^-$ than does nitrous oxide. This is evident from the initial slope of the curve of about 40. At very low iodine concentrations, the simple competition mechanism should hold at least approximately, and the slope would then mean that $k_{I_2}/k_{N_2O}$ is approximately equal to 80. This
Figure 39. Plot of $1/G(N_2)$ versus $[I_2]/[N_2O]$ for $[N_2O] = 0.077$ M.
is only a factor of 9 greater than that measured for hydrated electrons in water where $k_{I_2}/k_{N_2O} = 9$. Assuming that reaction (10) occurs at a rate similar to the rate of reaction of hydrated electrons with iodine in water ($k_{e_{aq} + I_2} = 5 \times 10^{10} \text{M}^{-1}\text{s}^{-1}$) this would imply that species $X^-$ reacts with nitrous oxide with a rate constant of about $5 \times 10^8 \text{M}^{-1}\text{s}^{-1}$. Since 0.02 M nitrous oxide was required to scavenge half of the species, the natural lifetime of $X^-$ can then be estimated to be approximately $10^{-7}$ seconds (100 nsec).

The fact that acid at 0.3 M $H^+$ was able to reduce the nitrogen yield significantly is supplementary evidence for the anionic character of the reducing species in PC. The product of the $H^+$ scavenging reaction with species $X^-$ does not appear to be molecular hydrogen as indicated by the lack of an increase in the hydrogen yield. However, it is conceivable that hydrogen atoms (formed by reaction of $H^+$ with a solvated electron) might react with the $\text{C}=\text{O}$ system of PC preferentially to give a non-volatile product rather than abstracting a hydrogen atom to form molecular hydrogen. This argument is partially supported by the experiment in which methanol was added and a slight increase in the hydrogen yield was observed. (Methanol is known to be a good $H$ atom scavenger in aqueous systems, producing hydrogen in the scavenging reaction.) On the other hand, if a molecular anion is the reducing species in PC then an increase in the $H_2$ yield would not be expected on addition of acid. In any event, since acid is known to cause hydrolysis of PC these results are not particularly reliable. Carbon dioxide and propionaldehyde are among the
hydrolysis products$^{40a}$ and both are good H atom and electron scavengers. It was mainly because of this hydrolysis problem that a systematic examination of the competition between $H^+$ and $N_2O$ was not made.

On the basis of the results discussed above, it appears that $\gamma$-radiolysis of liquid propylene carbonate produces the primary molecular products; hydrogen, carbon monoxide and carbon dioxide with yields: $G_{H_2} = 0.75 \pm 0.05$, $G_{CO} = 1.2 \pm 0.1$, and $G_{CO_2} = 3.3 \pm 0.2$, and methane via a secondary process involving methyl radicals with a yield $G(CH_4) = 0.20 \pm 0.02$. In addition, an ionic reducing species is formed with a yield $G_{X^-} = 2.0 \pm 0.2$. This species is most likely a solvated electron although because of the limited amount of data available, a molecular anion cannot be ruled out. The best arguments in favour of the solvated electron hypothesis are: (a) the lack of reactivity of PC with alkali metals suggesting that electron attachment to PC is not favoured, and (b) the large permanent dipole moment of PC would supply ample solvation energy to allow stabilization of the thermal electrons if they survived long enough to allow dipole relaxation. The measured yield of the reducing species is in good agreement with that found by Hayon$^{14}$ and with that expected on the basis of the empirical relationship between the yield of free ions and the static dielectric constant of the liquid (see Figure 5 in Chapter I).
PART III - GENERAL CONCLUSION AND SUGGESTIONS FOR FURTHER STUDY  
OF THE RADIATION CHEMISTRY OF PROPYLENE CARBONATE

The preliminary investigations reported here for the effects of radiation on the very polar propylene carbonate system have provided some interesting results. Trapped electrons were identified in the low temperature glass and it is very likely that the ionic reducing species formed in the liquid phase were also stabilized electrons.

From the physical properties shown by the trapped electron it is possible to make a prediction about the optical absorption maximum of a solvated species in the liquid phase. In most systems where both trapped and solvated electrons have been observed spectroscopically, \( \lambda_{\text{max}} \) consistently shows a blue shift of between 50 and 200 nm on going from the solvated to the trapped species at 77 °K. Thus on the basis of the assigned absorption band for trapped electrons in PC, \( \lambda_{\text{max}} \sim 370 \text{ nm} \), the solvated electron would be expected to absorb preferentially in the visible region with a \( \lambda_{\text{max}} \) in the region of 400 - 600 nm. This prediction is contrary to that expected from the proposed correlation between the iodide ion "charge-transfer-to-solvent" absorption maximum and the \( \lambda_{\text{max}} \) of solvated electron spectra. This correlation places \( \lambda_{\text{max}} \) for solvated electrons in PC at about 1200 nm, a value difficult to accept on the basis of the polarity of PC. If the solvated electron absorption does represent a distribution profile of the different trap depths, then
electrons in PC should be bound in relatively deep traps due
to its large dipole moment and thus should absorb somewhere
in the visible region and not in the infrared. Hence an
experiment of particular importance to identifying the
reducing species in PC is an investigation of its pulse rad-
iolysis to determine if any transient optical absorption occurs
which can be attributed to $e_\text{s}^-$.  

