PRNC-I05 ' PUERTO RICO NUCLEAR CENTER Radiolysis of Gaseous Hydrogen Halides Rupert A. Lee June 1967 ‘OPERATED BY UNIVERSITY OF PUERTO RICO UNDER CONTRACT NO. AT (40-1-833) FOR U.S. ATOMIC ENERGY COMMISSION ---Page Break--- RADIOLYSIS OF Gaseous HYDROGEN HALIDES by Rupert Archibald LEE A thesis submitted for the degree of DOCTOR OF PHILOSOPHY in the Faculty of Science, University of London. Puerto Rico Nuclear Center, Mayaguez, Puerto Rico. June, 1967, ---Page Break--- ABSTRACT Two pair yields of 4.1 and 4.7 have been measured for the radiolysis of pure gaseous hydrogen chloride and hydrogen bromide respectively, using Co-60. These yields, together with the W values for HCl (24.8 eV) and HBr (24.0 eV) obtained, lead to calculated G-values of 8.3 and 9.6 respectively, for the two gases. The effect of the scavengers bromine and sulfur hexafluoride on the radiolysis of the two gases revealed that there are at least two hydrogen forming species present. One of these is a 'thermal' hydrogen atom which may not have the electron as its precursor, the other is a ‘hot’ hydrogen atom which cannot be scavenged. The results with chlorine as a scavenger on the HCl radiolysis brought out the importance of back reactions taking place as the concentration of chlorine builds up during the irradiation of pure gaseous hydrogen chloride. A study of the effect of an applied electric field showed that during the radiolysis of the two gases, reactions involving the recombination of ions were unimportant as a means of producing hydrogen. ---Page Break--- This study has shown that adiabatic excitational processes are as important as ionization processes in the decomposition of these two hydrogen halides. The Br molecule appears to undergo dissociative excitational processes more readily than the HCl molecule. ---Page Break--- contents SECTION I = INTRODUCTION 1.1 Interaction of ionizing radiation with matter 1.2.1 Electromagnetic radiations 1.2.2 Fast electrons 1.2.3 Secondary electrons Fundamental processes in radiation chemistry 1.3.1 Primary

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mechanism for the radicalytic decomposition of hydrogen chloride SECTION V - DISCUSSION OF HBr RESULTS 5.1 Radiolysis of pure gaseous hydrogen bromide 5.2 The scavenging effect of bromine and sulfur hexafluoride on the radiolysis of gaseous hydrogen bromide 5.3 Applied electric field effect 5.4 Proposed mechanism APPENDIX I APPENDIX II REFERENCES 120 126 128 129 132 139 136 ---Page Break--- section 1 Introduction 2a. GENERAL It will be worthwhile to review briefly the historical development of radiation chemistry; it reflects both the shifting interest and interpretations which have marked the steady growth of this subject. With the discovery of X-rays and radioactivity towards the end of the 19th century, chemists became aware of the chemical changes brought about by various types of radiation. At the turn of the century, Sir William Ramsay, working in this field on the decomposition of simple gases in the presence of radon, wrote that "whenever radiation produces chemical action, then, other conditions being unaltered, each particle of emanation as it disintegrates produces the same amount of change." This statement made radiation chemists realize that there was some quantitative relation between energy absorption and chemical change. At first, most of the research in the field of radiation chemistry was carried out on gases, as evidenced by the pioneer work of Lind and Mund, their study of gaseous reactions involved the use of radon (i.e., alpha particles), and it was therefore natural for them to relate the observed chemical changes to the amount of ionization produced in the system. Thus, the term ion pair yield (IPY), i.e., the number of molecules destroyed or formed per ion pair produced, developed to illustrate the connection between the physical and the chemical actions of radiation. Since this ratio was only measurable in the case of gases, the term G-value, defined as the number of molecules changed per 100 electron volts of energy absorbed by the system, was introduced.

so that workers in the condensed phases could have a means of comparing yields. The G-value and ion pair yields are related by the equation e+ 100. W = W where W is the mean energy required to form an ion pair in the irradiated gas. Values of W for gases found to be approximately twice their ionization potential. This led to the point to point out that part of the chemical action of high energy radiation may be due not only to ions but also to the reactions of electronically excited species. The classic paper of Fyring, Hirschfelder and Taylor, in which they discussed ortho-para hydrogen conversion and hydrogen-bromine combination, demonstrated firstly, the importance of molecular ions having the valency properties of free radicals and secondly, the importance of neutral free radicals and atoms as chain carriers. It further stated that it was unnecessary to put forward the existence of ion-molecule clusters to explain large ion pair yields. This led to the almost complete rejection of ion-free processes in radiation chemistry until the recently proven occurrence of ion molecule reactions in the mass spectrometer. Within the last two decades due to the development of the nuclear reactor and various machines for producing high energy radiations, research in this field increased tremendously and has been centered mainly on aqueous solutions (thanks to Fricke for laying its foundation) and organic compounds. At present, studies in this field are carried out both for their intrinsic interest and their possible industrial use. 1.2. INTERACTION OF IONIZING RADIATION WITH MATTER The chemical effects produced by high energy radiations in an attenuating medium result from the interactions of fast charged particles. The particles may constitute the incident radiation such as alpha or beta rays, or be produced by the primary interaction of uncharged species such as gamma rays, X-rays or neutrons. It is imperative that the radiation chemist should have some knowledge of the physical processes involved in

the above interactions, only a brief description of the primary energy loss processes of electromagnetic radiation, and electrons will be considered. 1.2.2 Electromagnetic radiations The effect of an absorbing medium on a beam of electromagnetic radiation is to reduce the number of photons passing through. This reduction in beam intensity (-dt) is given by the relationship I = I■ e^(-µx) where I is the intensity of the incident radiation, dI is the reduction in intensity of the beam after passing through a distance x of the medium and µ is called the total linear absorption coefficient. This coefficient is the sum of a number of partial coefficients representing various processes of absorption. These processes are the photoelectric effect, Compton effect, pair production, coherent scattering and photonuclear reactions. Coherent scattering only occurs at low photon energies (<0.1 MeV) and in high atomic number (Z) materials and even so is negligible in comparison with the photoelectric effect at these low energies. Photonuclear reactions take place with photon energies above 10 MeV and therefore will be of no consequence in this study. (a) Photoelectric effect In this type of interaction, which occurs mainly with low energy photons, the entire energy of the photon (E■) is transferred to a single atomic electron. This electron is ejected from the atom with an energy (E■) equal to the difference between the photon energy and the binding energy (E_b) of the electron in the atom. At low photon energies, the electrons are ejected mainly at right angles to the direction of the incoming photon, but as the energy of the photon increases the distribution shifts increasingly towards the forward direction. To conserve energy and momentum, the remainder of the atom is recoiled. This means that photoelectric interaction is not possible with free electrons. At sufficiently high energies, K-shell interactions account for 80% of these events, the rest being L-shell interactions. The vacancy created in the

K-shell, or L-shell, is filled by an electron from an outer shell with the emission of characteristic X-radiation or Auger electrons. For low Z materials, the binding energy of the inner electron shells is relatively small, and therefore the secondary X-rays and Auger electrons will have low energies and will be absorbed in the immediate vicinity of the original interaction. The atomic absorption for this effect varies approximately as 4°c and is therefore important only at low photon energies and materials with high Z. (>) Compton effect: If the X- or gamma-ray energy is sufficiently large, rather than interacting with the atom as a whole, the X- or gamma-ray may interact with any of the orbital electrons as though they were essentially free electrons. Only a fraction of the photon energy will be transferred to the electron, and a modified photon of longer wavelength emerges from the collision in a direction differing by an angle θ from the original photon. These Compton electrons produced from radiation of given quantum energy have a very broad spectrum of energies which can be calculated from the Klein and Nishina formula. This spectrum is a continuous one, extending over a range given by $\Delta\lambda = (h/(mc))\ (1 - \cos\theta)$, where $h\nu$ and $\Delta\lambda$ refer to the incident photon and $\Delta\lambda$ is the change in wavelength after collision. On applying the law of conservation of energy and momentum, it can be shown that where h and mc have their usual significance. For a medium containing exclusively light elements, Compton absorption predominates for photon energies between 0.2 and 2 MeV, and the total energy absorbed per gram of the medium is nearly proportional to its electron density. (©) Pair production: For electromagnetic radiations of energies greater than $2m_ec^2$ (1.02 MeV), a fraction of the energy is absorbed in the production of an electron-positron pair. The available kinetic energy ($h\nu - 2m_ec^2$) is shared unequally by the two particles formed. Both of these particles are slowed down by interactions with the medium. Eventually the

A positron and an electron will combine, annihilating themselves and producing two photons of 0.51 MeV energy each, in opposite directions. The atomic absorption coefficient for this process is approximately proportional to 2° and increases with increasing photon energy. The relative importance of these three processes is shown in fig. 1 for the media water, aluminum, and lead. It can be seen that for gamma rays of energy 1.25 MeV, Compton scattering is the predominant process.

1.2.2 Fast Electrons

In the three processes described above, it is seen that electromagnetic radiation upon interaction with matter produces high-energy electrons. These fast electrons lose their energy by the following processes: emission of radiation (Bremsstrahlung), inelastic and elastic scattering, and polarization. The relative importance of these processes depends on the electron energy and to a lesser extent on the composition of the medium. The rate at which electrons lose energy in a particular medium is referred to as the stopping power or Linear Energy Transfer (LET) and is denoted by -dE/dx. For non-relativistic velocities, the simple equation can be developed where N is the number of atoms per cubic centimeter, v is the electron velocity, and I is the mean excitation potential of the medium.

The author has modified the above equation for the case of electrons at relativistic velocities to the following:

$$-\frac{dE}{dx} = \frac{2}{3} \int x R_e$$

where R is a complex function of $\rho (Y/e)$ and the electron energy. According to Bragg's law of additivity of stopping powers, the stopping power of an element is independent of its state of chemical combination. Thus, the stopping power of a hydrogen halide is equivalent to the sum of

the Stopping power of an equimolar mixture of hydrogen and halogen, The Bethe equation above does not take into account contributions to LET from the emission of bremsstrahlung or polarization effects: For an electron of energy E MeV, the ratio of the energy loss by radiation to the loss by collision is ---Page Break --- given by (aE /ex) rad 7 Ez, whereas, for col. Therefore, for electron energies below 1 MeV and low atomic number materials (<16), the contribution of bremsstrahlung is less than 28, 1.2.3 Secondary electrons charged particles, on traveling through a medium, leave ions and excited molecules along their tracks. Many of the electrons ejected by the incident fast particle will possess enough energy to cause additional ionizations and excitations. Since the electrons (referred to as secondary electrons) will have relatively low velocities, their rate of energy loss will be extremely high(!?), for secondary electrons of energies less than 100 eV, the formation of a few ion pairs will be sufficient to reduce the electron to sub-excitation energies (5 eV). The mean energy involved in the formation of an ion pair is about 30 + 10. This means that a secondary electron of 100 eV energy on being moderated will produce clusters of about 3 to 4 ion pairs along with several excited molecules. For low LET primary particles, ---Page Break --- -a2- the clusters will appear as widely separated beads along the particle track, whereas for densely ionizing radiation (e.g. alpha-particle), the clusters will be produced so close together that they will form a columnar envelope of ion pairs. When the kinetic energy of the secondary electrons is in excess of 100 eV, they can produce their own tracks which diverge from the direction of the primary track. These secondary electrons are referred to as delta-rays, ---Page Break --- -ue 1.3 FUNDAMENTAL PROCESSES IN RADIATION CHEMISTRY Ionizing radiation, on passing through matter, transfers its energy to the molecules of the absorbing medium by the various physical mechanisms described

Briefly in section 1.2, the chemical aspects of the various processes immediately following the primary radiation act (i.e. dissipation of energy) must now be considered. This stage, often referred to as the physico-chemical stage, can be classified into (2) primary processes and (2) secondary processes.

