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Radiolysis of Gaseous

Hydrogen Halides

Rupert A. Lee

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. RADIOLYSIS OF Gaszous

HYDROGEN HALIDES

dy

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A thesis submitted for the degree of

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Puerto Rico Nuclear Center,
Mayaguez, Puerto Rico.

June, 1967,

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ABSTRACT

Ton pair yields of 4,1 and 4.7 have been measured

for the radiolysis of pure ¢

jous hydrogen chiorige and

hydrogen bromide respectively, using Co®° ¢: 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 ¢

The effect of the scavengers bromine and sulphur

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
Ay oF may not have the electron as its precursor, the

other is @ ?hot! hydrogen atom which cannot be scavenged.

The results with chlorine ai

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 ga

jous hydrogen chloride.
A etudy of the effect of an applied electric field

showed that

during the radiolysis of the two ga
reactions involving the recombination of ions were un-

important as a means of producing hydrogen.

---Page Break---

This study has shown that a4:

jecfative exeitational

proc

sare as important as fonfzation processes in

the decomposition of these two hydrogen halides, The

Br molecur:

appear to undergo dissociative exeitational

S more readily than the He) molecul

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ary of the pre:

of hydrogen halide:

Aim and scope of the present investigation

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Apparatus

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sample

2.2.2 Analysis Line

82

a2

4s

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24

2s

cents

Materials and purity

2.241 Hydrogen chloride

2.2.2 Hydrogen bromide

2.2.3 Chlorine

2.2.4 Bromine

2.2.5 Sulphur hexafluoride

2.2.6 Ethylene

2.2.7 Argon

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pt and sample preparation

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3.2

Dovinetry

Radiolyses of pure hydrogen chloride and hydrogen bromide

The effect of chlorine on the radiolysis of hydrogen chloride

Radiolyeis of hydrogen chloride with bromine as scavenger

Radiolysis of hydrogen chloride with sulphur

45

so

50

si

sa

st

82

52

82

52

82

53

su

ss

87

69

79

83

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---Page Break---

Free radical reactions

---Page Break---

sectrow 1

Inrropueriox

2a. GENERAL

Tt will be worthwhile to review briefly the

historical development of radiation chenistry

it

reflects both the shifting interest and interpretations which have marked the steady grovth of this subject, With the discovery of X-rays and radioactivity towards the end of the 19th century, chenists became avare of the chemical changes brought about by various types of Fagiations, At the turn of the century Sir Willfan

Ramsey 2)

a working in this field on the decomposition of simple gases in the presence of radon, wrote that,

mwhenever radiun

mation produces chemical action, then, other conditions beinr unaltered, each particle of emanation as it disintegrates produces the same amount of change." This statenent nade radiation chentete Fealize that there was sone quantitative relation between energy absorption and chemical change.

At first most of the research in the field of radiation chenistry was carried out on gases as evidenced by the pioneer work of tind(?) ana mund(?), their study of gaseous reactions involved the use of radon (i.e.a-

---Page Break---

particles) and it was therefore natural for then to relate the observed chemical changes to the anount of tonization produced in the syste

Thus the term ion pair yield

(CUM, ise, the nunber of molecules destroyed or formed per fon pair produced) developed to illustrate the connection between the physical and the chemical actions of radiation. finee this ratio was only neasurable in the case of gases, the term G-value, defined as the number of nolecul changed per 100 electron volte of energy absorbed by the systen, was introduced ao 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. ¥

¥

where W is the mean energy required to form an {on pair

in the irradiated gas, Values of W for gai

found to be approximately twice their ionization potential.

This 1ed

x") to point out that part of the chemical

action of high energy radiation may be due not only to

fons but also to the reactions of electronicly excited

species,

The classic paper of Fyring, Hirschfelder and

(5)

taylor(S), in which they discussed ortho-pars hydrogen

---Page Break---

conversion and hydrogen-bronine combination, demonstrated

Firstly, the importance of molecular ions having the valency properties of free radicals and secondly, the importance of neutral free radicals and atons as chain carriers. It further stated that it was unnecessary to put forward the existence of fon-molecule clusters to explain large ion pair yields. This led to the almost complete rejection of fonfe processes in radiation chemistry until the recently proven occurrence of fon polecule reactions in the mass spectroneter®),

Within the last two deca

due to the develop-
Rent 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 conpounds. 7)

At present, studies in this field are carried out both for their intrinsic interest end their possible

industrial use

---Page Break---

1.2. INTERACTION OF TONIZING PADIATION VITH MATTER

?The chemical effects produced by high enersy radiations in an attenuating medium result fron the inter-

actions of fast charged particles. Th

particles may constitute the incident radiation auch as a+ or forays, on be produced hy the prinary interaction of unchanged species such as yerays, X-rays or neutrons, It ie imperative that the radiation chenist should have sone knowledge of the physical processes involved in the above interactions, Cniy a brief description of the prinary energy loss processes of electronagnetic radiation, and electrons will be considered.

1.2.2 Electromagnetic radiations

The effect of an absorbingmedium on a bean

of electromagnetic radiation is to reduce the number of photons passing thrush. This reduction in beam intensity

(-dt) fs etven by the relationship

nate ty wax

where I, is the intensity of the incident radiation, dr

is the reduction in intensity of the bean after passing

through a distance éx of the nedium and w is called the

total linear absorption coefficient. This coefficient is

the sun of a nunber of partial coeffic

nts representing

---Page Break---

woe

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 ve) and in high atonie nusber (2) materials and even so is negligible in comparison with the photoelectric effect

at these low energies. Photonuct

v reactions take place with photon energies above 10 MeV and therefore will be of no consequence in this study.