In light of the above remarks, some trial experiments
were performed on the pulse radiolysis apparatus designed by
a colleague, Dr. G.A. Kenney-Wallace. This system used the
light from a helium-neon laser to monitor absorption at 633 nm
in a sample pulse irradiated with a 3 nsec pulse of 0.5 MeV
electrons from a Febetron accelerator. A significant,
short-lived absorption was detected at 633 nm for liquid PC
and acid increased the rate of decay markedly. The species
observed could conceivably have been the solvated electron,
however, CO$_3^-$ and HCO radicals are both known to absorb in this
region and these species could not be excluded as the source
of the transient absorption on the basis of the data obtained.
The author hopes to pursue these leads at The Ohio State
University where pulse radiolysis equipment is available to
determine complete visible and infrared absorption spectra.

An interesting opportunity also exists with propylene
carbonate to investigate the effects of changes in dielectric
constant on the yield (and spectra) of solvated electrons.
Since PC shows such a large change in dielectric constant
over a comparatively small temperature range (90 at - 60 °C
to 60 at +30 °C), this effect may be observable in variable
temperature studies. Some effects are certainly evident in
the steady state radiolysis where trial experiments at -40 °C
showed that the yields of gaseous products decreased sub-
stantially with $G(\text{CH}_4) = 0.10 \pm 0.02$, $G_{\text{CO}} = 0.9 \pm 0.1$ and
$G_{\text{CO}_2} = 2.6 \pm 0.3$ as compared with $G(\text{CH}_4) = 0.20 \pm 0.02$,
$G_{\text{CO}} = 1.2 \pm 0.1$ and $G_{\text{CO}_2} = 3.3 \pm 0.3$ at 25 °C. In addition,
the nitrogen yield for a sample containing 0.08 M nitrous
oxide decreased to $G(\text{N}_2) = 1.6$ as compared with $G(\text{N}_2) = 2.0$
at 25 °C. Some of these changes may of course be due to
viscosity effects since the viscosity increases substantially
on cooling. However, one would have expected the dielectric
constant increase to cause an increase in $G(\text{N}_2)$ and the obser-
ved decrease must have resulted from a combination of different
temperature effects.

Further studies of the radiation chemistry of PC in
the solid state are clearly warranted to unravel the mystery
of the abnormal spontaneous decay of $e^-_{tr}$. Optical kinetic
studies of the irradiated glassy material and correlation of
these data with the ESR measurements would be helpful, part-
icularly in confirming the assignment of the violet absorption
band to $e^-_{tr}$. Experiments with deuterated propylene carbonate
could also help in the identification of the primary radical
species, as would studies of the ESR of other organic carbon-
ates such as ethylene carbonate and tetramethyl ethylene
carbonate.
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APPENDIX 1

FERROUS SULFATE DOSIMETRY

A. THEORY

Fricke ferrous sulfate dosimetry was used to determine the dose rate delivered by the $^{60}$Co Gammacell. The Fricke dosimeter utilizes the oxidation of ferrous iron to ferric iron in acidic, oxygenated aqueous solution to measure the dose absorbed. In 0.8N acid solution containing atmospheric oxygen, the two radiolytically generated primary reducing species, $e_{aq}^-$ and H atoms, are converted to oxidizing species by reactions (A-1) and (A-2).

$$e_{aq}^- + H_{aq}^+ \rightarrow H + H_2O \quad (A-1) \quad k = 2 \times 10^{10} \text{ M}^{-1}\text{s}^{-1}$$

$$H + O_2 \rightarrow HO_2 \quad (A-2) \quad k = 1 \times 10^{10} \text{ M}^{-1}\text{s}^{-1}$$

The HO$_2$ radicals formed via reaction (A-2) and the primary OH radicals and molecular hydrogen peroxide then oxidize the ferrous iron to ferric via reactions (A-3), (A-4) and (A-5).

$$H_{aq}^+ + HO_2 + Fe^{+2} \rightarrow H_2O_2 + Fe^{+3} \quad (A-3)$$

$$H_{aq}^+ + H_2O_2 + Fe^{+2} \rightarrow Fe^{+3} + OH + H_2O \quad (A-4)$$

$$H_{aq}^+ + OH + Fe^{+2} \rightarrow Fe^{+3} + H_2O \quad (A-5)$$

Thus each primary reducing species leads to the oxidation of three Fe$^{+2}$ and each primary OH radical oxidizes one Fe$^{+2}$. For $^{60}$Co $\gamma$-rays the total yield of Fe$^{+3}$ has been determined accurately using calorimetry as the standard, and $G(Fe^{+3}) = 15.5$.  