1.9.2 Primary processes

(a) Ionization

When a fast electron or any charged particle gets close to a molecule of the absorbing medium, a

Coulombic field is set up. This field will strongly polarize the molecular electrons in their orbitals. If the energy released in this interaction is larger than the binding energy of an electron in its parent molecule, then the electron can be expelled leaving a positive ion; XY^+ (which designates a primary radiation chemical process). The observed induced conductivity of gases provides evidence for the presence of such ionizations. The positive ion XY^+ produced above may or may not carry an excess of energy; moreover, if XY is a large polyatomic molecule, then the XY^+ would be unstable and dissociate into smaller fragments. This type of fragmentation process has been observed in the mass spectrometer. It occurs with a high probability, e.g., the hexane ion dissociates (below) $C_6H_{12}^+ \longrightarrow C_5H_{11}^+ + H^+$ to give smaller ions and radicals, or even radical ions and neutral molecules.

Alternatively, the interaction of a fast electron with a molecule may lead to a dissociative ionization process in which reactions (1) and (2) occur simultaneously.

The minimum amount of energy for process (1) is known as the ionization potential of the molecule and this can be accurately measured by electron impact methods. Since the energy required to form an ion pair is usually about twice the ionization potential, this excess energy may be used up in forming excited species.

(>) Excitation

If the energy transferred to a molecular electron is less than the ionization potential, it may still be large enough to displace the

electron from its ground state to an “excited state." [r ‘The excited state here is similar to that produced by the absorption of a quantum of Light AB + hν and therefore much information on the behaviour of ABY can be obtained from photochemical study. 1.3.2 Secondary processes (a) Reactions of ions Positive ions and their daughter ions are continuously produced in a system under irradiation. Along with these, there is an equivalent number of negative charges (i.e., free electrons or negative ions), and therefore two possible neutralization processes must be considered (G) electron recombination and (UL) positive ion-negative ion recombination. Besides these, the ions may interact chemically with neutral molecules or else undergo charge transfer with impurities. (2) Positive ion-electron recombination If an electron, ejected from primary ionization, becomes "thermalized" in the vicinity of a positive ion, recombination occurs owing to the strong Coulombic interaction and an excited molecule is produced; $XY + e > XY^*$. The excited molecule here has gained energy equal to the ionization potential of the molecule XY (10 to 15 eV). Consequently, the molecule will undergo dissociation and will lead to a permanent change. Samuel and Magee(2®) have calculated that an electron of kinetic energy below 5 eV becomes thermalized and recombines with its parent ion in less than 10^{-8} sec, in the case of water (adsorbing medium). Conflicting with the above view is the Lea(1®), Cray(1®) and Rietzman(1?) theory which says that the electron will escape from the Coulombic field and will attach itself to a neutral water molecule becoming an aquated electron. In the case of gases, either an ion or electron may become separated and react individually with the neutral molecule XY. (id) Positive ion-negative ion recombination If ions of opposite charge are to recombine, their total internal energy must decrease as a result of the reaction. The energy released.

fe may be achieved through an increase in the kinetic energy of the neutralized particles by transfer of energy to a third body, by emission of electromagnetic radiation, or by electronic excitation of the neutralized species. Hence recombination may proceed by any one of the following mechanisms (20): three body recombination (1) is the most important mechanism at pressures greater than a few mm. He. Radiative recombination (2) and mutual neutralization through charge exchange (3) will predominate at very low pressures (72), since only two bodies are involved. If one or both of the forms are molecular, then there is the possibility of dissociative mutual neutralization thus xy sex yes ow (4st) Ion-molecule reactions. Mass spectroscopic studies have provided evidence beyond doubt for the occurrence of ion-molecule reactions. The theory of this type of reaction has been well developed by Schissler and Stevenson (32) so much so that for the (D)* + Dp) reaction, kegs is 8.7 x 202 + per mole per sec. compared with k,(3.6 x 102 1, per mole per sec.). There is also excellent agreement for the (ar" + H) reaction; the theory further predicts that rates of ion-molecule reactions are so large that there is a high probability of reaction upon every encounter. These reactions are temperature independent and are mostly exothermic. Ion-molecule reactions are of two kinds (A) hydrogen transfer reactions R + yet ee where R is a free radical and Ma stable molecule and (B) condensation reactions Ms cp ——e act + > where AC is a condensation product and D a stable molecule. These reactions are becoming more and more important in the interpretation of many radiation chemical processes. (iv) charge transfer process. If an impurity or a substance in very small amount is present during the irradiation then the following process may occur Map —eaten where A is the main component of the mixture. For this reaction to occur at ordinary temperatures the lowest

The ionization potential of A must be higher than that of B. This type of reaction was invoked to explain the increased ionic yield when acetylene was irradiated in the presence of Argon. Ae (1515.7 eV) + C2H2 (811.9 eV) (b) Electron capture by neutral species. The electrons ejected in the primary ionization of a molecule of the absorbing medium lose their kinetic energy either by further ionization or by exciting other molecules. These electrons then lose their freedom by two processes: (1) combination with a positive ion (already discussed) and (2) electron capture by a neutral species. There are at least five mechanisms by which electrons may react: (1) Radiative capture by a neutral atom, (2) capture by an atom with a third body taking up the excess energy, (3) capture by a molecule with the vibrational excitation of the molecule ion, and its subsequent stabilization in a collision with another molecule, (4) dissociative attachment, and (5) ion pair production: the non-captive dissociation of a molecule into positive and negative ions by electron impact. A simple calculation can show that mechanism (4) cannot compete with (1), (2), and (3) at ordinary temperatures and pressures. For electrons of energies above 20 eV, mechanism (5) will become important and at low pressures (1) and (3) become unimportant compared with (4). A more complete discussion of the (2a) process is given by Massey. Figures (2) and (3) taken from the work of Frost and Wepower display the possibility of dissociative attachment occurring with chlorine and bromine. The main difference in the two halogens is that the threshold energy for electron capture by chlorine is about 1.6 eV whereas bromine has a zero energy threshold. This means that bromine will be a much more efficient scavenger for thermal electrons than chlorine. (c) Reactions of excited species. Excited species formed by the primary radiation process may

undergo the following reactions, ---Page Break--- Energy POTENTIAL -22- NUCLEAR SEPARATION FIG. 2 ---Page Break--- ENERGY POTENTIAL, 23 ---Page Break--- =e (2) dissociation into free radicals The free radicals X and Y formed from the dissociation of highly excited molecules may carry an excess of kinetic energy and are referred to as "hot" radicals. The radicals are highly reactive, (44) Dissociation into "molecular products" where A and B are saturated or unsaturated molecules. This is possible for excited states formed from positive ion electron recombination. (444) Reaction with other molecules xy" + co products Little is known about this type of reaction except for a suggestion by Burton et al. to explain condensation reactions involving hydrocarbons. (2v) transfer of excitation The reaction may be written x sy Here molecule Y must possess at least one excited state ---Page Break--- = 25 below the energy level of x". In certain gas phase photolyses where the increased ionic yield could not be explained by a charge transfer process, excitation transfer has been suggested. Burton pointed out that if the electron is attracted back to its parent ion in less than 10^-7 sec, then primary ions will have an extremely short lifetime and hence the observed energy transfer process should be mainly due to transfer of excitation rather than charge. ---Page Break--- ° - 2.4 Positron emission The radiation chemist requires to know the effectiveness of a particular chemical action of ionizing radiation. This is usually measured by (a) the ion pair yield (W/N) in the case of gases and (b) the 100 eV yield for condensed phases. Both of these terms have already been defined, where it was pointed out that they are related by the equation. It is not very difficult to obtain ion pair yields in gaseous systems; however, for a determination of G, an accurate value for Y is required. By an application of the Bragg-Gray cavity ionization chamber theory, the quantity of ionization observed in a small cavity can be

related to the energy absorbed by the cavity walls during exposure to ionizing radiation. It is expressed simply by the equation es ee ss gw mo Se ES Se Me where FE and E are energies absorbed per unit mass in E and Ey Pr the wall and gas respectively, S" is the ratio of the mass stopping powers of the wall to that of the gas and ---Page Break--- -27- J, 48 the number of ions produced per unit mass of gas in the cavity. Since the energy absorbed by the wall is independent of the characteristics of the gas, then by filling the chamber with various gases successively, the equation 2 172 Sat He ey can be obtained, where the subscripts (1) and (2) apply to two different gases. It follows that, the unknown can be calculated from measurements of the saturation ion currents and the stopping power ratio (s3), calculated from the Bethe equation(20). The Bragg-Gray theory of cavity ionization is depicted in fig. & (a) where it can be seen that the radiation chemical reaction is carried out only by electrons emanating from the walls due to Compton interaction of the Y-rays. A more general picture appears in figs 4 (b), Spencer and Attix(®) were able to modify ---Page Break--- ~ 28 7 RAY GAS FILLED cavity (2) SOLID MEDIUM a bes BRAGG-GRAY THEORY OF CAVITY IONIZATION RAY SOLID MEDIUM GENERAL CASE OF CAVITY = IONIZATION PROBLEM FIG. 4 ---Page Break--- -29- the Bragg-Gray picture to take into account the processes (8) and (c). In their calculation "fast" secondaries of the type (B) are added to the primary electron spectrum and their effect subtracted from the stopping power of the medium, whereas the "slow" secondaries of the type (C) are not added to the electron spectrum but their effect is subtracted from the stopping power of the gas. The ratio of the energy dissipated per unit mass in a small gas filled cavity to that in the surrounding wall (due to Spencer and Attix modifications) is given by the equation(29) CaP), x f, 1a) 2 [tte ad an eg OTD ° GM, . where subscripts and g refer to wall and gas respectively.

Zand A to atomic numbers and weights, and I to the mean excitation potential. The term ¢, (1) is a polarization correction to energy lo 1s im the wall and depends only on wall material and the initial electron energy Ty. C,(Tged) is a function of the average wall separation and the pressure of the cavity gas. The pressure dependence results from its dependence on 4, which is the energy of an electron of range in the cavity gas equal to the average wall separation. This expression predicts ---Page Break --- = 30 departure from the constancy of the ratio of saturation ionization currents to pressure at low pressures, and for materials with z differing from 2. For z, wait < 2 > 2 eae Ht wall gas’ gas the departure decreases and for Z, wall increase ---Page Break --- sae 245A SUMMARY OF THE PRESENT STATE OF THE RADIOLYSIS OF HYDROGEN HALIDES The three hydrogen halides hydrogen chloride, hydrogen bromide and hydrogen iodide have all been irradiated in the gas phase by various workers. The ionic yields obtained increase in order of increasing atomic number of the halogen (=Myo)/¥ 135 Mupe/ wMyy/N= 6). Hydrogen iodide has been irradiated both with a-particles and with X-rays independently by different workers (2°) and in each case the ion pair yield was approximately 6 within experimental error. Following is the proposed mechanism Hr ——-utee @ e+ kr ener @ wr 4 ener @ Beer ened om rerew— ene ro) ‘This mechanism gives an ion pair yield of 4. However, if line 4 of reaction (3) the ten molecule reaction ---Page Break --- -32- ars att grt er 6) is chosen, followed by ur? ¢ Te ons or om an ion pair yield of 6 is obtained. In the X-radiolysis of gaseous hydrogen bromide, ion pair yields varying from 4.6 to 5.221) were obtained. Hamiz1 put forward a similar chain to reactions (1) to (5) above and suggested that the yield above 4 may be due to contributions from the excitational processes which may be depicted as follows MBy > yar* @ ce # wEr*——> par’ «) Worn + Br ao) The only work published on gaseous hydrogen chloride before this.