(a) Photoetectric effect

Th this type of interaction, which occurs

mainly with low energy photons, the entire energy of the

Photon (5) is transferred to a single atonic electron. This electron te ajected fron the aton with an energy (FQ) equal to the difference between the photon energy and the

binding energy (£,) 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 towarce the forward direc

conserve energy and nomentun, the remainder of the ator

is recoiled, This means that photoelectric interaction

---Page Break---

is not possible with free electrons, At sufficiently high

energies, X-shell interactions account for 80% of these

events, the rest being L-shell interactions. The

vacancy created in the K-shell, or Leshell, is filled by

an electron from an outer shell with the emission of

characteriatic X-radiation or Auger electrons, For low

ZB 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 inter-

action, The atomic absorption for this effect, varie

approximately as 4°c" and is therefore important only at

low photon energi

and materials with high 2.

(>) compton effect

If the X- or y-ray energy is sufficiently Large,

rather than interacting with the atom as a whole, the x=

or y-ray may interact vith any of the orbital electrons as

though they were essentially free electrons, only a

fraction of the photon energy will be transferred to the

stectron and a modified photon of longer wave length

emerges fron the collision in a direction differing by an

angle @ from the original photon. These Compton electrons

Produced from a radiation of given quantun energy, have

---Page Break---

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

a

c= nv (?_

+e

where hv and 1 refer to the incident photon and 6h is the change in wave length after collision. on applying

the law of conservation of energy and monentum, it can

be shown that

where hand mac have their usual significance, For a

medium containing exclusively light elenents, Compton

absorption predomina

for photon energies between 0.2

and 2 MeV and the total energy absorbed per gran of the

medium is nearly proportional to its electron density.

(©) Pair production

Tor electromagnetic radiations of energies

greater than 2m,c7 (1,02 MeV), a fraction of the energy ie

absorbed in the production of an electron-positron pair.

The available kinetic energy (hv-2m,c7) is shared unequally

by the two particles formed, Both of theee particle:

are slowed down by interactions with the medium.

Eventually the positron and an electron will combine

---Page Break---

annihilating themselves, and producing two photons of

0.51 MeV energy each, in opposite directions, The atomic

absorption coefficient for this process is approximately

2

proportional to 2° and increases with increasing photon

energy.

The relative inportance of these three processes

Ae shown in fig. 1 for the media water, aluninun and

ow)

aead'®), re can be seen that for co®° gannas of

energy 1.25 MeV, Compton scattering is the predominant process.

1.2.2 Fast electrons

In the three proce:

described above, it is

seen that electromagnetic radiation on interaction with

matter produces high energy electrons, These fast electrons

au

Apate their energy by the following proce:

emission of radiation (Brensstrahlung), inelastic and

eu (20),

tic scattering, and polarization| The relative

importance of th

prec! @epends on the electron

energy and to a lesser extent on the composition of the

pediu

The rate at which electrons lose energy in a

Particular medium is referred to as the stopping power

ae

or Linear energy transfer (LET) and {8 denoted by - Ze.

For non-relativistic velocities the simple equation

---Page Break---

Fre. 2

---Page Break---

%

%

corrriciant

a

on

«we

MEReY (nev)

MASS ABSORPTION COEFFICIENTS FOR (a) WATER

(8) ALUMINUM (6) LEAD AS FUNCTIONS OF THE QUANTUM

ENERGY OF THE INCIDENT RADIATION

FIG. 1

---Page Break---

-10-

2

ae, 2ve'N 2 an MoV

a a a

can be developed where ¢, m, and Z have their usual

significance, is the number of atom:

per cubic centinetre,

V is the electron velocity and I the mean excitation

potential of the medium. pethe(10) nas modified the above

equation for the case of electrons at relativietic

velocities te the following

ae Lane [ ]

-£ + 2[@-2 int

x Re

where @ is a complex function of ¢(¥/e) and the

electron energy.

According to Bragg's law of additivity of stopping

powers,?11) the stopping power of an elenent is independent

of its state of chemical combination, Thus the stopping

Power of a hydrogen halide ic 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 te LET from the emission of

etrablung or polarization effect:

For an electron of energy E MeV, the ratio of

the energy loss by radiation to the loss by collision is

---Page Break---

eae

given by

(aE /ex)

rad 7 Ez,

wares, reer

col .

Therefore, for electron energies below 1 MeV and low

atomic number materials (<16), the contribution of

Brensstrahlung is less than 28,

1.2.3 Secondary electrons

charged particles, on travelling through a nediun, leave fons and excited molecules along their tracks, Many of the electrons ejected by the incident fast particle will poss. enough energy to cause additional fonizations and excitations, Since th electrons (referred to as secondary electrons) will have relatively low velocities, their rate of energy loss will be extrenely high(!?), ror secondary electrons of energies less than 100 eV, the formation of a few fon pairs will be sufficient to reduce the electron to Sub-excitation energies (5 eV), The nean energy involved in the fornation of an fon pair ie about 30 + 10 This means that a secondary electron of 100 eV energy on being Boderated will produce clusters of about 3 to 4 ion pairs along

with several excited molecules. For low LET primary particles,

---Page Break---

the clusters will appear as widely separated beads

along the particle track, whereas for densely fonizing

radiation (e.g. a-particie), th

fe clusters will be Produced so close together that they will form a columnar envelope of son-paire.

When the kinetic energy of the secondary electrons

is in excess of 100 eV, they can produce their ovn
tracks which diverge fron the direction of the primary
track. These secondary electrons are referred to as

deita-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 mediun by the various physical mechanisns
described briefly in section 1.2, The chenfeal
aspects of the various processes innediately following
the primary radiation act (i.e. dissipation of energy)
must now be considered. This stage, often referred to
je the physico-chemical stage, can be classified into

(2) primary process:

and (2) secondary prec

1.9.2 Primary processes

(a) Tonization

When a fast electron or any charged particle

P

es close to a molecule of the absorbing medium, a

coulombic field is set up. This field wii strongly

polarize the molecular electrons in their orbitale. 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 « positive ion;

XY mer ne @

ine

ignates a primary radiation

chemical process), The observed induced conductivity

---Page Break---

oe

of gases provid:

evidence for the presence of such

ionizations,

The positive ion x¥* produced above may or

may not carry an excess of energy; moreover {f XY is «

Jarge polyatomic molecule, then the x¥* would be unstable

and dissociates

xt ext ny @

This type of fragmentation process has been observed in

the nase spectrometer !), re occurs with a high

probability e.g. the hexane ion dissociates (below)