The ferrous sulfate dosimeter is very sensitive to traces of organic impurities. Oxidation of the organic material
by OH radicals and subsequent reaction of the organic radical with oxygen via reactions (A-6) and (A-7) produces an organic

\[
OH + RH \rightarrow R^* + H_2O \quad (A-6)
\]

\[
R^* + O_2 \rightarrow RO_2^* \quad (A-7)
\]

peroxide. The organic peroxide then reacts with the Fe\(^{+2}\) in an analogous way to HO\(_2\) to produce three Fe\(^{+3}\) instead of the normal one for each OH radical. Thus in the presence of organic substances \(G(Fe^{+3}) > 15.5\). To suppress reaction (A-6) chloride ion is normally added to the dosimeter solution. OH radicals react very efficiently with chloride ions via reaction (A-8).

\[
OH + Cl^- \rightarrow OH^- + Cl^- \quad (A-8) \quad k = 4 \times 10^9 \text{ M}^{-1}\text{s}^{-1}
\]

The resulting chlorine atom oxidizes only one Fe\(^{+2}\) via reaction (A-9)

\[
Cl^- + Fe^{+2} \rightarrow Fe^{+3} + Cl^- \quad (A-9)
\]

B. PROCEDURE

A stock solution of ferrous sulfate was made by dissolving 0.4 g of analytical grade ferrous ammonium sulfate, 0.065 g of analytical grade sodium chloride and 22.0 ml of analytical grade sulfuric acid in triply distilled water to a total volume of 1.00 litre. All apparatus and cells used in the dosimetry work were scrupulously cleaned using the permanganic acid - hydrogen peroxide - distilled water routine.

The ferrous sulfate solution was irradiated in the sample cells using the appropriate volumes and positions in the Gammacell cavity. The irradiations were automatically
timed with the built-in timer on the Gammacell. The times ranged from 0.1 second to 10 minutes with the corresponding doses of about 1000 to 50,000 rads. Longer irradiation times were avoided because above 50,000 rads oxygen depletion in the solution causes $G(Fe^{+3})$ to decrease.

After irradiation, the ferric ion concentration was determined spectrophotometrically by measuring the absorbance at 304 nm using either 1 or 5 cm cells and a Cary 14 spectrophotometer. The irradiated samples were measured with an unirradiated "blank" in the reference beam of the spectrometer. The absorbed dose was then calculated using the equation:

$$Dose = \frac{0.965 \times 10^9 \times (A_{net}^{304})}{\varepsilon_{304} \rho l G(Fe^{+3})} \text{ rads}$$

where $A_{net}^{304}$ is the net absorbance of the irradiated sample at 304 nm, $\varepsilon_{304}$ is the molar absorptivity of $Fe^{+3}$ at 304 nm, $l$ is the optical path length and $\rho$ is the density of the ferrous sulfate solution ($1.024 \pm 0.001$ between 15 and 25 °C). $G(Fe^{+3}) = 15.5$ was used in all calculations. $\varepsilon_{304}$ was taken to be $2174 \text{ M}^{-1}\text{cm}^{-1}$ in one series of experiments, while in the other series (radiolysis of liquid PC) $\varepsilon_{304}$ was measured experimentally.

C. **RESULTS**

1. **Nitrogen Fixation Experiments**

The dose rate for the syringes inside the stainless steel high pressure cell was determined using the above procedure with 15 ml of the ferrous sulfate solution in the syringe.
On December 3, 1969 the dose rate was found to be 2500 rads min$^{-1}$ assuming $\epsilon_{304} = 2174$ and $G(Fe^{+3}) = 15.5$. $A_{304}^{\text{net}}$ was determined as a function of time by irradiating samples for various time intervals and the slope of the plot of $A_{304}^{\text{net}}$ versus time was used in the dose rate calculation. The intercept of this line was positive rather than zero because the samples received a dose equivalent to about 1/10 minute during the lowering and raising of the Gammacell cavity into the radiation field. (The micro-switch which activated the automatic timer was not engaged until the Gammacell drawer was fully lowered.) This small correction factor was taken into account in subsequent dose calculations. Since the dosimetry for this experimental setup was done at ambient temperature and without checking the value of $\epsilon_{304}$, it was probably not accurate to more than $\pm$ 5%. This uncertainty was however tolerable since precise G value determinations were not involved.