Investigation was undertaken, is that of Vandamne(??). An ion pair yield of about 3.3 was obtained for α-radiolysis. No attempt was made in this paper to put forward a mechanism. In the context of radiolysis of hydrogen halides in the condensed phases, Arastrong and his group have studied the effects of scavengers on product yields. They have proposed the following possibilities in accordance with the Samuel-Magee model. Hel was Hert + e Heat + eHca* + anor) + en () Hen Ae eat be Hea + Her” + ker? + ca HCl? + (not) + Her + Winot) Both of these mechanisms are likely to produce "hot" hydrogen atoms. The effects of the scavenging of chlorine and bromine on both hydrogen chloride and hydrogen bromide suggest the following electron capture process. These papers show clearly the presence of two hydrogen forming species. Table I summarizes the kinetics of the radiolysis of hydrogen chloride in the presence of chlorine and bromine on the assumption that one of the following competitions occurs. The C values for liquid hydrogen chloride and hydrogen bromide were found to be 6.5 and 12.4, respectively. Results (Ref. 93) of liquid phase radiolysis of hydrogen chloride, chlorine, bromine: first species 2.3, 1.7 x 10^7, second species 4.2 e10.

ATM AND SCOPE OF THE PRESENT INVESTIGATION In the previous section it can be seen that the mechanism for the radiolytic decomposition of hydrogen halides in the condensed phase differs considerably from that proposed for the gas phase radiolysis. From his study, Armstrong has obtained evidence for the presence of two hydrogen forming species. In the condensed phase radiolysis, he has placed emphasis on the occurrence of excited species as a precursor to "hot" hydrogen atoms. In view of the above differences, it was considered desirable to reinvestigate the gas.

phase radiolysis. Also, the irradiations in the previous gas phase studies had been carried out to high percentages of decomposition where the accumulated products would interfere with the initial yields, and hence G values quoted in previous publications may have been too low. Since the appearance of the first communication on this investigation, it has been pointed out by Dr. Henry J. Gomberg, Director of the Puerto Rico Nuclear Center, that due to the high G values obtained with hydrogen halides, these gases would be ideal for use in a regenerative type fuel cell. The hydrogen halide would be decomposed by ionizing radiation and the products hydrogen and halogen recombined in a closed system type fuel cell. The efficiency of the fuel cell could be over 90%, the theoretical E.M.F. produced with a hydrogen-chlorine type fuel cell is 1.36 volts. Assuming a G(HCl) value for hydrogen chloride to be 8.3, an energy conversion of 11.3% is obtained. This appears more attractive than the present SWAP systems. These systems for Nuclear Auxiliary Power are of two types: reactor systems and radioisotope systems. In the radioisotope systems, energy conversion is carried out mainly by a thermoelectric process. The overall RTG (radioisotope thermoelectric generator) efficiency is only about 5%. A thorough investigation of the mechanism of the decomposition of these hydrogen halides would prove to be of immense value towards the adoption of this idea.

SECTION 11 EXPERIMENTAL 2.2, APPARATUS The same pieces of equipment used in this investigation consisted of two high vacuum systems, a variety of irradiation cells, several radiation source and a diaphragm gauge, and instruments both for applying an electrical potential and for measuring very small electrical currents. The following is a description of these and other relevant pieces of apparatus. Mercury-free vacuum system for purification of sample A mercury-free vacuum line (figs. 566) was constructed for purifying and storing.

gaseous samples. A high vacuum of about 10^7 San.tz. was maintained by a new Seal forepump and a water-cooled oil diffusion pump. The low pressures were monitored by an ionization gauge. The oil diffusion pump was arranged in such a way that hydrogen from the irradiated samples could be transferred from the vacuum system to a conventional hydrogen analysis line. In this way, irradiated samples could be re-irradiated without coming into contact with mercury vapor from the analysis line. This was to prevent hydrogen halides or scavengers from forming undesirable products by reacting ---Page Break--- Fig. 5 ---Page Break--- s ‘914 NOLWOISId «=3IdNVS «40s = NIT WNNOWA ---Page Break--- = 398 = Fig. 6 ---Page Break--- 9 91 W31SAS a ONINNSVIW ---Page Break--- - 40 with mercury. The hydrogen halides were introduced into the line directly from Matheson tanks via stopcock 0 (fig. 5) and condensed after purification (to be described later) in the sample storage F. The bulbs B and C (fig. 6) were calibrated and used for measuring out quantities of scavengers. The pressures of the hydrogen halides and scavengers were measured using a metal diaphragm gauge E (fig. 6) connected to a mercury manometer. The diaphragm separated the measured gas from coming into contact with mercury vapor. 2.2.2 Analysis Line The analysis line is shown in fig. 7, and consists of a calibrated McLeod gauge, a Toepler pump, and a palladium thimble which could be heated. The irradiated sample was put either into the mercury-free line and the hydrogen to be analyzed pumped via the line, or else a diffusion pump into the analysis just placed at the sample inlet V and the hydrogen toeplered into the McLeod gauge while liquid nitrogen was placed around the U trap K to condense any mercury vapor. The volume of the McLeod gauge and associated dead space were measured accurately. Pressures of hydrogen as low ---Page Break--- see = Fig. 7 ---Page Break--- see £ old W32LSAS SISAIVNY N3ASONGAH ---Page Break--- as 2x10^-9 nm,lig. could be measured. 2.1.9 Metal

diaphragm gauge This gauge (fig. 8) had a diaphragm made from steel of 0.002" thickness and a 6" circular piece of 316 stainless steel: The diaphragm was held between teflon and stainless steel annulars as shown in the figure. To each of the outside steel plates were soldered Kovar glasses. Inside one of these Kovar glasses was a screw with a minute hole through the center. This screw could be adjusted to increase the sensitivity of the gauge. The whole system was held together by equally spaced bolts (not shown in the diagram). The diaphragm and the screw were connected to a milliammeter and a 6 volt dry cell. By means of equilibrating the pressure on both sides of the diaphragm with the aid of the milliammeter, pressures could be measured to an accuracy of 0.05 cm. Radiation sources (a) 4,200 curie cobalt-60 source This source was contained in a lead castle mounted into the side of a concrete cave. The cave door was fixed on a movable trolley which could slide in such a way as to position samples on the trolley ---Page Break--- FIs. ---Page Break--- RY ay SSSSSS METAL DIAPHRAGM GAUGE FIG. 8 ---Page Break--- opposite the source when the source was out of its lead castle. The source could be activated by lowering the isotope. Safety precautions were such that the door could neither be opened if the source had been lowered nor could the source be lowered if the door was open. Samples to be irradiated had to be placed in special containers and bolted onto the trolley. This was done to ensure reproducibility of dose rates. (b) Gamma-ray Samples were prepared and sent to Atomic Energy of Canada Limited, Chalk River, to be irradiated at high doses using their 12,000 curie cobalt-60 source. (c) X-ray machine Samples were subjected to 87kV X-rays supplied by a conventional therapeutic machine at the Holy Cross Hospital, Calgary. (d) 4,1200 curie cobalt-60 source This was the source used at the Puerto Rico Nuclear Center. The source was contained in twelve pencil-type capsules, each containing

approximately 100 curies. The capsules were inserted into twelve hollow aluminum cylinders. The cylinders were positioned to form a Hollow Cylinder Variable Geometry Irradiator. The irradiator was remotely controlled and could be adjusted to form a hollow cylinder from § to 19 1/2 inches in diameter. The shielding was provided by water in the form of a pool 9! x @* and 14 1/2" deep. The capsules were about 10! under water. Samples to be irradiated were placed in special containers and lowered into the pool.

2.1.5 Electronic equipment Ionization currents were measured with a Keithley 410 C micro-microammeter which covered current ranges from 10 to 10°? anp. The applied potential was supplied by a Hamner 113 high voltage supply capable of producing 5000 volts. Both of these instruments were connected to the irradiation cell via coaxial cables.

2.1.6 Ionization chambers and irradiation cells Two types of ionization chambers were used (a) a concentric cylindrical chamber (b) a parallel plate chamber. The concentric cylindrical ionization chamber (similar in design to Pack's(37)), used for measuring ionization currents, is shown in fig. 9. The 2.5 mm thick cylindrical wall was coated internally with colloidal graphite to form the collecting electrode. The central high voltage electrode A, which consisted of a 9 7 mm outer diameter pyrex tube, and a guard ring B, were coated in a similar manner. After the coatings had been applied through the tube D, this end was sealed to form a thimble trap for condensing the hydrogen halide using a liquid nitrogen bath. Tungsten wires passing through the glass wall provided contact between the graphite coatings and shielded electrical leads A", B", and C'. Gas was admitted to the irradiation cell via a stopcock attached to a 30 cm extension of tube E. This stopcock was shielded during irradiations.

The parallel plate cell shown in fig. 10 was made by

flattening the ends of a cylindrical tube. The distance between plates varied from 2 to 3 cm from cell to cell. These flat faces were coated with colloidal graphite through the end I which served the same purpose as the end D in the previous description. Platinum leads were soldered to tungsten, and the joint encased in glass for the metal-glass seals. Within the cell, a platinum rod came into contact with the graphite face. On the outside, the tungsten leads were connected via coaxial cables to the electronic equipment. The irradiation cells not used for the measurement of ion current are shown in fig. 11. These were ---Page Break--- - Mea - FIG. 10 ---Page Break--- YAGNVHD NONVWZINO! 31V1d T3ATIVEVd or “Ola ---Page Break--- CELL IRRADIATION ---Page Break--- - 50 - made from Pyrex round bottom flasks and had a side arm with a stopcock and a thimble for admitting gases and freezing hydrogen halides respectively. The cell volume varied around 230 cc and one large cell had a volume of 9690 cc. This type of cell was used both with the 200 curie Co-60 gamma source and the X-ray machine. For the Chalk River irradiations at high dose rates, the cells were similar in shape to the cylindrical ionization chamber. They were uncoated and carried no electrode attachments. In these, the stopcocks were replaced by break seals. 2.2. MATERIALS AND PURITY 2.2.1 Hydrogen chloride Hydrogen chloride gas of 99.08 minimum purity obtained from Matheson & Co. was degassed several times after being introduced into the vacuum line through stopcock C (fig. 5) directly from the Matheson gas cylinder; it was then purified from hydrogen bromide by pre-irradiation in the solid phase for one day in the presence of about 1% chlorine. This procedure oxidized the hydrogen bromide to bromine which, together with excess chlorine, was removed by trap-to-trap distillation through copper. The hydrogen chloride was finally distilled from an alcohol/liquid nitrogen bath to a liquid nitrogen bath, retaining ---Page Break--- only the middle fraction. It was then

stored in the aoiié state whenever possible. Silicone grease was used in all stopcocks which were to be in contact with the hydrogen halides for long periods. 2.2.2 Hydrogen bromide hydrogen bromide gas of 99.88 minimum purity, also obtained from Matheson and Co., was pre-irradiated overnight and thereafter treated in exactly the manner as hydrogen chloride. 2.2.3 Chlorine chlorine (99.58 minimum purity) was obtained from several sources. The lecture bottle was then purified further by bulb-to-bulb distillations from a trap at -80°C to a liquid nitrogen trap. After each distillation, the non-condensable gases were pumped away from the nitrogen-cooled solid. The chlorine was then stored as a solid at liquid nitrogen temperature in storage A (fig. 6). 2.2.8 Bromine bromine (reagent grade) was obtained from the Aker and Adamson Co. It was further purified by distilling through phosphorus pentoxide and collected at dry ice. After several times, it was stored ---Page Break--- - 32 - in a storage trap similar to trap A (fig. 6) and cooled by a dry ice/alcohol mixture. 2.2.5 Sulfur hexafluoride Sulfur hexafluoride obtained as a compressed gas from Matheson and Co., was subjected to several bulb-to-bulb distillations from -80°C to liquid nitrogen temperature. The sample was degassed after each distillation and finally stored in a one-litre flask R (fig. 5) as a gas. 2.2.6 Ethylene Research grade ethylene (Phillips Petroleum Co.) was further purified by distilling over phosphorus pentoxide and by bulb-to-bulb distillation. It was then stored as a gas in a large 4-litre flask (fig. 5). 2.2.7 Argon Research grade argon (obtained from Matheson and Co.) was used without further purification. 2.3 IRRADIATION TECHNIQUES 2.3.1 Cell treatment and sample preparation The Pyrex irradiation cells were left overnight in a glass blower's oven at 600°C before use. The cells were then attached to the mercury-free vacuum line and evacuated for over an hour to a pressure of about 1076 mmHg. During the evacuation, the cells were flamed.