BCsHy2? ??> Cglty? + Colts

on So oatlg? + Cag

to rive smaller fons ané radicals, or even radical ions and Reutral molecules. Alternatively, the interaction of a fast electron with a molecule nay teed to a éiseociative fonization process in which reactions (1) end (2) cceur simettaneously

KY 3x Fv se + rnerey @

The minimum amount of energy for process (1) is known ex the fonization votential of the molecule and

thi

ean be accurately measured by electron impact

---Page Break---

-as-

an,

methods Since the energy required to form an ion

pair is usually about twice the jonization potential(?5), this excess energy may be used up in forming excited

specie:

(>) Excitation

If the energy transferred to @ 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

ap ?» as® os)

eaten excited species]

absorption of a quantum of Light

AB + hye an?

and therefore much information on the behaviour of ABY

can be obtained from photochemical studi

1.3.2 Secondary processes

(a) Reactions of ions

Positive so

and their daughter ions are

continuously produced in a system under irradiation,

Along with these, there is an equivalent number of

---Page Break---

negative charges (1.e, free electrons or negative ions)

and therefore two possible neutralization processes

must be considered

(G) fon-etectron reconbination and

(UL) positive ion-negative fon recombination,

Besides these, the ions may interact chemically with

neutral molecules on else undergo charge transfer with

impurities.

(2) Positive fon-electron recombination

If an electron, ejected from « primary

fonization, becones "thernalized" in the vicinity of a

positive ion, recombination occurs owing to the strong

coulombic interaction and an exeited molecule is produced;

xy +e > xt

The excited molecule here has gained energy equal to

the fonization potential of the molecule XY (10 to 15 eV).

Consequently the molecule will undergo dissociation and will

lead to a per

calculated that an electron of kinetic energy below

nent change. Samuel and nagee(2®) nave

5 eV becomes thermalized and reconbines with its parent

fon in less than 10°** sec, in the case of water

(adsorbing medium), Conflicting with the above view is

---Page Break---

the Lea(l7), cray(1®) and rietzman(t?)

theory which says

that the electron will escape fron the coulombic field

and will attach itself to 2 neutral water molecule becoming an aquated electron. In the case of gases, either an fon or electron nay becone separated and react individually with the neutral molecule XY.

(id) Positive fon-negative fon recombination

If Sons of opposite charge are to recombine,

their total internal energy suet decreas

sa result

of the reaction. The energy rei

fe may de achieved

through an increai

in the kinetic energy of the neutra

Lized particles by transfer of energy to a third body,

by enission of electromagnetic radiation, or by electronic

excitation of the neutralized species. tence recombination

nay proceed by any one of the Following mechaniene(20)

xterra zs ere a

xt re @

+r et @

?The three body recombination (1) is the most important

nechaniam at pressures greater than a few mm. He.

Radiative recombination (2) and mutual neutralization

---Page Break---

- ae.

through charge exchange (3) will predominate at very low

pressures(72), since onty two bodies are invelved,

If one of both of the fons are moleculay, then

there is the possibility of dissociative mutual neutrali-

zation thus

xy sexe yes ow

(4st) Ton-nolecule reactions

Mass spectroscopic studies have provided

evidence beyond doubt for the cecurrence of ion-molecule

reaction:

The theory of this type of reaction has been

Well developed by Schissier and Stevenson(?2) so much so that for the (D)* + Dp) reaction, kegs i8 8.7 x 202 + per mole per sec. compared with k,(3.6 x 102 1, per mole per sec.). There is also excellent agreenent for the (ar" +H) reaction, the theory further predicts that Fates of 11 Son-nolecule reactions are so large that there 4s @ high probability of reaction upon every encounter, These reactions are temperature independent and are mostly exothernic.

Ton-nolecule reactions are of two kinds

(A) fydrogen tranafer reactions

Rut + yet ee

---Page Break---

where R is @ free radical and Ma stable solecule and

() 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 proce

If an impurity or a substance in very anall

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 te occur at ordinary temperatures the lowest

fon{zation potential of A must be higher than that of Bs

This type of reaction was invoked to explain the

incre:

ed ionic yield when acetylene was irradiated in

the presence of Argon.

Ae? (1515.7 av) ¢ cpt ?eare CoH," (811.9 ev)

(b) Electron capture by neutral species

ML the electrons ejected in the primary jon-

---Page Break---

ization of a molecule of the absorbing mediun lose their

Kinetic energy either by further fonizing or by exciting

other molecules. These electrons then lose their

freedom by tvo processes (1) combination with « positive

ton (already discussed) and (2) electron capture by a

neutral species.

There are at least Five mechanions by which

electrons may react

(2) Radiative capture by @ neutral aton

eth rey

(44) capture by an aton with a third body taking up the

excess energy

eth eB e eaeE,

(444) Capture by @ molecule with the vibrational

excitation of the molecule ion, and its subsequent

stabilization in a collision with another molecul.

ey xr)*

os et en rr

(Civ) Dissociative attachment

etre ory eee

(¥) Ion pair production: the non captive dissoctation

---Page Break---

sae

of a molecule into positive and negative ions by electron

impact

eres er eye

A simple calculation can show that mechanism

(4) cannot compete with (41), (411) and (iv) at ordinary

peratures and pressures, For electrons of energies

above 20 eV, mechaniem (v) will become important and at

low pressures ({1) and (iff) become unimportant compared

with (iv), A more complete discussion of th

(2a)

proce!

is given by Massey

Figa. (2) and (3) taken from the work of Frost

and wepowel'?") afsplay the possibility of dissociative attachment occurring with chlorine and bromine, The main

aifference 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 bronine will be a much more efficient scavenger for

thermal electrons than chlorine.