2. Radiolysis of Liquid PC

The determination of the dose rate for this experimental setup was done more precisely to minimize the uncertainty. The radiolysis cell containing 17.9 ml of the ferrous sulfate solution was thermostated at 25 $\pm$ 0.1 °C during the irradiations and absorbance measurements for $Fe^{+3}$ were also made at this temperature. The latter was required since the value of $\epsilon_{304}$ for $Fe^{+3}$ has a large temperature coefficient and uncertainty in the temperature can introduce significant error into the dose calculations. In addition the value of $\epsilon_{304}$ was experimentally determined using the same spectrometer and cells. Solutions of known $Fe^{+3}$ concentration were made from fresh
analytical grade (> 99% pure) ferric ammonium sulfate. The data obtained are plotted in Figure Al-1 and from the slope of the line $\varepsilon_{304}$ was determined to be $2184 \pm 8$ at 25 °C. This in in good agreement with the value of 2194 calculated from data given in reference 3 for 25 °C.

The dosimetry results for irradiations of the sample cell are plotted in Figure Al-2. From the slope of the line, the experimentally determined value of $\varepsilon_{304}$ and taking $G(\text{Fe}^{+3}) = 15.5$, the dose rate was calculated to be 4545 rads min$^{-1}$ for the ferrous sulfate solution on August 1, 1970. The intercept was found to be equivalent to 725 rads or about 10 seconds irradiation time.

3. Dose Correction Procedures - Computer Program

Corrections for "electron density" differences between the ferrous sulfate solution and the experimental liquid were incorporated in a computer program which automatically corrected for the natural decay of the source activity. This program was devised by a colleague and will be published elsewhere.* It corrected for the electron density difference by taking the average Z/A value for the ferrous sulfate solution (0.5533), water (0.5551) and propylene carbonate (0.5289) and multiplying the dose calculated for the ferrous sulfate solution by the ratio of the Z/A values of the experimental liquid and the ferrous sulfate solution. Correction for the natural radioactive decay of the $^{60}$Co was made from the known half-life

*footnote 3. G. J. Flynn, this laboratory, communicated.
**Figure A1-1.** Plot of the absorbance of Fe$^{3+}$ at 304 nm as a function of Fe$^{3+}$ concentration at 25 °C.
Figure Al-2. Ferrous sulfate dosimetry results for the "bubbler" cell used in the liquid phase radiolysis of PC.
using the formula:

\[ \text{Dose}_{\text{corr}} = \text{Dose}_{\text{orig}} \cdot e^{\frac{-\text{days} \times 0.693}{1924.9}} \]

where "days" is the elapsed time in days from the date of the original dosimetry, 1924.9 is the half-life of \(^{60}\text{Co}\) in days and 0.693 is a constant equal to \(\ln 2\).
APPENDIX 2

INDOPHENOL BLUE AMMONIA ANALYSIS

A. THEORY

The method used to produce the indophenol blue dye involves reaction of ammonia with sodium hypochlorite and phenol in a very alkaline solution as described by Tetlow and Wilson.

The reaction mechanism is believed to involve the following series of reactions (A-10), (A-11) and (A-12).

\[
\text{NH}_3 + \text{OCl}^- \rightarrow \text{NH}_2\text{Cl} + \text{OH}^- \quad \text{(fast)} \quad \text{(A-10)}
\]

\[
\text{NH}_2\text{Cl} + \text{O}^+ + 2 \text{OCl}^- \rightarrow \text{Cl-} - \text{N=O} + 2 \text{Cl}^- + 2 \text{OH}^- \quad \text{(slow)}
\]

\[
\text{O}^+ + \text{Cl-} - \text{N=O} \rightarrow \text{O}^+ - \text{N=O} + \text{Cl}^- \quad \text{(A-12)}
\]

indophenol blue

The indophenol blue dye has a broad asymmetric optical absorption band with a maximum at 630 nm as illustrated in Figure A2-1.

B. EXPERIMENTAL PROCEDURE

1. Reagents

A stock solution of sodium hypochlorite with 1.00% available chlorine was prepared from Fisher reagent grade NaOCl solution and doubly distilled water. The available chlorine in the undiluted reagent (4 - 6 %) was determined
Figure A2-1. Absorption spectrum of the indophenol blue dye in alkaline aqueous solution.
precisely by reaction with iodide and titration of the free iodine with standardized sodium thiosulfate in acid solution using a starch indicator.\textsuperscript{36} The sodium thiosulfate solution was standardized using solid potassium iodate as the primary standard as described in Vogel.\textsuperscript{36} The 1.00\% (weight/volume) available chlorine stock solution was stored in a darkened volumetric flask in a refrigerator until immediately before use. It was stable under these conditions for at least 4 months.

Stock solutions of sodium phenate were made fresh before each run by dissolving 62.5 ± 0.1 g of reagent grade phenol in 135 ml of 5N sodium hydroxide solution and then diluting this with doubly distilled water to a total volume of 500 ml. This solution was also protected from light and was stable only for about 6 hours.

Acetone used as a "catalyst" in the procedure was Fisher spectrograde.