to ---Page Break--- = 53 - release any moisture that may have been absorbed by the glass. The appropriate hydrogen halide was distilled from the copper mesh storage reservoir into a tube adjacent to the cell. It was then allowed to vaporize slowly, filling the cell and dead space. The pressures were monitored by the diaphragm gauge. When the desired pressure had been reached, the cell and dead space were isolated from the rest of the system. The differential pressure across the diaphragm gauge was now reduced to zero and the pressure read from the mercury manometer. When a scavenger had to be introduced, it was measured in a small calibrated bulb at the pressure calculated to give the mole percent required. The scavenger was then condensed into the irradiation cell. The procedure for filling an ionization chamber was similar to the above. In this case, the chamber was heated overnight in an oven at 110°C instead of at 500°C. 2.9.2 Irradiation procedure After the cells were filled, they were removed from the vacuum line and allowed to come to equilibrium at room temperature (23-24°C). They were then placed in ---Page Break--- - sue cell holders and carefully positioned on the trolley of the concrete cave or attached to the X-ray machine. When using the gamma pool source, the parallel plate type ionization chamber was always employed. This was placed in a stainless steel cylindrical can 5 inches in diameter. A rubber gasket was clamped onto the can by the cover with 6 evenly spaced bolts. The cover had a concentric hole through which passed the coaxial cables for electrical measurements. The cables were enclosed in a 1" internal diameter Tygon tubing 15' long. This tubing was in turn clamped onto a tube in the cover of the steel can. The whole can was lowered into the pool rods and these were immediately adjusted to grasp the steel can tightly. The open end of the Tygon tubing was always kept out of the pool, enabling the system to be water-tight. 2.4 MEASUREMENTS OF IONIZATION CURRENTS The Hamner high voltage power supply and

the Kedehiey nicro-nicroanneter were connected to the ceil before irradiation. As soon as the steel can was in position the voltage was applied and ionization currents 4. In the where a clear saturation curve was not obtained the saturation ionization currents were ---Page Break--- = 55 calculated from a plot of 1/i versus i/y? in accordance with Greening and Scott(*®), 2.5 MEASUREMENT OF HYDROGEN YIELDS After the sample had been irradiated, it was attached to the mercury free line via a 10/30 joint, or glass blown on in the ¢ of the 3690 ce cell and those that were irradiated at Chalk River. The whole hydrogen analysis line was pumped to a pressure of 10-Sam.Hg. When this pressure had been maintained for some time, the thimble of the cell was frozen with liquid nitrogen. With the system isolated in such a way that any gas from the cell would go directly to the diffusion pump, the stopcock to the cell was opened (or the break seal broken for the Chalk River experiments by means of a steel bar and magnet). After pumping for about 3 minutes, all the non-condensable gas (mainly hydrogen) would have been transferred from the cell to the analysis line. The gas was then sampled a few times into the McLeod gauge. By opening tap B (fig. 7) to the atmosphere, the mercury was forced into the capillary section of the McLeod. The differences in the heights of the mercury columns in the were measured with a cathetoneter and the pressure ---Page Break--- - 56 - calculated. The gas was now allowed to expand by pulling the mercury down in the gauge and the palladium thimble heated for a few minutes by means of nichrome wire or an infrared lamp. The measuring process was repeated until there was no further decrease in pressure. This decrease was due to the loss of hydrogen through the heated palladium thimble. The number of molecules measured pressure hydrogen was then calculated from the mass and temperature of the gas and the volume of the McLeod, assuming ideal behavior for the gas. ---Page Break--- were SECTION 117 RESULTS The principal method of

studying the radiation-induced reactions obtained by a determination of hydrogen yields as described earlier. All the results presented in this section are due solely to the interaction of radiation with the specified systems. Irradiation of an evacuated sample cell with and without a silicone greased stopcock did not produce any detectable hydrogen. Also, no hydrogen could be detected in unirradiated cells which had stood for several hours at room temperature. 2.2 DOSIMETRY It has already been pointed out that the simplest and most direct method of dosimetry for gaseous systems is by the measurement of saturation ionization currents. These can then be converted to absorbed energy provided the value of W, the energy required to form an ion pair in the gas, is known. W values for hydrogen halides are unavailable; however, there are reliable measurements of W for the inert gases. It follows from the equation ---Page Break--- = see a (5), = ratio of stopping power: Jp/J, = ratio of saturation ionization currents developed in section 1.4, that by comparing hydrogen halide gas with the inert gas adjacent to the particular halogen in the periodic table, the W values for the hydrogen halides can be determined. A definite advantage of choosing the inert gases for comparison lies in the fact that they would be isoelectronic with the corresponding hydrogen halides. This would mean that their electron stopping power will not differ appreciably and their Compton scattering cross-section will be the same. The ratio of stopping powers for hydrogen chloride to argon, and hydrogen bromide to krypton have been calculated using the Bethe equation and Bragg's law of additivity. Table 2 shows these ratios as a function of electron energy. Ionization current measurements were made with both the parallel plate and the concentric plate chamber. Tables 2 and 5 display typical measurements of ionization currents with applied electrical field at various pressures. Table 4 is depicted graphically in fig. 12. In the cases where saturation has not been

reached, & Greening type plot of 1/1 against i/v? has been de and ---Page Break--- -50- TABLE 2 Calculated stopping power ratios from the Bethe equation: 2 Fea, HBP E(MeV) 0.5 s Ar ke 0.02 0.0739 29.64 1.033 1.021, 0.05 0.1708 22.83 1.028 2.027 0.20 0.3008 23.15 1.023 2.015 0.20 0.48936 24.48 3.022 2.018 0.30 0.6032 25.20 2.022 1.022 0.40 0.6854 25.90 1.019 1.022 0.50 0.7446 26.42 1.019 0.60 0.7805 26.83 1.018 0.70 0.829 27.20 2.018 0.80 0.847 27.53 2.016 1.010 0.90 0.8688 27.83 2.018 1.010 1.00 0.9887 28.09 1.018 1.008 2.20 0.9995 28.38 1.027 1.010 1.20 0.9109 28.58 1.028 1.010 excitation potential used Bpp = 274 eV 269 eV Tain 0.05 eV 1, dm wx = 27.9 eV Ipp = 959 eV 960 eV ---Page Break--- = 60 TABLE 3 Typical ionization current measurements for hydrogen chloride (p=26.8 cm Hg) in parallel plate chamber v (volts) I (Amps x 10°) Polarity Reversed Start end 300 0.48 500 0.58 0.87 0.58 800 0.75 1000 0.80 0.79 0.78 1300 1500 0.06 0.85 1800 2000 0.08 0.88 2300 0.90 2500 0.90 0.88 3000 0.90 0.89 3800 0.92 0.90 0.90 4000 0.92 0.90 0.90 4500 0.92 0.90 0.90 5000 0.92 0.82 ---Page Break--- =o - TABLE 4 Typical current-voltage measurements Applied Voltage Current (Amps x 10°) (volts) 0.70 0.68 1.0 0.97 1.08 2.0 1.55 1.65 1.20 2.0 1.70 3.2 4.72 3.8 1.74 2.8 1.78 4.0 1.42 1.78 4.5 1.79 4.5 2.79 ---Page Break--- a Old S1OId FOVIIOA- LNBYYND IWIIdAL (S210A011M)-39Y110A aaitday s ’ © z ‘ So OH up c-gz © TOHy oF o8 ANauunD (4004 sanv) ---Page Break--- = 63 the saturation ionization current obtained by extrapolation to i/v? = 0. This type of analysis is only reliable for current measurements that are in excess of 0.7 of the true saturation current. Table 5 displays typical results used in a Greening type plot. A plot of the current versus voltage for this table is shown in Fig. 13. Fig. 14 is a typical Greening plot. The results for Figs. 15 and 16 were obtained using the concentric plate.

chamber. It should be noted that here the dose rate is much lower than the previous set of results obtained with the parallel plate chamber. As a test to the equation 8 be) % the W values for air (33.7 eV) and argon (26.2 eV) were inserted along with a calculated value of 1.19 for the Shir energy of 0.15 MeV. This value corresponded to a weighted mean electron, which was calculated to be 1.46, in excellent agreement with the experimental value of Lue (fig. 26). Carrying out the measurements for hydrogen chloride, argon, hydrogen bromide, and krypton (p, #25.0), ---Page Break--- - TABLE 5: Typical ionization current measurements for hydrogen chloride (p273.0 em He) in parallel plate chamber Camps) 2 v (volts) ‘ 2/4 (Amp sv? Camp: x 10) x 10 x 10 500 0.58 - - 1000 - - 1500 - - 2000 - - 2500 2.08 - - 3000 2.28 0.438 2.53 . 3200 2.38 425 2.29 3500 2.42 1.98 3800 2.49 0.40 1.72 4000 2.53 0.395 4200 2.56 0.390 4500 2.60 0.388 1.28 4800 2.64 0.378 5000 2.66 0.278 2.07 ---Page Break--- €b 91d (811000114) —-BOVLIOA —-O3ITdd¥ s ’ € z ‘ - 65: oo oz Awauuno (08 « sanv) ---Page Break--- = 66 1078 ontnaa’ Gs110n-sanvy gees s Ivolwas v 3 5 3 ---Page Break--- st Old {s110A011m)-BOVLTOA GaITda os oo oF so {8H = €02) NOOMY + (SH wo 6°6e) vIV (SH w> o'¥9) 19H AWaWuND —-NOLLVZINOT (08 « san) ---Page Break--- oe Ob (8H 9) ov 13 wv (6) Noeuy (2) yoH UH) Awawund — NOLLVENAYS (obx sanv) ---Page Break--- - 69 eV and G values can now be computed from the ion pair yields. These are given in table 6 for hydrogen chloride and hydrogen bromide. 3.2. RADIOLYSES OF PURE HYDROGEN CHLORIDE AND HYDROGEN BROMIDE. The radiolysis of each of the gases, hydrogen chloride and hydrogen bromide was carried out in a cell of volume 228 cc (fig. 11). These were all performed in exactly the same position on the trolley to ensure the dose rates. Various pressures and doses were used. The formation of hydrogen from the two gases is shown in tables 7 and 6 to delineate on pressure and dose. These results are also illustrated in