(©) Reactions of excited species

Excited species formed by the prinary radiation

process nay undergo the following reactions,

---Page Break---

Enerey

POTENTIAL

NUCLEAR SEPARATION

FIG. 2

---Page Break---

ENERGY

POTENTIAL,

23

---Page Break---

=e

(2) dissociation into free radicale

wr ee

The fr

radicals X and ¥ formed from the dissociation of highly excited molecules may carry an excess of

Kinetic energy and are referred to as "hot" radicale.

Th

radicals are highly reactive,

(44) Dissociation into "molecular products

xy* eae

where A and B are saturated or unsaturated molecules.

This is possible for excited states formed from positive

fon electron recombination.

(444) Reaction with other nolecute

xy" + co» products

Little is known about this type of reaction except for

@ suggestion by Burton et ai??®?

to explain condensation

reactions involving hydrocarbons.

(2v) transfer of excitation

The reaction may be written

x sy mere

Here molecule Y must possess at least one excited state

---Page Break---

= 25

below the energy level of x", In certain gas phase

padfolyses where the increased ionic yield could not be

explained by @ charge transfer process, excitation

transfer has been suggested. Surton(?6)

pointed out

that if the electron ie attracted back to its parent fon

in lese than 1072* gec,, then primary fons will have an

extremely short 1ifetine and hence the observed energy transfer process should be mainly due to transfer of

excitation rather than charge.

---Page Break---

° -

2.4 posrmerey

The radiation chenist requires to know the

effectiveness of a particular chemical action of

fonizing radiation, This is usually m

ured by (a)

the fon pair yield (W/N) in the case of gases and (b) the

100 eV yield (6) for condensed phases. Both of these

terms have air

ay Deen defined, where it was pointed

out that they are related by the equation

It ie not very difeicult to obtain ion pair yields in gaseous systems; however for a determination of G, an accurate value for ¥ is required.

By an application of the Bragg-Gray cavity

donization chamber theory(?7) the quan:

y of ionization observed in a small cavity can be related to the energy absorbed by the cavity walls during exposure to ionizing

vadiation. It is expressed sinply 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---

J, 48 the nunber of dons produced per unit mass of gas

in the cavity,

Since the energy absorbed by the wall is ind

Pendent of the characteristics of the gas, then by

Lling the chamber with various ga

successively, the

equation

2

can be obtained, where the subseripts (1) and (2) apply

to two different gases.

It follows that

,

tees)

for an unknown can be calculated from measurenents of the

saturation ion currents and the stopping pover ratio

(s3,), calculated from the Bethe equation(20), The Bragg-Gray theory of cavity ?onization ie depicted in fig. & (a) where it can be seen that the radiation chenical reaction {s carried out only by electrons emanating fron the walls due to Compton interaction of the Y-rays. A more general picture appears

in figs 4 (b), Spencer and Attix(?®) vere able to rodify

---Page Break---

~ 28

7 RAY GAS FILLED cavity

(2)

SOUD MEDIUM

a

bes

BRAGG-GRAY THEORY OF CAVITY IONIZATION

RAY

SOLID MEDIUM

GENERAL CASE OF CAVITY = IONIZATION PROBLEM

FIG. 4

---Page Break---

the Brarg-Gray picture to take into account the processes

(8) and (c), In thefr calculation "Fest" secondaries of

the type (B) are added to the prinary electron spectrum

and their effect subtracted fron the stopping power of

the medium, whereas the "rast" secondaries of the type

(?) are not added to the electron spectrum but their

effect is subtracted from the stopping power of the gas.

The ratio of the enersy dissipated per unit

nase ina small gas filled cavity to that in the sur-

rounding wall (due te Spencer end Attin modifications)

is given by the equation??9)

CaP), x

f, 1a) 2 [tte ad an eg OTD

° GM, . w/e

Re

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 vail and depends only

on wall nater{ai and the initial electron enercy Ty.

C,(Tged) is a function of the average wall separation and

the pressure of the cavity ras. The pressure dependence

Fesuits fron its dependence on 4, which is the energy of

an electron of range in the cavity gas equal to the

average wall separation. This expr

sion predicts

---Page Break---

= 30

departure fron the constancy of the ratio of saturation

ionization currents to pressure at low pressures, and for

materials with z,

@iffering fron 2, For 2,

wait <

2 > 2 eae Ht

wal gas?

gas the departure decreases and for Z,

wal

increai

---Page Break---

sae

245A SUMMARY OF THE PRESENT STATE OF THE RADIOLYSIS

OF HYDROGEN HALIDES

The three hydrogen halia

hydrogen chloride,

hydrogen bromide and hydrogen fodide have ali been

irradiated in the gas phase by various workers, The ionic

yields obtained increase in order of iner

ing 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 mechanion gives an ion pair yield of 4,

However, if ine?

4 of reaction (3) the fen 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 fron 4.6 to 5.221) vere

obtained, Hamiz1

put forward a sinilar

chanien

to re

jetions (1) to (5) above and suggested that the yield above 4 may be due to contributions fron the

exeitational proc:

jes 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 wa: obtained for a-radiolysis. Mo attempt was made in this Paper to put forward a mechanism.

In the oi

'¢ of radiolysis of hydrogen halides in

---Page Break---

the condensed phases, Arastrong and his group?) have

studied the effects of scavengers on product yields. they

have prope

4 the following possibilities in accordance

with the Samuel-Magee mode1(16)

@ Hel was Hert +e

Heat + @ ?eHca* ?~ anor) + en

()) Hen Ae eat be

Hea + Her? ??+ ker? + ca

Hcl? + © ???w(not) + Her

??~ Winot) ee cr

Both of these mechanisms are 1ikely to produce Mhot?

hydrogen atone.

The effects of the scavenging of chlorine and

bromine on both hydrogen chloride and hydrogen bromide

Suggest the following electron capture process

CF HK ete Se ne eH

along with

Hak? + xen x7 + ax

These papers show cl

rly the presence of tuo

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

---Page Break---

= one

the following competitions occur

Hea + en

Hey ee x

ROhot) + Her en, + en

H(hot) +X, enn ex

The C values for liquid hydrogen chloride and

hydrogen bromide were found to be 6.5 and 12.4,

respectively.