Doubly distilled water was used to make up all solutions. The first distillation was from tap water and the second from acidified dichromate solution.

Standard ammonia solutions were prepared from reagent grade ammonium sulfate.

2. \textbf{Analysis Procedure}

All glass apparatus used in the procedure (i.e. flasks, pipettes, burettes \textit{etc.}) were initially cleaned with the
normal permanganic acid - hydrogen peroxide - distilled water routine. Subsequently the apparatus was washed well with doubly distilled water after each use and allowed to air dry. The volumetric flasks were stored filled with doubly distilled water.

The reagent solutions were delivered into 50 ml volumetric flasks using fast flow burettes. The ammonia standard (or unknown sample) was first added to the flask and diluted appropriately so that the total sample volume was 25 ml. If the unknown solution was strongly acidic or basic, it was first neutralized using standard H₂SO₄ or NaOH. To the 25 ml of sample 0.30 ± 0.05 ml of acetone was added and the solution mixed well. Then 10.0 ± 0.2 ml of the sodium phenate solution was added, immediately followed by 5.0 ± 0.2 ml of the standard hypochlorite solution. The sample was quickly mixed and diluted "to the mark" with doubly distilled water. The volumetric flask was then stoppered, shaken vigorously and placed in a darkened constant temperature bath at 25 ± 0.5 °C for 60 ± 5 minutes during which time the indophenol dye developed. The absorbance was then measured (within ± 5 minutes of 60 minutes development time) in a 5 cm cell versus distilled water at 630 nm using a Cary 14 recording spectrometer.

The absorbance values obtained above were corrected for the absorbance of the reagent solutions by determining the absorbance of a "reagent blank". Tetlow and Wilson found that if the reagents were mixed together first and allowed to stand for several minutes before adding an ammonia solution,
then no indophenol blue was developed except for that produced by any traces of ammonia in the reagents. This reagent blank procedure also allowed for the determination of the ammonia concentration in the "pure" doubly and triply distilled water samples.

C. RESULTS

The corrected absorbance at 630 nm was found to be linear with ammonia concentration up to at least $10^{-4}$ M $\text{NH}_4^+$ as shown in Figure A2-2 where the results of a typical calibration run are plotted. The concentrations quoted here are the original undiluted concentration of $\text{NH}_4^+$ in the 25 ml of sample before adding the reagents. (This is twice the effective concentration of $\text{NH}_4^+$ in the final 50 ml of solution.) From the slope of the calibration line the response factor was calculated to be:

$$\text{Response} = 0.156 \text{ absorbance units/} 10^{-5} \text{ M } \text{NH}_4^+$$

for a 5 cm pathlength cell. Since the minimum practical absorbance which could be measured was 0.005 units, the absolute sensitivity of the technique was about $5 \times 10^{-7}$ M $\text{NH}_4^+$.

The pure water samples always gave identical absorbance readings to those of the reagent blank solutions indicating that the water contained less than $5 \times 10^{-7}$ M $\text{NH}_4^+$.

Since the sensitivity of the method depended on the age of the phenate reagent and the particular batch of acetone used$^{37}$, the calibration curves were rechecked frequently. Each time an unknown sample was analysed, an internal
Figure A2-2. Typical calibration graph for the indophenol blue ammonia analysis procedure.
standard as well as a normal standard were run to be sure that the procedure and reagents were alright.

It was found on analysis of irradiated solutions which contained oxygen during the irradiation, that hydrogen peroxide formed during the radiolysis interfered quite markedly with the analysis. In fact analysis of a sample containing only $6 \times 10^{-4}$ M hydrogen peroxide gave an orange coloured solution which had an absorbance of 0.8 at 630 nm in a 5 cm cell. This absorbance was due to the tail of an intense UV band. Oxidation of the phenate reagent to give a quinone was thought to be responsible for this UV absorption. Because of this interference, the working sensitivity of the analysis procedure was about $5 \times 10^{-6}$ M $\text{NH}_4^+$ when a definite peak could be observed at 630 nm indicating the absorbance was due to indophenol blue and not caused by hydrogen peroxide interference.
APPENDIX 3

ELECTRON SPIN RESONANCE*

A. BASIC THEORY

By virtue of its intrinsic angular momentum and its charge, an electron has a magnetic moment associated with it. In the presence of an externally applied magnetic field, \( H \), the alignment of the electron's magnetic moment has a preferred direction, i.e. parallel to the external field. From quantum mechanics it is known that the electron has a spin quantum number of \( \frac{1}{2} \) which means that its spin angular momentum can have only two orientations with respect to a given axis. Thus the magnetic moment associated with the electron's spin angular momentum may either be aligned with the external field or against it. Since the parallel configuration is preferred, an energy difference exists between the two spin orientations. Transitions in which the electron changes its spin orientation may be induced by supplying the appropriate amount of electromagnetic energy. This is basically what ESR measures; the energy required to reverse the spin of an unpaired electron.