fig and 18, The hydrogen yields are expressed in moles of hydrogen formed per cm Hg pressure of gas used, per minute. 3.3 THE EFFECT OF CHLORINE ON THE RADIOLYSIS OF HYDROGEN CHLORIDE. Hydrogen chloride was next irradiated with various concentrations of chlorine present, in cells of volume 228.8 cm^3 and 3690 cm^3 respectively, using Co™ y ---Page Break --- = 70 - TABLE 6 . i) ax. fon pairs H molecules © (M/N)_——GC, . (cm Hg) G0=37) corhy oH ® (2) Hea results 26.80 3.42 ras we a owns 3.25 6.50 4.0882 17.20 2.67 sar sao as mean 8.12 + 0.1 8.3 + 0.2 (21) HBP results 22.25 1.98 asa 46s 5 22.25 1.86 4.29 8.62 . 22.28 2427 5.40 4.80 28.50 2.26 5.38 we 7 40.60 2.7% 3.58 4.767 mean 4471 40.2 9.6 4 0.2 ---Page Break --- -n- TABLE 7 Hydrogen formation from y-radiolysis of pure hydrogen chloride and hydrogen bromide gases (228.8 cm^3 cell) HX Pressure Irradiation time R(rate of H■ formation) (cm Hg) (mins) $x10^{12}$(moles /cm^3/min) Hydrogen chloride 46.05 995 2.78 50.90 9a8 2497 sine 668 2.93 59.95 1072 2.66 95.90 1038 2.62 218.90 450 2.79 120.20 480 2.79 mean 2.79 ± 0.13 Hydrogen bromide 18.70 asaa 7.86 18.70 izes 7078 36.00 seo 739 38.00 731 60.30 2095 60.30 ean 60.30 437 7.69 60.30 869 7.80 sean 7.59 ± 0.18 ---Page Break --- Table 8 Hydrogen formation from y-radiolysis of pure gaseous hydrogen chloride and hydrogen bromide (3690 cm^3 cell) HX pressure Irradiation time Rx 10^2 (cm Hg) (mins) (moles /cm^3/min) Hydrogen chloride 91.30 auto 23.85 91.30 an26 2eane 91.30 368 28.98 49.95 2160 23.80 19.90 16s 23.45 19.90 ass 23.80 mean 24.1 ± 0.5 Hydrogen bromide 1.65 ne 66.59 53.15 439 67.76 50.55 ase 66.79 sous 978 66.12 40.45 1020 67.05 mean 66.0 ± 0.5 ---Page Break --- ao (OH FO) XH 40 SUnSSIMd ---Page Break --- me 0hx XH dO Junssaud SH wo uae NIN dda GaKUos 7H 40 S310n 40 waGHON 1000 1200 1400 IRRADIATION ‘800 600 (ans) or TIME 18 FIG ---Page Break --- rays. Chlorine has the effect of lowering the yield of hydrogen and this sensing effect may be attributed to competition between the two following reactions, i Weer, 2 ewer oe A kinetic

treatment of the above would produce the relationship (see appendix 1): where AG(H2) = G(iy)nax = SUQ)e oy is the yield of Hs (CUID), and C(Hig)e are the yields of hydrogen in the absence and presence of the scavenger respectively. Pa, are the partial pressures Puea 12 of hydrogen chloride and chlorine. Table 9 gives the results of the scavenging effect of chlorine on hydrogen chloride using two cells of different sizes. Fig 19 is drawn from the results in table 9. The results obtained with the large cell have been normalized to those of the small cell, and a plot of the above equation is shown in fig. 20. From the ---Page Break--- -76- TABLE 9 Radiolysis of gaseous hydrogen chloride with water Rx 108? Cl, (moles/centigram) 226.8 ce cell 3690 ec cell 0.00 2.79 23.80 0.102 2.27 19.38 0.18 2s - 0.306 37% - 0.327 172 14.78 04550 aes - 0.700 2.25. 10.68 0.986 2.09 - 1.97 0.95 - 2.50 0.735 5.75 was 0.708 - 980 662 327 306 162 awa 102 sa 40 22 chlorine 0.980 0.938 0.735 0.649 0.588 0.517 0.898 0.429 ---Page Break--- 61 ‘Old UBONTAVS 1NBDU3d ZION “7 y1a9 99 1199 99 oss 199 99 eat amimous amos nO} x 19H 40 3unssaud SH we Yad NIN 83d O3HYO4 7H 40 S3T0W 40 RENAN ---Page Break--- oz ‘914 (v3]/ ow) cos | 00SEC = 78 - ost ---Page Break--- -19e slope of the line in fig. 20, a value of (3.80 + 0.15) x 207? can be calculated for k,/k, and a value of 6.75 for 4, ys The value for k,/k, is not in agreement with 1.07 x 107? calculated from the equation K/h = (0.187 + 0.033) exp-(1540/RT) at 29°C put forward by Klein and Wolfberg 4) for competition reactions of hydrogen chloride and chlorine for thermal hydrogen atoms. It can be concluded that the # represented above is not a thermal hydrogen atom, but some other species which will be referred to 3.4 RADIOLYSIS OF HYDROGEN CHLORIDE WITH

BROMINE AS SCAVENGER The radiolysis of hydrogen chloride in the presence of bromine was carried out in cells of different sizes at different pressures. These results are given in tables 10, 11, and 12. The results of table 10 are plotted in

fig, 19 to show the comparative effect of bromine and chlorine as scavengers. It is clear from this figure that bromine is a much more efficient scavenger at low mole percentage concentrations; however, at high concentrations it does not reduce the hydrogen yield as ---Page Break --- ~ 80 - TABLE 10 y-Radiolysis of gaseous hydrogen chloride with bromine as scavenger in 228.8 cc cell HCl pressure Irradiation time Mole # Fx 1027 (cm He) (mins) Br 219.90 450 - 2.79 219.90 938 0.10 2.32 229.90 1000 0.20 1.19 219.90 1500 0.30 1.05 219.90 1190 0.50 0.98 219.90 1067 0.70 0.95 219.90 1010 0.05 1.54 219.90 1010 0.05 1.00 229.90 1060 1.0 0.92 229.90 980 2.0 0.90 229.90 872 5.0 0.08 ---Page Break --- -a- TABLE 12 y-Radiolysis of gaseous hydrogen chloride with bromine as scavenger in 3690 cc cell HCl pressure Irradiation time Mole # Fx 1022 (cm He) (mins) Br (moles/gm/min) 92.30 1000 - 2H.46 91.30 366 - 26.90 91.30 1208 0.05 33.05 92.30 1228 0.05 32.77 92.30 1080 0.20 32.00 92.30 2126 0.20 10.88 91.30 1090 0.20 2.68 92.30 1500 0.80 9.28 91.30 2205 0.60 8.79 91.30 1170 0.40 8.38 91.20 1000 2.0 8.07 91.30 900 0 7.86 92.30 600 6.0 119 ---Page Break --- -82- TABLE 12 y-Radiolysis of gaseous hydrogen chloride with bromine as scavenger in 3690 cc cell HCl pressure Irradiation time Mole # Fx 1022 (cm He) (mins) Br (mole/gm/min) 19.90 1.65 - 23.45 19.90 1000 - 23.90 29.90 1000 0.05 12.02 219.90 1045 0.05 12.12 19.90 950 0.20 20.35 19.90 1096 0.35 9.56 29.90 1286 0.20 9.10 39.90 1213 0.40 8.50 19.90 1400 0.60 7.98 29.90 1205 0.60 8.08 20.10 800 1.0 7.00 20.10 1020 2.0 7.42 20.10 2293 4.0 6.97 20.10 977 4.0 7.28 ---Page Break --- - 83 - much as chlorine. Fig. 21 is a similar plot to fig. 20 using the results of tables 10 and 11 normalizing the pure hydrogen chloride yield to unity. Values of 1.96 x 10^7 and 5.65 are obtained for (k+ He) and Gye respectively, Keg Bee) assuming a competition for H* by hydrogen chloride and bromine. The comparison of these results with those of art cs) strong and Runferar, provides further evidence for the

assumption that H* is not a thermal hydrogen atom. An immediate possibility appears to be that the scavengers may be scavenging electrons which could be the precursor for H atoms. 3.5 RADIOLYSIS OF HYDROGEN CHLORIDE WITH SULPHUR HEXAFLUORIDE AS SCAVENGER. The foregoing results have indicated that the species H* was not a thermal hydrogen atom, but could be a mixture of thermal hydrogen atoms and thermalized electrons, in which case the rate constant ratios obtained would be complex rate constant ratios. Sulphur hexafluoride, a good electron scavenger, was therefore chosen. The activation energies for the two competing reactions (a) H+ $\rightarrow$ e + Ar and (b) H2 + He $\rightarrow$ He + e are about 10 K cal/mol and 3 K cal/mol respectively. Sulphur hexafluoride would therefore be unable to compete with hydrogen chloride for thermal hydrogen at room temperature and at the sulphur hexafluoride concentrations used. The same technique was used as in the cases of chlorine and bromine. The results are presented in table 19 and plotted in fig. 22. On comparing fig. 19 and 22 it can be seen that the sulphur hexafluoride has reduced the hydrogen yield more rapidly than either bromine or chlorine at low concentrations; however, the plateau obtained with sulphur hexafluoride is somewhat higher than with either chlorine or bromine. Both bromine and sulphur hexafluoride at low concentrations must be scavenging mainly electrons, since they both have maximum electron capture cross section for electrons at zero energy. If it is now assumed that the sulphur hexafluoride will only scavenge electrons, then from fig. 22 about 46% of the total hydrogen formed will have thermalized electrons as its precursor. 9.6 RADIOLYSIS OF HYDROGEN CHLORIDE WITH ETHYLENE Ethylene is known to react with thermal H atoms to form an ethyl radical. It was therefore thought --- Page Break --- 86 Table 13 y-Radiolysis of gaseous hydrogen chloride with

Sulfur hexafluoride as scavenger in 3690 cc cell Hel pressure Irradiation time Mole § Rx 101? (om He) (eins) SPz (molee/emig/min) 39.05 aan. - 22.62 39.75 aes - 22.69 39.75 1098 0.03" 12.96 39.75 1160 0.069 12.68 39.75 1072 0.102 12.60 39.75 1022 0.305 32.29 . 39.05 aa72 o.weo 32.83 39.05 1080 1.28 11.86 39.05 aio 2.56 aaa2 39.05 1068 3.10 20.88 39.05 1200 5.01 20.63 39.05 ais? 6.86 10.65 ---Page Break--- -87- sunfOoe no ‘armH 2 x7y gO NOLLYMWOs sO JLVY bY FIG. 22 ---Page Break--- Necessary to see what scavenging effect this gas would have on the radiolysis of hydrogen chloride. Little was done on this reaction and before it could be discussed a more systematic and thorough investigation would have to be carried out. The results obtained are given in table 14, from which it can be seen that the higher the mole per cent ethylene used the lower the hydrogen yield, and also that this yield increases with time of irradiation since the concentration of ethylene would have decreased with time. The preliminary experiments indicated (a) a scavenging effect of ethylene on the hydrogen yield and (b) consumption of the ethylene in a chain reaction (i.e. S.coty $8 of the order of several thousand). This suggested that the mechanism was quite complex and would need a detailed study. Before this study could be pursued further a publication appeared on this reaction putting forward a 3.7 vol% RATE EFFECT. Three similar cells (fig. 9) without electrical connections, all containing break-off seals, were sent to chatk Ri T (ALE.Csis) to be irradiated with a Gann cell. These cells were filled with pure hydrogen chloride ---Page Break--- -e9- sort we crot ses. ontan oar us we see ouras ost zn a6 oan onten ere ere ts 096 sarns tere ore orn eee serns zert ere ers ore oeres sure - - 566 seron (a7e/Shu2/seTew) | dn pasn aye (sary) (3H us) oT Xa "NED y eTon 4 erou TeF3ruz our2 woFseFpeaar ounssosd q3H a 1192 99 graze UF sosusawos Se oust Ay29 YazH epraoTy> ussospAy enossey 50 syshtorped. at guava ---Page Break--- = 90 - at first

and then various mole percentages of bromine were introduced. The reduced hydrogen yields are shown in table 15 together with a comparison of the results obtained with a 200 Curie Co-60 source. The nature of the experiment made it difficult to carry out too many runs. The samples had to be carefully packed and shipped each time for their journey to and from Chalk River. The few runs, however, indicate that there was very little difference in the scavenging at the higher dose rate. 3.8 EFFECT OF COATING THE CELL The cell used here was coated with colloidal carbon in a manner similar to that described by Pack et al. (37). These results compared with those from uncoated cells are given in table 16. It was found that the coating had a tendency to absorb bromine and therefore the cells had to be baked out under vacuum to remove absorbed bromine if a second series of runs were to be carried out. These results demonstrate that coating had little or no effect (within experimental error) on the relative reduced hydrogen yields. 3.9 RADIOLYSIS OF A MIXTURE OF HYDROGEN CHLORIDE AND HYDROGEN BROMIDE CONTAINING BROMINE AS A SCAVENGER. Measured amounts of a mixture of hydrogen chloride and hydrogen bromide were first irradiated in a manner similar to those already described. Several amounts of bromine were then added to observe its effect on the above mixture. on the assumption of the following competing