: rasLe

Results (Ref. 93) of liquid phase radiolysis of

hydrogen chloride

chiorine Bromine

o *nea!! vn,

nea/Fen, ce *nea/*se,

Piret species 2,3 1.7 x 107 24

Second species 4.2 e.10 wea -

---Page Break---

-as-

266° ATM AND SCOPE OF THE PRESENT rnvESTzcATION

In the previous section it can be

yn that the

Rechanisn for the radiclytic decomposition of hydrogen halides in the condensed phase differs considerably from that proposed for the gas ph

radiolysis.

Fron his study, Armstrong has obtained evidence for the presence of two hydrogen forming species. In the condensed phase radiolysis he has placed enphasis on the cccurrence of excited specie:

@ precursor to "hot" hydrogen atons,

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 ySelds and hence G values quoted in previous

publications may have been too low.

Since the appearance of the first communication

fon this investigation(®*), it has bi

n pointed out by

Dr. Nenry 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

@ regenerative type fuel cell. The hydrogen halide would

---Page Break---

be decomposed by ionizing radiation and the products

hydrogen and halogen recombined in a clo!

a aysten type

fuel cell, The efficiency of the fuel cell could be over 908(95), the theoretical E.M.P. produced with

a hydrogen-chiorine type fuel cell is 1.36 volte.

a

wuning a G(H,) value for hydrogen chloride to be 8.3, an energy conversion of 11.3% is obtained, This appears nore attractive than the present SWAP ayetene. These systens for Nuclear Auxiliary Power are of to types reactor eystens and radioisotope systens. In the radio-

isotope systems energy conver:

fon is carried out mainly by a thermoelectric process. The overall FTG (radioisotope

(38)

thermoelectric generator) efficiency is only about 5%.

A thorough investigation of the mechanian of the decomposition of these hydrogen halides would prove to be of inmense value towards the adoption of this idea,

---Page Break---

SECTION 11

EXPERIMENTAL

2.2, APPARATUS

The sain pieces of equipment used in this

investigation consisted of two high vacuum systens, a

variety of irradiation cells, several radiation source

adi

phragn gauge, and in

trunente 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.

2sled Vacuun syaten for purification of sample

A mercury-free vacuun line (figs. 566) was constructed for purifying and storing gaseous samples. A high vacuun of about 107San.tz. was maintained by a nue-Seal forepump and a water-cooled ofl diffusion pump. The low pressures were monitored by an ionization gauge. The ofl diffusion pump was arranged in such a way that hydrogen from the irradiated samples could be transferred fron thie vacuum systen to a conventional hydrogen analysie line.

In thie way irradiated eanples could be re-irradiated without coming into contact with mercury vapour fron the

analysis line, This vas to prevent hydrogen halides or

scavengers fron forming undesirable products by reacting

---Page Break---

Fic. 5

---Page Break---

s ?9l4

NOLWOISId «=3IdNVS «40s = NIT WNNOWA

---Page Break---

= 398 =

Fis. 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 conde:

4 after purification (to be described Later)
in the sample storage F, The bulbs B and ¢ (fig. 6)

were calibrated and used for measuring out quantities

of scavengers, The pressures of the hydrogen halides and
Scavengers were measured using # metal diaphrage gause

E (#ig. 6) connected to a mercury manometer. The diaphragm

Separated the measured ¢

jes fron coming into contact
with mercury vapour.

2.2.2 Analysie Line

The analysis line is shown in fig. 7, re
consists of a calibrated Meteod gauge, a Toepler pump,
and a palladium thimble which could be heated, The
ivradiated sample was put either into the mercury free

Line and the hydrogen to be analyzed punped via the

Line, or else w

@iffusion pump into the analys: just

Placed at the sample inlet V and the hydrogen toeplered

into the MeLeod gauge while Liquid nitrogen was placed

around the U trap K to condense any mercury vapour. The

volume of the McLeod gauge and asseciated dead apace

were measured accurately. Fr:

ures of hydrogen as low

---Page Break---

saa =

Fre. 7

---Page Break---

sae

£ old

W32LSAS SISAIVNY N3ASONGAH

---Page Break---

oe

as 2x10" nm,lig. could be measured.

2.1.9 Metal diaphragn gauge

This gauge (fig. 8) hed a Ataphragn made fron steel of 0,002"

a 6" circular piece of 316 stainl

thickne:

The diaphragn was held between teflon and

stainless et:

2 (926) annulars alternately ae shown in

the figure. To each of the outside steel plates were

soldered Kovar glace s:

1s. Inside one of these Kovar

1s was a sorew with a minute hole through the center.

This screw could be adjusted to increase the sensitivity

of the gauge. The whole systen wi

held together by

eax

ply spaced bolts (not shown in the diagram). The

Afaphrage A and the screw were connected to a miiiii

eter

and a 6 volt dry cell, By means of equilibrating the

pressure on both sides of the aiaphragn with the aid of the nillianmeter, pressures could be measured to an accuracy

of 0.05 emstig.

2s144 Radiation sources

(a) 4 200 curse cof ganna source

This source was contained in a lead castle

mounted inte the side of a concrete cave, The 1

cave door was fixed on # movable trolley which could

s1fde 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---

re

opposite the source when the source was out of its lead

castle, The source could be acti

ted by lowering the

isotope, Safety precautions were such that the door

could neither be opened {f 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 on to the trolley. This was done

to ensure reproducibility of dose rat;

(>) Gamma-ce2

Samples were prepared and

nt to Atomic Energy

of Canada Limited, Chalk River, to be irradiated at high

using their 12,000 curse co®° ganna coll.

dose ra

(e) X-ray machine

Sample:

were subjected to 87kV X-rays supplied

by @ conventional therapeutic machine at the Holy Cross

Hoapital, Calgary.