Normally in ESR a constant energy source in the form of microwave radiation is used and the external magnetic field is varied until the unpaired electron "resonates". When the difference in energy between the two spin states equals the energy of the microwave radiation, there is an exchange of

*footnote 4. Prepared from references 48, 53 and 63.
energy between the two energy systems which is effectively a "resonance" process. This resonance condition is normally written as:

\[ h \nu = g \beta H \]  \hspace{1cm} (A3.1)

where \( h \nu \) is the microwave energy, \( H \) is the external field and \( \beta \) is the Bohr magneton. \( g \) is called the spectroscopic splitting factor and it is the parameter which describes the position of the resonance absorption. The value of \( g \) for an electron with only spin angular momentum, i.e. the "free-spin" \( g \)-factor, is 2.0023. (The deviation from the integral number is due to relativistic velocity corrections.)

For the X-band spectrometer used in this research, the microwave frequency was about 9.3 GHz for which the field corresponding to the resonance of a free electron is about 3300 G.

In most radicals unpaired electrons have orbital angular momentum in addition to spin angular momentum. The effect of the orbital angular momentum is to shift the \( g \)-value of the resonance from the free-spin value. The degree of spin-orbit coupling determines the magnitude of the shift. For most organic radicals the deviations are small and may be thought to arise through an additional small perturbing magnetic field caused by a very slight orbital motion. This modifies the effective field that the unpaired electron experiences by vectorially adding to the externally applied field and thus causes positive or negative \( g \)-factor shifts.

Therefore equation (A3.1) may be rewritten as:

\[ h \nu = g \beta (H_e + H_i) \]  \hspace{1cm} (A3.2)

where \( H_e \) and \( H_i \) are the external and internal fields respectively.
From equation (A3.2) it is evident that the $g$-factor depends both on the magnitude of the external field and its orientation with respect to the local internal fields. This anisotropy of the $g$-factor is the reason that it is customarily expressed as a tensor with principal values: $g_{xx}$, $g_{yy}$, and $g_{zz}$, where the axes are generally chosen to correspond to the symmetry axes of the radical.

Hyperfine splitting of the electron's resonance line into multiplets is the result of interactions of the electron with the magnetic moments associated with those nuclei having nuclear spin. Since the orientation of nuclear spin is quantized, the nuclear fields do not cause a displacement of the resonance but rather split it into a number of components corresponding to the different orientations of the nuclear moment with respect to the external field. In the simplest case of the interaction of an unpaired electron with a nucleus with spin $\frac{1}{2}$ (e.g. a proton) there are two orientations of the nuclear magnetic moment, one opposing and the other adding to the external field. The unpaired electron then experiences a field of $H \pm \delta H$ where $\delta H$ is the field due to the nucleus. Thus two lines are observed equally spaced about the position where the resonance would have occurred if there were no hyperfine interaction. In general for a nucleus of spin $I$, the spectrum will consist of $2I+1$ lines of equal intensity. A much more complex situation exists when the unpaired electron interacts with more than one magnetic nucleus, particularly when they are not equivalent.
Since hyperfine splitting results from the interaction of two dipoles, this effect depends on their mutual orientation. Thus for electrons in orbitals which are not spherically symmetric, e.g. p-orbitals, the hyperfine interaction is anisotropic and this gives rise to a hyperfine tensor, $A$, where the principal values are usually calculated for the same axis system used for the $g$-tensor, i.e. $A_{xx}$, $A_{yy}$ and $A_{zz}$. Because of the spherical symmetry of electrons in s-orbitals, all the dipolar interaction with the nucleus average to zero. However, since s-orbitals have a non-zero wavefunction at the nucleus, this permits a hyperfine interaction which is known as the Fermi contact interaction and it is isotropic. Consequently if an electron is in a sp-hybrid orbital on an atomic nucleus there will be both an isotropic term with an anisotropic component superimposed on it.

B. APPLICATION OF ESR TO AMORPHOUS SYSTEMS

For radicals formed in amorphous or polycrystalline matrices there is a complete randomization of the radical orientations with respect to the external magnetic field; although in the polycrystalline system there is an ordered environment on the microscopic scale. In these systems, the ESR spectrum obtained is an envelope containing all the features for all possible orientations of the radical. The type of line shape that one observes will depend on the magnitudes of the anisotropies of the $g$-factor and hyperfine interactions. It will also depend on contributions to line width from dipolar interactions. Figure A3-1 shows some of the theoretical
Figure A3-1. Theoretical ESR derivative line shapes for amorphous samples when the radical is characterized by: (a) an axially symmetric $g$-tensor and no hyperfine structure, (b) an asymmetric $g$-tensor and no hyperfine structure, and (c) axially symmetric $g$- and $A$-tensors with the same symmetry axes and a large hyperfine splitting of a spin $\frac{1}{2}$ nucleus.