Reactions we need, +e We were too Hl, + Br Wg ey Ae made + oe @ similar calculation to that given in appendix T can be carried out and the following equation obtained, «(ery kine) a. ae +o Su Ry Grp *) Gr) The results are presented in table 17. rij depicts the scavenging effect and fig. 24 is the reciprocal plot of fig. 23. The rate of production of hydrogen in the absence of bromine was normalized to 100. From fig. 24, k,/k, can be evaluated using the previously obtained value for ky/kyy to be 1.96 ± 0.15 x 10^7, the calculation gives the value ky/ky = 6.1 ± 0.3 x 10^7% which is net in agreement with the ratio 0.12 for thermal H atoms obtained by conventional gas kinetic techniques (50). This provides further evidence for ---Page Break--- ~ oye TABLE 17. y-Radiolysis of a mixture of hydrogen chloride and hydrogen bromide containing bromine in 3690 cc cell Heh pressure Mole $ Irrad, time ole & R x 10^1? (eB He) HBr (mins) Bry (motes/entig/min) 16.80 5.32 1187 - 27.12 16.40 san 2066 0.050 19.50 16.40 5.32 ane2 0.099 16.97 . 16.40 5.31 126 0.198 16.98 16.40 5.31 asa 0.207 ae.us . 39.95 5.33 1082 - 26.88 : 39.95 5.33 3209 0.53 13.58 39.95 5.33 aise 1.02 11.96 39.95 5.33 1206 1.86 11.28 ---Page Break--- RESENT s . 3 3 x 3 nObt 10K 40 aunSSIud 8H Wo aE NIN Wad anos *H 40 S3I0N 40 WANN FIG. 23 ---Page Break--- 0003 008s 0008 00s 369 - 49H iNa0uae 370H ---Page Break--- -97- referring to the species ll above as H 3.10 HYDROGEN BROMIDE IRRADIATED WITH X-RAYS IN THE PRESENCE OF BROMINE Three similar cells A, B and C (fig. 11) were used. The cells were each filled with hydrogen bromide and irradiated with X-rays from a standard X-ray therapeutic machine using 87kv. These irradiations were all carried out at the Holy Cross Hospital, Calgary. The volumes of the cells were all about 230 cc differing by only about 3 cc. Next, small amounts of bromine were added and the cells re-irradiated. A treatment of the results (table 18) similar to those of hydrogen chloride with bromine gives the equation Kk, (Br) 2 eo far 2 Fa By Ror Figs. 25

and 26 show the scavenging effect and the reciprocal plot. From the reciprocal plot a value of (5.9 ± 0.9) x 10^7 for (H+ HBr) is obtained. This provides further justification for referring to the scavenged species as H’ rather than H2. ---Page Break--- - oe TABLE 18 Radiolysis of hydrogen bromide containing bromine using X-rays in a cell of approximately 290 cc at pressure Irrad. time Mole % Cell Rx 1027 (cm He) (mins) Br2 (moles/cent/min) ss. as - 8 2.97 55.08 as - 8 2.97 55.68 10 - 2.98 55.68 5 : s 2.95 : 56.26 as - e 3.01 . 56.28 as 0.20 4 2.77 . 55.88 as 0.508 2.60 . 55.88 as eo. 2.47 seu as 2.028 2.47 56.26 3s orc 2652 55.50 as 2.03 2.39 55.50 as 2.03 ¢ 2.3L 55.50 as wor oc 2.20 55.42 as 6.038 2.84 55.4 as 6.038 1.87 ---Page Break--- ys aH 40 BUNSSBud 8H HO ad NI wad camuod "H 40 $370M 40 wBENNN FIG. 25 MOLE % SCAVENGER ---Page Break--- = lou = ---Page Break--- - 101 = 3.21 RADIOLYSIS OF HYDROGEN BROMIDE WITH SULPHUR HEXAFLUORIDE USING X-RAYS. This was carried out in exactly the same manner as the previous irradiations using sulphur hexafluoride instead of bromine. If the following equations are assumed e+ HBr → H + Br e+ srg sre” then by treating the results similarly to the previous section a value for K(e + HBr) can be calculated. K(e + s) The results are given in table 19 and plots are shown in figs. 25 and 27. From fig. 27 the value of the above ratio is (6.4 ± 0.3) x 10^7, this is within experimental error of the value for K(e + Br) and therefore it is not unreasonable to conclude that the species represented above is not a thermal H atom but may be the thermalized electron. The scavengers have a lesser effect in reducing ---Page Break--- = 02 = ‘TABLE 18 Radiolysis of hydrogen bromide containing sulphur hexafluoride using X-rays in a cell of approximately 230 cc at pressure Irrad. time Mole % Cell — Rx 1027 (cm He) (mins) SF6 (moles/cent/min) $5.77 20 - 2.97 55.77 as 0.27k 2.70 55.77 as 0.27 A 2.74 55.83 as 0.58 oc 2.59 55.83 as lose 2.87 55.83 as ssc 2.37 55.72 as

3.088 2s 55.72 as 7.038 1.98 55.72 7 7.038 1.97 ---Page Break--- “2 la [fas] an] = 103 - "ss 49H ‘sav =x ---Page Break--- = Lon the hydrogen yield in the case of hydrogen bromide than in hydrogen chloride. 9412. THE EFFECT OF AN APPLIED ELECTRICAL FIELD ON THE RADIOLYSIS OF HYDROGEN CHLORIDE AND HYDRO BROMIDE. The cells used in this investigation are shown in fig. 10. They were filled with the desired amount of hydrogen chloride or hydrogen bromide separately, and as soon as they were placed in the irradiator, the saturation ionization currents were obtained. This was achieved by measuring ionization current with applied voltages in intervals of 500 volts at first and smaller intervals after 3000 volts. This took about 2 minutes. The applied voltage required was then set and the radiolysis carried out for 7 to 8 hours.

At the end, the ionization currents against voltage were rechecked. After this, the cells were analyzed for hydrogen to obtain ion-pair yields. The results are shown in tables 20 and 21. Plots of (a) ion pair yield of hydrogen against applied voltage and (b) ionization currents against applied voltages are demonstrated for hydrogen chloride and hydrogen bromide in figs. 28 and 29 respectively. ---Page Break--- = 105 - z Cw, oztn gntn eetn oth auth TOR CusH) uw mere sero no's oss ws ers ot x setnoetou prers %y oz save + sot eure usrz thre gr-ot sap aor ro roy hare ostz atte, ote et eur cert 1Br0 3303/09/4 preys pertddy ostez osrae oprsz osrsz oerae oztee oztee ozree ores oz ee ozs oar By us Tou, ---Page Break--- oz sorn ost cure zree 3 sore nom sore cute est ur RETR AEP TEP ve stave = 901 = ---Page Break--- = 107 - ez ‘ola swv01 /to 21100 ---Page Break--- at sanv oF wos / wo/ *1708 sae—(/) or oe on ---Page Break--- = 109 - section 1v DISCUSSION OF THE HYDROGEN CHLORIDE RESULTS N21 RADIOLYSIS OF PURE HYDROGEN CHLORIDE GAS In the introductory section the similarity of mass spectrometric studies to radiation chemistry was pointed out. Therefore, in considering the possible ionic reactions which are likely

To occur in irradiated hydrogen chloride, it would be worthwhile to review briefly the mass spectral data on hydrogen chloride. When hydrogen chloride is subjected to electrons of 150 eV impact energy, the principal ions observed are HCl■, HeI**, Cl■, Cl**, and H■(52), the approximate relative abundance of the first four ions are estimated to be 100:11:10:3. The parent ion (HCl■) is predominant in the mass spectrum and should also be the predominant primary ionic species formed in the radiolysis of gaseous hydrogen chloride. Since the ionization potentials of Cl and H (12.96 and 19.60 eV respectively)(52) are slightly higher than that of the HCl molecule (22.74 eV)(52), the ions Cl■ and H■ should rapidly undergo the following charge transfer processes at high hydrogen chloride pressures:

Cl■ + HeI → Cl + H■ + ΔE = -0.22 eV
Cl■ + H■ → Cl + H + ΔE = -0.86 eV

The doubly charged HCl^{2}■ and Cl^{2}■ ions, because of their larger values of second ionization potentials (e.g., second I.P. of Cl^{2} is 23.8 eV(52)), would be capable of far more highly exothermic charge transfer processes with hydrogen chloride molecules. These processes (given below) may lead to excitation and dissociation of the product ions:

Cl■ + He → Cl + H + Heat ΔE = -3.7 eV
HCl + Cl■ → HCl + Cl + ΔE = -8.9 eV

These reactions would obviously be followed by reactions (2) and (3). The overall stoichiometry for the primary ionization processes can therefore be represented as follows:

(Cl + x)He → Heat + e■ + x + x

The value of x would obviously depend on the ion distribution in the radiolysis and on the fraction of energetic charge transfers leading to dissociation. If it is assumed that every charge transfer of HeI^{2}■ and Cl■ leads to dissociation, a value for x (0.26) can be estimated using the ion distribution obtained in the mass spectral data. Before considering the possible reactions which the species HCl■, e■, H■, and Cl■ can undergo, the results of the experiments with

scavengers will be discussed: 4.2 THE SCAVENGING EFFECTS OF CHLORINE, BROMINE AND SULPHUR HEXAFLUORIDE ON THE RADIOLYSIS OF GASEOUS HYDROGEN chapter: It is quite clear from the results that the three scavengers used decrease appreciably the hydrogen yield in the radiolysis of gaseous hydrogen chloride. However, it is obvious (from the plateaux in figs. 19 and 22) that not all the hydrogen yield is being scavenged. This means that the scavengers must be competing with the hydrogen chloride for some species H* which can eventually lead to hydrogen formation. There must also be another species H* which accounts for the unscavengeable yield, and for which the scavengers cannot compete. On this basis the following competitions can be envisaged H0 + HeI + cr) H+ 8 → products other than H2 a) ws ner ea, + cn ao) ---Page Break--- - 12 = uM 4s —e products other than H2 ay (S denotes scavenger) Now if the species H* is a thermal hydrogen atom, reaction (a2) will be unable to compete with reaction (20) at the scavenger concentrations used in these experiments. Reaction (9) must then be responsible for the reduction of hydrogen yields. A summary of the results is shown in table 22 assuming the competitions depicted above. It can be seen that both kg/kg and Gy vary from one scavenger to the next. Table 22 Scavenger Gye Gye kg/kg Radiolysis Heaton -3(55 cig 0:75 188880 a0? 10.7 20 Br, S68 2465 1.96 x20 6.5 x 2079058) srg 9:80 4.50 <2 x 30 >t The last two columns in table 22 permit a comparison of the values of kg/kg obtained from radiolysis and from conventional studies in which H* is a thermal ---Page Break--- - ua hydrogen atom. The disagreement in the two sets of ratios indicates that the species H* is not a thermal hydrogen atom. Since it is known that sulphur hexafluoride is an extremely good scavenger for thermal electrons (57) and that it will not react with thermal H atoms at the sulphur hexafluoride concentrations used, it can be concluded that the Gy value obtained with sulphur hexafluoride should be