(a) 4 1200 curse co®° ganna source

?This was the source used at the Puerto Rico

Nuclear Center, The co®? w:

contained in twelve pencil.

type capeulee, each containing approximately 100 curies.

the

capsules were inserted into twelve hollow aluminum

cylinders, The cylinders were positioned to form a

Hollow cylinder Variable Geonetry Irradiator. The

---Page Break---

= use

irradiator was remotely controlled and could be adjusted

to form a hollow cylinder from § to 19 1/2 inch in

diameter, The shielding was provided by water in the form

of @ pool 9! x @* and 14 1/2" deep, The capsules were

about 10! under water, Sanples to be irradiated were

placed in special containers and lowered into the pool.

2.1.5 Electronic equipment

Tonization currents were measured with a Keithley

410 C micro-microanmeter 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. Soth of these instruments we:

connected to

the irradiation cell via coaxial cables

2.1.6 Ionization chambers and irradiation cells

Two types of ionization chanbers were used

(a) © concentric cylindrical chamber

(®) a paraiiel plate chanber

(2) The concentric cylindrical ionization chamber (eimilar

in design to pack's(37)), used for ne.

uring ionization

currents, is shown in fig. 9, The 2.5 mm thick eylinérical

wall was coated internally with colloidal graphite to

Form the collecting electrode. The central high voltage

electrode A, which consisted of 9 7 mn outer dianeter

---Page Break---

FIG. 9

---Page Break---

= 46

CYLINDRICAL IONIZATION CHAMBER

FIG. 9

---Page Break---

<4

pyrex tube, and a guard ring 8, were coated in a sintler manner. After the coatings had been applied through the tube D, this end was sealed to form a thinble trap for condensing the hydrogen halide using a liquid nitrogen bath, Tungsten wires passing through the glass walle

provided contact betw

yn the graphite coatings and

shielded electrical leads A", BY, and c'. Ga

admitted to the irradiation cell via a stopcock attached to a 30 on extension of tube E, This stopcock was shielded during irradiations.

(>) The paraitel plate ceil shown in fig. 10 wae made by flattening the ends of a cylindrical tube. The Afstance between plates varied fron 2 to 3 en from cell to cell.

These flat faci

were coated with colloidal graphite through the end I which senved 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. ¥ithin the cell a platinum rod

cane inte contact with the graphite face. On the outside

the tungsten leads were connected via coaxial cables to the electronic equipment.

The {rradiation cells not used for the measure=

ment of fon 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---

jade from pyrex round bottom flaske and had a aide arm

with a stopcock and a thimble for admitting gases and freezing hydrogen halides respectively. The cei volume

vari

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® 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 re-placed by break seals,

2.2. MATERIALS AND PURITY

2.2.1 Hydrogen chloride

Hydrogen chioride gas of 99.08 minimum purity

obtained from Math

jon & Coy was deg:

ed several tines

after being introduced into the vacuum line through stopcock

© (#ig. 5) directly from the Matheson gas cylinder:

qe

was then purified from hydrogen bronide by pre-irradiation

in the solié phase for « day in the pri

nce of about 1%

chiori:

This procedure oxidized the hydrogen bromide

to bromine which, together with excess chlorine, removed by trap to trap distillation through copper =

he

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 Mathi

on and Co. was pre-irradiated

overnight and thereafter treated in exactiy the

manner as hydrogen chloride.

2.2.3 Chiorine

chiorine (99.58 minimum purity) obtained from

2 several times. It

theson lecture bottle was dese:

wae then purified further by bulb to bulb distillations fron a trap at -80°C to a liquid nitrogen trap, After each distillation the non-condensable gases were punped avay from the nitrogen cooled solid, The chierine was then stored as @ solid at liquid nitrogen temperature in etorage 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

ing several times it was stored

---Page Break---

in a storage trap similar to trap A (fig. 6) and cooled by a

ary ice/alcohol mixture.

2.2.5 Sulphur hexafluoride

Sulphur hexafluoride obtained as a compressed

gas from Matheson and Co, was subjected to several bulb

to bulb distillations from -80°C to 1iquid nitrogen

?

perature, 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.)

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 £1.

ks (fig. 5).

2.2.7. Argon

Re

veh grade argon (obtained from Katheson 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 celis were then attached to the mercury free vacuum line ané evacuated for over an hour to a pressure of about 1076

mn.tig. During the evacuation the cells were flamed to

---Page Break---

elease any moisture that nay have been absorbed by the glass.

The appropriate hydrogen halide was distitied fron 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

wore monitored by the éfaphragn gauge, When the desired

pressure had been reached the cei and dead space were

Asolated fron the rest

f the syst

The differential

pressure acro:

the dfaphragm gauge vas now reduced to

zero and the pressure read from the mercury manometer.

When a scavenger had to be introduced, it was measured in a snail 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 chanber was heated overnight in an oven at 110°C instead of at s00%c.

2.9.2 Irradiation procedure

After the cells were filled, they were removed fron the vacuun line ané allowed to come to equilibrium

at room temperature (23429C), 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 sachine.

When using the ganma pool source, the parallel plate type lonization chamber was alvays employed. This was placed in a stainless steel cylindrical can 5 inches in diameter, A rubber gasket was clanped on to the can

by the cover with 6 evenly spaced bolts, The cover had

a concentric hole through which pa

ed the coaxial cables

for electrical m

surements. Th

cabu

were enclosed

in a 1" internal diameter tygon tubing 15* long. This

tubing wai

in turn clamped on to a tube in the cover of

the steel can, The whole can was lowered into the pool

rods and these were innediately

adjusted to grasp the steel can tightly. The open end of the tygon tubing was always kept out of the pool, enabling the aysten to be water tight.