(after Figures 9.3, 9.4, 9.7 in Ayscough, reference 63, pages 324, 325, and 327)
line shapes for the the more simple cases: (a) an axially symmetric g-tensor (i.e. $g_{xx}=g_{yy}=g_\parallel$ and $g_{zz}=g_\perp$ with $g_\parallel \neq g_\perp$) and no hyperfine structure, (b) an asymmetric g-tensor and no hyperfine structure, and (c) axially symmetric g- and A-tensors with the same symmetry axes and with the hyperfine splitting of a spin $\frac{1}{2}$ nucleus being much larger than the quantity $\beta_H(g_\parallel-g_\perp)$. Analysis of the line shapes for totally asymmetric g- and A-tensors with more than one interacting nucleus is not easily accomplished.

When the magnitude of the dipolar broadening of the lines is greater than the anisotropies of the g- and A-tensors then the line broadening results in loss of the individual features corresponding to $g_\parallel$, $g_\perp$ etc. and the formation of a line of approximately a Gaussian shape. In this case, the peak-to-peak separation corresponds fairly closely to the isotropic component of the hyperfine splitting. This is the situation most often encountered for organic radicals trapped in low temperature matrices. The observed line widths are generally 10 -15 G at 77 °K, although tumbling or partial rotation of the radicals can reduce the line widths to some extent by time averaging the dipolar interactions.
APPENDIX 4

PURIFICATION AND ANALYSIS OF PROPYLENE CARBONATE

Propylene carbonate was purified using the following procedure:

7 litres of Eastman Kodak practical grade propylene carbonate was dried for several weeks over Linde 4A molecular sieves. (The molecular sieves were previously dried by heating to 300 °C under a dynamic vacuum overnight.) The dried solvent was vacuum fractionated in two 3.5 litre portions using a clean, dry, still with a 5 litre still-pot and a 4 foot by 1 inch column packed with 3/16 inch glass helices. The distillations were carried out at less than 1 mm pressure with a column head temperature of 86 ± 1 °C and a distillation rate of about 0.4 litres per hour. From each of the two 3.5 litre batches, about 0.7 litre fore-run was rejected and about 1.8 litres of the middle fraction was collected, leaving about 1 litre in the still-pot. The two 1.8 litre middle cuts were combined and dried overnight with molecular sieves. The 3.6 litre first distillation fraction was then redistilled, rejecting 0.8 litres of the fore-run and collecting about 1.9 litres of the middle fraction in a thoroughly cleaned 2 litre round bottom flask.

This doubly distilled PC was immediately deoxygenated and flushed for several hours with dry helium (dried via a liquid nitrogen trap) and then sealed in the 2 litre storage
flask. A sintered glass bubbler - dispenser unit as shown in Figure A4-1 was used in the 2 litre flask to flush and dispense the PC. This single sample of purified PC was then used for all experiments reported in this thesis. The required quantity was dispensed by applying helium pressure above the liquid. The flask was then well flushed with dry helium via the sintered glass bubbler and sealed under the helium atmosphere with the teflon stopcocks.

The distillation and drying procedure most probably reduced the water content to less than 1 ppm \((6 \times 10^{-5} \text{M})\) since it was more elaborate than that used by Jasinski and Kirkland\textsuperscript{42a} who found that double vacuum fractionation lowered the water content to less than 2 ppm. In addition, the continued flushing procedure with dry helium helped to remove traces of low boiling organic impurities as well as water.\textsuperscript{42a}

The physical analyses made on the purified PC included a mass spectrum, ultraviolet spectrum, nuclear magnetic resonance spectrum and infrared spectrum as shown in Figures A4-2, A4-3, A4-4 and A4-5 respectively. The refractive index of the PC was found to be \(n^2_0 = 1.4213\) as compared with the literature values of 1.4214\textsuperscript{40b} and 1.4212\textsuperscript{40d}. 
Figure A4-1: Storage - dispensing flask used to keep the purified PC under a helium atmosphere.
Figure A4-2. Mass spectrum of doubly distilled propylene carbonate (PC).
Figure A4-3. Ultraviolet absorption spectra of Eastman Kodak practical grade PC and its singly and doubly distilled fractions.
Figure A4-4. 60 MHz nuclear magnetic resonance spectrum of doubly distilled PC.
Figure A4-5. Infrared absorption spectrum of doubly distilled PC.
APPENDIX 5

GAS CHROMATOGRAPHIC ANALYSIS SYSTEM

A Varian Aerograph A-90-P2 gas chromatograph was specially modified to measure the gaseous product yields from the radiolysis of liquid PC. The system was designed to separate and measure quantitatively nitrogen, methane, carbon monoxide and carbon dioxide. Hydrogen could also be detected by this technique but with very poor sensitivity.