identified with G. A value of 3.8 (estimated from the plateau in fig. 22) is in good agreement with 4.0 calculated from the W value for hydrogen chloride (24.8 eV). Bromine reacts rapidly with thermal electrons as well as thermal hydrogen atoms, and therefore the G# (2.65) value obtained with bromine can be considered as being due entirely to processes not involving either thermal electrons or thermal hydrogen atoms as precursors. The difference between Gy for bromine and G implies that there is a source of thermal hydrogen atoms whose precursor is not the electron. A yield G of 1.85 thermal hydrogen atoms per 100 eV can be calculated from the difference in the G value obtained in the bromine and sulfur hexafluoride results. The ke/kg ratios obtained with chlorine and bromine as scavengers are really functions of keueuery/*cues) 84 ¥cegncry/*cessy? are best treated as "complex" rate ratios. It has been suggested that at high doses and high chlorine concentrations, the back reaction $H_2 + Cl_2 \rightarrow HCl + H_2$ with an activation energy of 5.48 kcal/mol may cause a slight reduction in the observed hydrogen yield. With bromine, the analogous reaction $H_2 + Br_2 \rightarrow HBr + H_2$ is less likely to occur since its activation energy is 19.7 kcal/mol. Consequently, the differences in G for these two scavengers may be ascribed to the effects of reaction (12). The scavengers chlorine, bromine, and sulfur hexafluoride, and the hydrogen chloride molecules can all react with electrons thus $e + H_2O \rightarrow H_2 + Cl^–$ (and $e + Cl_2 \rightarrow e + Cl^– + Cl$) $e + Br_2 \rightarrow e + Br + Br^–$ (and $e + S_2 \rightarrow e + S + S^–$). The energy thresholds for the above electron capture reactions are 0.65, 1.60, 0.00, and 0.00 eV respectively. Since the electrons would be expected to thermalize quite rapidly, reaction (15) could hardly compete effectively with reactions (1sacb) unless chlorine molecules were present in very high concentrations. The chlorine must therefore be competing with the H_2 molecules for hydrogen atoms which are

formed in reactions (14a) or (4B). € + 2iic1 —> electron-HCl complex HF cay csp) A study of the effect of chlorine on the radiolysis of a mixture of HeI and SF,(7) has shown that chlorine reacts with the electron-HCl complex and with thermal hydrogen atoms, but not with thermal electrons. The other two scavengers, bromine and sulfur hexafluoride, would undoubtedly react with all the thermalized electrons. It is obvious from the curve in fig. 19 that the accumulation of chlorine during the radiolysis of pure hydrogen chloride would cause a depletion in the radiolytic yield. The results obtained here can therefore be used in an empirical manner to correct those of Vandanne'®?), whose radiolyses were all carried out to a high percentage decomposition (>0.3%) relative to this work (0.018). If R is the dose rate in eV per unit volume per unit time, then the equation for the rate of formation of hydrogen: ---Page Break--- = 11a - eto 7 we eto F The central ueow ere ere we osto oruee areot —oreok aston ste we ste tst0 oveat Test orsse os ton en ve geo over eine ovnTe ose on ze anro sree Tan ortet.gatze ue etn ere orto ores erte | cree ate (ze) 508 eaep s,ouuepuen tro Fete tio F The sentes ueee ete ooTtn 600° ons uote ozree cre ote zooro ont ort soteg ze gotm zooro zert get sorne cre gotm zt0°0 este sere shton we atth seoro ste ene oaraz Apngs sty3 go eaeg dq Pe39eaa09 aueueddy Gr-0t) Gqs0T) (gq-08) ¢ OM . 4 tox _soffdotou safbd vor Sho BH Cayay press 279 30 2H esog ee steve ---Page Break--- = 116 = at any time t, and any given chlorine concentration, is a0) sca, a tty faxfay ecw © He + Hel where G(H■) is the ‘true’ initial total hydrogen yield and A the proportion of hydrogen formed by H* (6.75/8.3 = 0.815). Assuming that the value of Kenes nery/Kenre 29) (2.8 x 107%) and of A for the a-particle radiolysis and y-radiolysis are the same, the above equation can be integrated (appendix IT) to give the relationship 2 fer.) (ea) CH■ = ~*~ 0.208 (wer) rogyy } aeue.7 2 p | d.165 Head where D is the do: Vandanne's reauite were

corrected using the above equation. Table 23 shows these corrections and displays the close agreement in hydrogen yields between the α-particle and γ-radiolysis of pure hydrogen chloride. The results with Br and Sf reveal that 56g + Gy + Gye = 8.3, 3.8, 1.85, 2.65, and therefore the mechanism for the radiolytic decomposition of hydrogen chloride must include reactions which provide that (1) about 46.4% of the total yield of hydrogen molecules ---Page Break --- have thermal electrons as their precursors (2) about 22.3% are formed from "thermal" hydrogen atoms (not originating from electrons) and (3) the remaining 31.7% originate from the thermal hydrogen atoms. 4.9 THE EFFECT OF BROMINE ON A MIXTURE OF HYDROGEN CHLORIDE AND HYDROGEN BROMIDE, with the value of 8 x 10^7 obtained in the liquid phase (8 keV/mole) is greater than F (0.9 keV/mole). The gas phase ratio would be expected to be larger if the same species were involved. It is therefore apparent that bromine is not scavenging the same species in the liquid and gas phase radiolysis. The rate constant ratio for k at 25°C is known (HeBr, 264), from conventional studies to be 0.12 ± 0.01; this value has been made use of, by comparing it with that obtained in the radiolysis of a mixture of hydrogen ---Page Break --- chloride and hydrogen bromide containing varying percentages of bromine. A value of 6.1 x 10^7 has been obtained for k (Yuse/Fucalue), using the method outlined in section 3.9. This adds to the evidence already accumulated in establishing that the species is not a thermal hydrogen atom. 4.u THE EFFECT OF OTHER PARAMETERS The effect of scavengers on the radiolysis of hydrogen chloride has been studied under a variety of different conditions. The "plateau yield" obtained with over one percent of added bromine was independent of hydrogen chloride pressure, radiation cell volume, dose, and dose rate. It was also unaffected by coating the irradiation cells with colloidal graphite. These studies were useful in establishing that

the plateau was not due to contributions from heterogeneous processes. The rate at which reactive intermediates diffuse to the walls should be inversely proportional to the pressure of hydrogen chloride (P) and the square of the radius of the irradiation cell (r). However, the rate of homogeneous combination of the same species should be proportional to the dose rate (I). The value of IPr (which should be a measure of the heterogeneous process) varied in these experiments from 1.3 x 10^27 to 1.7 x 10^27, during which the plateau remained the same within experimental error. The hydrogen produced in the bromine concentration range corresponding to the plateau may therefore be attributed to a homogeneous process involving the species R* for which the bromine does not compete effectively.

4.9. APPLIED ELECTRIC FIELD RESULTS

This study was carried out in the hope of obtaining information on the fate of the ions produced during radiolysis. Since ions would be collected on application of an applied electric field, the use of this technique should interfere with the ion-recombination reactions. In the absence of an electric field, it would be expected that the HCl* ion would either undergo ion recombination with the electron or some other negative ion, thus leading to H+ + Cl- or else react with the neutral hydrogen chloride molecule as follows: H* + HCl → H_2 + Cl (20). Assuming an ion recombination coefficient of 10^7 cc/ion and the rate of ion formation to be 10^{22} ions/cc in these experiments, the steady state approximation would give a concentration of 10^{10} ions/cc and hence the calculated lifetime of the HCl* ion would be about 10 seconds. For the ion-molecule reaction (20), Schissler and Stevenson have found the specific rate constant to be 4 x 10^7 cc/molecule sec. At a hydrogen chloride concentration of about 10^{10} molecules/cc (in this study), the lifetime of the HCl* ion is about 10^{-7} seconds. Hence the ion-molecule reaction will undoubtedly be responsible for the removal of HCl" ions. The HCl* ion would be the principal positive ion collected at the cathode on application of an electric field. The scavenger studies have demonstrated the importance of electrons as a precursor to hydrogen formation in the radiolysis of hydrogen chloride. These electrons produced from the initial ionization process (2) should rapidly become thermalized and eventually disappear by any of the three following processes: ambipolar diffusion to the walls of the vessel, electron recombination (HCl* + e) and attachment to a neutral hydrogen chloride molecule to form a negative ion. The first-order decay constant for electron loss by ambipolar diffusion is given by D/A^2 where D is the ambipolar diffusion coefficient and A is a length characteristic of the vessel geometry. A typical value of D (0.09 cm^2/sec at 1 atm) and A (> cm) for the system used, lead to D/A^2 = 70/P mm per sec. This gives a diffusional loss time of at least 1 sec in this study. The electron recombination has already been discussed where the estimated lifetime of the electron for this process is about 10■ sec. The electrons will lose their energy initially in reactions (21) and (22) viz: e + HCl → H* + e and e + HCl → HCl* + e. (2) and finally to rotational and vibrational excitation of HCl molecules. They may also be captured in one of the following processes: e + HCl → H■ + Cl■ (a) H■ + HCl + He → electron-ion complex (b) Both reactions (21) and (23) have been observed in the low pressure mass spectrum of hydrogen chloride. The energy thresholds for the dissociative capture process (23) and the ion pair formation reaction (21) are 0.6 eV and 14.5 eV respectively. The ionization current of Cl■ coming from the low energy resonance capture process at its peak was at one order of magnitude greater than that for the ion pair formation reaction. The collection efficiencies for the Cl■ ion coming from the two reactions (21) and (23) should be the same, and therefore the cross section for the reaction (28) should be much greater than that for reaction (21). Now the absolute cross section for reaction (23) has been measured by Buchnel'Nikova to be 3.9 x 10^7 en? at the maximum. Using this and the data for energy loss per collision with hydrogen chloride as summarized by Healey and Read, it can be shown by the method of Magee and Burton that only a small fraction (58) of the subexcitation electrons which have energies in excess of 1.5 eV will be captured prior to thermalization. The excitation process (22) should occur at an energy of at least 4.5 eV. There is no information on the efficiency of this type of process. Davidow has obtained evidence that the electrons disappear in a termolecular reaction represented above as reaction (24). He estimates that the rate constant of this reaction is approximately 2.1 x 10^7 cn/molecule·sec, from which a mean lifetime for the electron would be of the order of 10^7 sec, at a concentration of hydrogen chloride molecules of about 10^10 molecules/cc. From the foregoing, it can be concluded that the ions HCl+ and Cl-, and maybe electrons would be collected at the electrodes on application of an electric field. At a field strength of 10 V/cm/torr, the effective electron energy in HCl may be estimated at 0.14 eV. This energy is much lower than the threshold energy of reaction (22), which requires an energy of at least 4.5 eV. This means that a reduction of hydrogen yield caused by neutralization of ions at the electrode should not be compensated for by the above process. The recent work of Kebarie on ammonia and water in the gas phase near atmospheric pressure has shown that both the MH4+ and H2O+ ions are heavily clustered. In view of this, it would be expected that the HCl+ and Cl- ions would also be heavily clustered. Consequently, in the absence of an electrical field, the occurrence of a non-dissociative