2.4 MEASUREMENTS OF TONTZATION 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 wai

not obtained the saturation fonization currents were

---Page Break---

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

lee glass blown on in the ¢

of the 3690 ce cell and

those that were irradiated at Chalk River. The whole

the hydrogen analysis line,

pumped

ure of 10-Sam.Hg. When this pressure had

been maintained for ome time, the thimble of the cell

frozen with liquid nitrogen. With the eysten isolated im such a vay 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 toeplered 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 NeLeod, The differences in the heights of the mercury columns in the re measured with a cathetoneter and the pressure

---Page Break---

calculated. The gas was now allowed to expand by pulling the mercury down in the gauge and the palladiun thimble

heated for a few minut

by means of nichrome wire or

an infrared lamp, The 08

suring process was rep:

until there wae no further decre

in pressure, This

deere

was due to the loss of hydrogen through the

heated palladium thimb.i of

?The number of molecul

sured pressure

hydrogen was then calculated fron the mi

and temperature of the gas and the volune of the McLeod

Assuming {deal behaviour for the gas.

---Page Break---

wore

SECTION 117

RESULTS

The principal method of studying the radiation

induced reactions hai

n by a determination of hydrogen

yields as described earlier. All the reaulte presented

in this

ection are due solely to the interaction of

radiation with the specified systems. Irradiation of an evacuated sample cell with amiwithout a silicone greased

stopcock did not produce any detectable hydrogen. Also,

no hydrogen could be detected in unirradiated cells which

had stood for

eral hours at room temperature.

2.2 DosIMETRY

Tt has alr

ay be

pointed out that the

simplest and moat direct method of dosimetry for gaseous

syste:

is by the measur:

nt of saturation fenization

currents, The: then be con

ted to absorbed energy

Provided the value of W, the energy required to form an

fon pair in the gas, is known. ¥ values for hydrogen

halides are unavailable; however there are reliable

Measurements of W for the inert ga

.

won (4),

It follows fron the

equation

---Page Break---

= see

a

(5), = ratio of stepping power:

Jp/J, = ratio of saturation

fonization currents) developed in section 1.4, that by

comparing @ hydrogen halide gas with the inert ¢1

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 ases for comparison lies in the fact that they would be

iseelectronic with the corresponding hydrogen halidi

This woud m

n that their electron stopping power will not differ appreciably and their Conpton scattering cross-section will be the sane.

The ratio of stopping powers for hydrogen chloride to argon, and hydrogen bromide to krypton have deen calculated using the Bethe equation and the Brage's

law of additivity, Table 2 shows these ratios as a

function of electron energy.

Tonization current measurenents were made with both the parallel plate and the concentric plate chanber:

Tables 2 and § 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---

TABLE 2

Calculated stopping power ratios from the Bethe equation????

: 2 Fea, HBP

E(Mev) ° 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 a.019 1.022

. 0.50 0.7446: 26.42 1.019 aon

0.60 0.7805 26.83 1.018 2eon2

. 0.70 o.e29 27.20 2.018 201

0.00 o.e4er 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 o.e995 28.38 1.027 a.o1e

1.20 0.9109 28.58 1.028 1.010

excitation potential used

Bpp = 274 av¥0 eye 269 ev(*)

Tain #05 ev") 1, dm wx = 27,9 ev)

oy cua)

Ipp = 959 ev = 960 ev?

---Page Break---

= 60

TABLE 3

?Typical ionization current measurements for hydrogen

chloride (p=26.8 em Hg) in parallel plate chanber

v (volts) I Anps x 10° Polarity Reversed

Start tnd

300 o.a - -

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 o.a9

3800 o.92 0.90 0.90

4000 o.92 0.90 0.90

4500 0.92 0.90 0.90

5000 0.92 oon o.s2

---Page Break---

=o -

TABLE 4

5 Typical current-voltage measurements

Applied Voltage Current (Amps x 10°)

(cLleveits) qryen ORM

os 0.70 0.68

1.0 aeas 0.97

as aes 1.08

2.0 1.55 Loe

. 25 1.65 1.20

2.0 1.70 aan

3.2 4.72 ane

. 3.8 1.74 aa2

2.8 1.78 -

4.0 Lr ans

42 178 -

4s 1.79 as

4s 279 -

---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---

the saturation ionization current obtained by extrapolation te i/v? = 0, This type of analysis is only reliable for current measurenents that are in excess of

0.7 of the true saturation current.

Table § displays typical results used ina Greening type plot. A plot of the current versus voltage for this table is shown in fiz, 13, Fig. 14 is a typical Greening plot.

The results for fies, 15 and 16 were obtained using the concentric plete chanber. It should be noted that here the dose rate is nuch lower than the previous set of results obtained with the parallel plate chamber.

As a teat to the equation

.

8 be) %

the W values for air (33,7 ev)'"?) and argon (26.2 ev){*?)

were inserted along with a ealevlated value of 1.19 for

ae

Shir

energy of 0.15 Hev

+ This value corresponded to a weighted mean electron

43) a

+ J,/3, was calculated to be 1.46,

in excellent agreement with the experimental value of

Lue (fig. 26).

carrying out the J measurenents for hydrogen

chloride, argon, hydrogen bromide and krypton (ip,#25.0)°"2),

---Page Break---

- ou

TABLE §

: Typical ionization current measurements for hydrogen

chloride (p273.0 em He) in parallel plate chamber

Camps) 2

v (veits) ? 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 ous 1.98

3800 2.49 0.40 1.72

4000 2.53 0.395 ase

4200 2.56 0.390 aus

4500 2.60 0.388 1.28

4800 2.64 0.378 Las

5000 2.66 0.278 2.07

---Page Break---

?b 91d (811000114) ?-BOVLIOA ?-O3ITdd¥

s ? ? z ?

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

ylelde, 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 out in a cell

of volume 228

ce (fig. 11), Theme were all performed

in exactly the same position on the trolley to ensure

the #1

dose rates, Various pressures and doses vere

used, The formation of hydrogen from the two gases is shown

in tables 7 and 6 to de Lin

oe on pre:

and do:

?These reauits are also {1lustrated 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 OW THE RADIOLYSIS oF HYDROGEN cutorrDE.