Figure A5-1 is a schematic drawing of the analysis system. An 8 foot by 1/8 inch Porapak Q column maintained at 0 °C outside the chromatograph was connected between the input of the sample side of the detector and the injection system via 1/8 inch copper tubing. The exit of the sample side of the detector was connected, through a flow reversing valve, to a 20 foot by ½ inch 13X molecular sieve column that was maintained at 100 °C in the chromatograph oven. Effluent from this column then passed through the reference side of the detector block and was vented into the atmosphere. The thermal conductivity detectors used WX filaments operating at 180 ma and 140 - 150 °C. The output of the detector bridge was connected via a polarity reversing switch to a Leeds and Northrup - Speedomax W 1 mV fast response chart recorder. (The polarity reversing switch allowed signals from the reference detector to be displayed in the normal "positive" manner.)
Figure A5-1. Schematic diagram of the modified Varian Aerograph gas chromatography system.
Prior to entering the 8 foot Porapak Q column, the carrier gas passed through a 1 foot section of 1/4 inch copper tubing, mounted externally, which could be cooled to liquid nitrogen temperature to trap out CO$_2$ and N$_2$O. The trap also had a heater section on the 1/8 inch tubing input and output connections to prevent blockage of this narrow bore tubing caused by conduction cooling and subsequent condensation of CO$_2$ and N$_2$O.

The external sample loop system was connected into the injector portion of the chromatograph via a stainless steel bypass valve and 1/8 inch copper tubing. It consisted of SL3 socket connections for the sample cell, a 2 foot by 1/8 inch Porapak Q "pre-column" vapour trap and a glass "in-line" standards gas sample loop of calibrated volume.

Helium, used as the carrier gas, was fed at 65 psig into the chromatograph via a liquid nitrogen trap which removed water vapour and traces of organic contaminants. Normal flow rate was 60 ml/min. With the columns at 0 and 100 °C, nitrogen eluted in about 10 minutes, methane in about 15 minutes and carbon monoxide in about 20 minutes. Carbon dioxide was subsequently measured by warming the external trap quickly to room temperature. It eluted from the Porapak Q column about 4 minutes later to be detected by the sample side of the detector as a sharp peak. It was then "trapped" in the molecular sieve column. Nitrous oxide had virtually the same retention time as CO$_2$ and thus prevented measurement of CO$_2$ in its presence. The flow reversing valve on the molecular sieve column allowed the CO$_2$ and N$_2$O to be "back-flushed" from it.
A typical chromatogram is shown in Figure A5-2. A nitrogen standard was routinely injected from the "in-line" sample loop before each sample to monitor any changes in detector sensitivity. Peak areas were measured by manual triangulation.

The linearity of the detector response and absolute sensitivity was determined by injecting known quantities of the sample gases using a second sample loop of calibrated volume which was filled on a vacuum line to known pressure. It was connected to the external sample loop system via the S13 sockets used for the radiolysis cell. The graphs of detector response (peak area) versus sample size (molecules) were all linear over a range of at least 100 from the limit of detection as shown in Figure A5-3. The response factors as determined from the slopes of these plots were calculated to be:

\[
\begin{align*}
N_2 &= 3.2 \pm 0.1 \times 10^{14} \text{ molecules mm}^{-2} \\
CH_4 &= 3.6 \pm 0.1 \times 10^{14} \\
CO &= 3.1 \pm 0.1 \times 10^{14} \\
CO_2 &= 2.7 \pm 0.1 \times 10^{14} \\
(H_2 \sim 220) &= 1 \times 10^{19} \text{ molecules (20 micro-moles)}
\end{align*}
\]

Since the minimum area which could be measured reasonably accurately was about 100 mm² for CO₂ and about 500 mm² for the other gases, the detection limits were thus approximately:

\[
\begin{align*}
(H_2 \sim 1) &= 1 \times 10^{19} \text{ molecules (20 micro-moles)} \\
N_2 &= 1.6 \times 10^{17} \text{ (0.3 " " )} \\
CH_4 &= 1.8 \times 10^{17} \text{ (0.3 " " )}
\end{align*}
\]
Figure A5-2. Typical chromatogram produced by the GC system shown in Figure A5-1 for a hypothetical sample containing N₂, CH₄, CO, and CO₂.
Figure A5-3. Detector response to $N_2$, $CH_4$, CO and $CO_2$ for the GC system shown in Figure A5-1.
$CO \sim 1.6 \times 10^{17}$ molecules (0.3 micro-moles)

$CO_2 \sim 0.28 \times 10^{17}$ " (0.04 " " )

The variation of detector sensitivity from day to day as monitored by the nitrogen standards was found to be less than $\pm 5\%$ from the mean. Since the majority of this deviation could be accounted for on the basis of uncertainties introduced by the manual integration technique and by atmospheric pressure and temperature changes, no corrections were applied to the experimental data for this apparent sensitivity variation.