combination, viz: ---Page Break--- 1H at +0, "2h Caneay * S cmneay is not unreasonable. This proposed reaction, whereby no > (nome) (26) hydrogen is formed, is in agreement with previous evidence obtained from a study of the scavenging effect of chlorine on a mixture of hydrogen chloride and sulfur hexafluoride. (99) The application of an electrical field during the radiolysis shows no effect on the hydrogen yield in the non-recombination region. One explanation is that the ions do not react to produce hydrogen, thus justifying the proposed reaction (26). The other explanation is that the clustered HCl■ ion on being neutralized at the cathode forms hydrogen. Very little is known about reactions taking place at electrodes in aqueous systems and until more is known, the first explanation appears quite reasonable and is in agreement with the experimental result. 4.6 FREE RADICAL REACTIONS The free radicals produced in the ionic reaction and in the excitation process are mainly the H and Cl radicals. These radicals would be expected to react as follows: He + He → Hy + O (en) He + Cl → (2a) Net pon, om (2s) ---Page Break--- = 125 - Cl + S → (30) Reaction (27) has an activation energy of about 3 kcals/mole whereas the others (28), (25) and (30) would be expected to have zero activation energy; however, since the radicals H and Cl would be present in very low concentrations, the reactions (28) and (29) would be unable to compete with reaction (27). As the products hydrogen and chlorine build up during the radiolysis (e.g. at high doses) the back reactions: We + Cl → Hy + Cl → (2) can be expected to interfere with the hydrogen yield. Their activation energies are 3.0 kcals/mole and 5.48 kcals/mole, respectively. In the stoichiometric equation: Ce + He → neat + e at + xen, an estimated maximum value of x was 0.26. Since W for hydrogen chloride is 24.8 eV, a contribution of up to 21.04 G units of H and Cl atoms can be expected from the ionization processes. The yields of H and I from reaction (7) may

vary between 0 and 1.04, depending on the value of x. With respect to the unscavengeable hydrogen = 126 - yield, this must be coming from processes such as e+ncr → ne + est scree (ss) ws norms, + ca oy) It can be postulated that some of the hot hydrogen atoms may be thermalizing before reaction. Very little is known about this type of phenomenon. 4.7 PROPOSED MECHANISM FOR THE RADIOLYTIC DECOMPOSITION OF HYDROGEN CHLORIDE. Ionization CexyHer > Her + e+ xe + xen am Hen + Her → uzcr* + cr @ Hyer? + ntter > H,01* aneyy a © + Hcl + Hel—pelectron-He1 complex Be ca oy - . (Her) G27 + ated → e2"Yauery os) N2C2* canery + C2" (qyeyy—> (n4m47 HCL (6) Excitation e+ cr → suea* + eon scree am * coliisionar 8 Geactivation (7a) Radical H+ Her 5H, + cr «@ * w+ Heron, +o (ea) ---Page Break--- -a27 cls creme ee o 6 G, = 100/24.8 = 4.0 is in Seer? * Sijea* fair agreement with 3.8 obtained from the scavenger studies. Assuming an x value of 0.26, reactions (1) and (4) can account for up to a 6, = 4.0 + 1.00 5.0K, the remainder to make G,, (5.65) may be coming from reaction (7a). The scavengers must be competing with reactions (4) and (8). At high doses the back reactions (10) and (21) become important Heel, > Hers cr ae) Weel + Here ay ---Page Break--- = 128 = SECTION v DISCUSSION OF HYDROGEN BROMIDE RESULTS 5.1 RADIOLYSIS OF PURE GASEOUS HYDROGEN BROMIDE When pure gaseous hydrogen bromide is irradiated with co® g, S, an don pair yield of 4.7 + 0.1 (Table ©) for the decomposition is obtained, this is in very good agreement with the work of Hamill et al. (S28) on the radiolysis of this gas using X-rays. It appears from the above result that X- and y-rays produce the same effect on HBr gas. This is to be expected since both of these rays are penetrating electromagnetic radiation only differing in their energies. Before a mechanism for the decomposition of the gas is attempted, all the pertinent data will be reviewed. The mass spectral data on HBr using electrons of 150 eV impact energy show the occurrence of the ions.

HBr*, uBr*t, Brt, and Br?* in the relative abundances of 100:7:46:10 S (91) charge transfer processes (shown below) similar to those postulated for HCl would be expected Br? + HBr ———+ Her? + Br ans-0,11 ey @ (E.R, of Breti.s ev'5?) ana 1.p, of HBreii.69 ev) Ys upr ene' + ates ev (2) Hert? 4 ur —enert + Hts Be (3) ---Page Break--- = 120 - art? 4 npr par' ses Br anesteev (uy (2nd T.P, of Bre19.2 ev'52)) These equations would lead to an overall stoichiometric equation (en) HBr nbet 6 ee nt exer os) where x can be calculated from the distribution of ions given above to be 0.0 5.2 THE SCAVENGING EFFECT OF BROMINE AND SULPHUR HEXAFLUORIDE ON THE RADIOLYSIS OF GASEOUS HYDROGEN BROMIDE In the radiolysis of gaseous hydrogen bromide, the scavengers bromine and sulphur hexafluoride reduce the hydrogen yield to about the same extent (Fig. 25) and also at low scavenger concentrations their effects are almost identical. On comparing the effects of the scavengers on the HBr radiolysis with that on the HCl radiolysis (Tables 22 and 24), it can be seen that the scavengers are much less effective in the case of HBr than in HCl, in both reducing the hydrogen yield and in competing for the reactive species H. A kinetic analysis similar to that used for the HCl scavenging results, assuming that the scavenger and HBr compete for the reactive species, ---Page Break--- = 130 - gives the results shown in Table 24. From the last two columns of this table it can be observed that the rate constant ratios kyesup,/k 20 ee snoe!Mirase, aE Rot in agreement with the ratios obtained from conventional Haar studies with 'thermal' hydrogen atoms. The scavengers must therefore be scavenging electrons since both bromine and sulphur hexafluoride are good electron scavengers having maximum capture cross sections at zero energy. Table 24 Scavenger out Kuen! Ks radiolysis # atom Bromine 2.6 7.0 5.9x10^7 0.12 Sulphur Hexafluoride 2.7 6.9 6x10^20 pa and t* represent the scavengeable and unscavengeable species, respectively, The scavenging results give a

Gy, value of 2.7 which should be equal to G,. However, from the W value for Br, a G,9.*G,=4.1 should have been obtained. This means that not all of the electrons are being scavenged as in the case of He. ---Page Break--- - as - During thermalization, the electrons may interact with the HBr molecule as follows e+ Br → on? + ar te (6) e+ H → snbr* + e en are om e+ mar oH + are ro) Finally, as in HCl, the three-body process e + 2ir → Electron-HBr complex « ue °F ane) may occur. The energies required for reactions (6) and (7) are 19.8 eV and at least 3.75 eV, respectively. Reaction (6) has a threshold energy of 0.1 eV with a maximum capture cross-section occurring at 0.21 eV, and reaction (9) should take place with thermalized electrons. The cross-section for electron capture by an HBr molecule in reaction (8) is 15 times larger than that for the corresponding reaction with HCl and also, capture occurs at a much lower energy. It must therefore play a much greater part in the HBr radiolysis than in the HeL radiolysis. Reaction (6) gives one which would be measured in the Y value, but not be scavengeable by sf.. hence it may contribute to the difference between G, from the scavenger data and G calculated from the W value for HBr. ---Page Break--- = 132 - The rate constant ratio Kysupe/Fyeae, #8 2068) and therefore at 6 mole & bromine concentration only one third of all the thermal hydrogen atoms formed in the system would be scavenged by bromine, in addition to the competition for electrons; therefore, depending on the yield of thermal # atoms, a difference would be expected in the scavenging effects of the two scavengers. Clearly, from an inspection of fig. 25, this is not the case. Hence the ‘thermal’ hydrogen atom yield cannot be large and most of the hot hydrogen atoms must be reacting before becoming thermalized. The H atoms resulting from the stoichiometric equation (7) of the previous section can contribute up to 1.6 6 units to the Gy yield. 5.9 APPLIED ELECTRICAL FIELD EFFECT The effect of an applied

Electric field on the radiolysis of gaseous hydrogen bromide is illustrated in Fig. 29. Here it can be seen that there is no change in the ion pair yield in the ion recombination region; however, as the field strength increases and before secondary ionization sets in, the ion pair yield increases. It has already been pointed out that the electrons on slowing down can undergo the following reactions. ---Page Break--- - 333 = e+ tron’ + e on saree om e+ Her on + are «sy The stoichiometry of reaction (#) is the same as reaction (9), i.e., one molecule per electron. Reaction (7) can explain the observed effect since a constant applied electric field would be expected to increase the average energy of the electrons in the gas. A fraction of them may attain the threshold energy of reaction (7). 5.4 PROPOSED MECHANISM The following mechanism has been put forward by Hamill et al. for the radiolytic decomposition of HBr using X-rays. HBr —> Br* + e (Qo) ef Br on 6 pee (a) wart + be” en + opr an out ea, + Be a2) Br + H oar, + m as) This scheme gives an ion pair yield of 4.0. These authors have attributed the yield in excess of 4.0 to a cooperative excitational process which may be depicted as e+ Wor Sense’ + e ent sore as) Since their investigation the rate constant for the formation of the molecule reaction ---Page Break--- ~ is HBr + HBr’ —> Br’ + e as) has been measured by Schissler and Stevenson to be 4.7 x 10^7 cm^3/molecule sec. On carrying out similar calculations to those for the HCl case, it is seen that reaction (15) is a preferred reaction to reaction (11). Since the applied electric field results show that there is no change in the ion pair yield for either the production of hydrogen or the destruction of HBr molecules in the ion recombination region, reaction (16) below must be proposed as the ion recombination reaction. nybe? + Br Hor ae For similar reasons to the HCl case, instead of reaction (16), reaction (27) would be expected. 2 Canpey * PF (anaes ——™ (otnt2dBE an With the above modifications to Hamill's mechanism, the

proposed mechanism for the radiolytic decomposition of gaseous hydrogen bromide should then be as follows. Tonic reactions HBr + e- → H + Br- + electron-iBr complex → HBr + e- → H + Br- + electron. The scavengers would be competing with reactions (b) and (c) for electrons. Reaction (h) followed by (j) is responsible for the unscavenged hydrogen yield. The energy to form an ion pair in HBr is 24.4 eV. The T.P. of HBr is only 11.67 eV and therefore 12.7 eV is available for excitation, hence there is no reason why the ratio of excitational processes to ionization processes cannot be 3:2, thus accounting for the high unscavengeable yield of hydrogen.

APPENDIX T: Consider the two competitions below. Let Gy be the yield of He then in the presence of the scavenger Cl, Cg = (aeons); A, B, Haein, ely) + The reduction in Gy, represented as ΔGy, is given by (kG GD) - (0-2 a 7) > 1 GP GeDen, GF Ie, te (x (ea) - ae) iWin er, (er) . (Kyrea / Rea : actH) =

APPENDIX II: At any given chlorine concentration the rate of hydrogen formation will be given by the equation a aH) Kyey eap(C22) at ke xjis ee cie 2) ee Wee Hen where G(H) is the "true" initial total hydrogen yield, A represents the proportion of hydrogen formed by the scavenged species "(A = 0.015; B= 1-a) and R is the dose rate in eV per unit volume per unit time. Putting ne 2000 x 7H 3.8 (Her wee wea POD rea) (1g) + (Hig) = x ang assuming that (HCl) is constant, the equation becomes a ax + ex + Bexeuy f sare va}

-13e - of piste BUH) e often [ee 5 7 4 + Bex) + R- n(l + Bex)| #1! Ho) t comme = 2 (Yan as tee ecm) = 2 | ip) _ 0.208 cer) 2084 {1 + 48.7 (ery o-b08 ey. where D is dose.

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