Hydrogen chloride was next irradiated with

various concentrations of chlorine pre

nt, in cells of

volume 228.8 ce and 3690 ce respectively, using Co? y

---Page Break---

TABLE 6

. i)

ax. fon pairs H molecules © (M/N)_??GC,

. (em Hg) G0=37) corhy oH ®

(2) Hea resuits

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 bronide gases (228.8 ce cell)

HX Pressure Irradiation time R(rate of Hy formation)

(en Hg) (mins) x1012(moies /entig/min)

Hy@rogen 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 4 0,18

---Page Break---

Tapur 8

Hydrogen formation from y-ra¢iolysis of pure gaseous

hydrogen chloride and hydrogen bromide (2690 ce cei1)

HX pressure Irradiation tine Rx 102?

Com Hg) (nine) (motes /entig/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 4 0.5

Hydrogen bromide

1.65 ne 66.59

53.15 439 67.76

50.55 ase 66.79

sous 978 66.12

4o.4s 1020 67.05

mean 66.0 3 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 sc

encing effect may be attributed to

competition between the two follewing reactions,

i

Weer, 2 ewer oe

A kinetic treateent of the above would produce the

relationship (see appendix 1)

:

where AG(H2) = G(iy)nax = SUQ)e

oy fs the yielé of Hs CUID),,, and C(Hig)e are the yields

of hydrogen in the absence and presence of the scavenrer

respectively. and Pa, are the partial pressures

Puea 12

of hydrogen chloride and chlorine.

Table 9 gives the reeulte of the scavenging effect of chlorine on hydrogen chloride using two cells of different sizes. Fig 19 i drawn fron the resuite in table 9, The results obtained with the Large celi have heen normalized to those of the snail cell, and a plot

of the above equation {s shown in fig, 20, Fron the

---Page Break---

TABLE 9

yeRadiolysis of gaseous hydrogen chloride with

wote Rx 108?
Cl, (motes/entig/ain)
226.8 ce cell 3690 ec call

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 o.9se -

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 fin, 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 Kiein and Wolfeberg 4)

for conpetition
Feactions of hydrogen chloride and chlorine for thermal
hydrogen atoms.

It ean 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

eines at different pressures, These results are given in

fables 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 fron this figure

that bronine is @ much more efficient scavenger at iow

mole percentage concentrations; however, at high

concentrations it does not reduce the hydrogen yield as

---Page Break---

TABLE 10

y-Padiolysis of gaseous hydrogen chloride with bromine

8 scavenger in 228.8 cc cell

FOL pressure Irradiation tine Mole # Fx 1027

(om He) (nine) Br

219.90 450 - 2.79

219,90 938 0.10 2.32

229.90 aoa 0.20 aa

119.90 1500 0,30 1.05

119.90 1190 0.50 0.98

119.90 1067 0.70 0.95

aanss ais 0.05 1.54

21s iias 0.05 Lee

3nn.ss 1060 Lo 0.92

ana.ss 980 2.0 0.90

aan.ss aa72 5.0 0.08

---Page Break---

-a-

TABLE 12

yoRadfolysis of g1

ous hydrogen chloride with bronine

as scavenger in 3690 cc cell

HOL prescure Irradiation time Mole § Fx 1022

(en He)	(ins)	Bry	(meles/emig/min)
92.30	an26	-	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	1ce7	0.80	9.28
91.30	2205	0.60	8.79
91.30	1170	ao	8.38
91.20	ais	2.0	8.07
91.30	at0a	0	7.86
92.30	ae	6.0	119

---Page Break---

TABLE 12

yeRadiolysis of g

ous hydrogen chloride with bromine

scavenger in 3690 ce ceil

HCL pressure Irradiation time Mole $ Rx 102?

(on Bg) (mins) Bra (mole/enlig/nin)

19.90 1.65 - 23.45

19,90 ass - 23.90

29,90 1000 0.05 12,02

. 219.90 1045, 0.05 12.12

19.90 98s. 0.20 20.35

19.90 1096 o.as 9.56

. 29,90 1286 0.20 9.10

39,90 1213 0.40 8.50

19.90 aaua 0.60 7.98

29.90 1205 0.60 8.08

20.10 aaa? Leo 7.00

' 20.10 1020 2.0 742

20-10 2293 4.0 6.97

20.10 977 4.0 7.28

---Page Break---

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 107% and

5.65 are obtained for ("+ Hel) and Gye respectively,

Keg Bee)

assuming a competition for H* by hydrogen chloride and

dromin

?The comparison of these results with those of

art cs)

trong and Runferar(*®), prowiai

further evidence

for the aseunption that H* is not « thermal hydrogen atom. An immediate possibility appears to be that the scavengers may be scavenging electrons which could de 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 atone and thermalized electrons, in which case the rate constant ratios obtained

would be complex rate constant ratios. Sulphur hexafluorid
ve)

2 good electron scavenger "®), was therefore chosen.
?The activation energies for the two competing reactions
(a) H+ srg ??e sre + ar

and (>) Hs Hea ??+ He er

---Page Break---
= ow

ooo

?Old

cost

foal /bon]

008

vivus @

aeuva o

---Page Break---

are about 10K cats/note?"?) and 3 K cals/moie(*®)

respectively, Sulphur hexefluoride would therefore be

unable to conpete with hydrogen chloride for thermal hydrogen at

eat room tenperature and at the sulphur

hexafluoride concentrations used.

The same technique was used ae in the cases

of chlorine and bromine. The results are presented in

table 19 and plotted in fiz. 22, On comparing fic:

19 and 22 it can be 5:

n that the sulphur hexafluoride

has reduced the hydrogen yield more rapidly than either

bromine or chlorine at tow concentrations; however, the

plateau obtained vith suiphur hexafluoride is sonewhat

higher than with either chlorine or bromine. Both bromine

and sulphur hexafluoride at low concentrations must be

scavenging mainly electrons, since they both have saxinum

electron capture cross section for electrons at zero energy, If it is now assuned 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 atom:

?to form an ethyl radical, It was therefore thought

---Page Break---

~ 86

Tabur 13

y-Radiolysis of ga:

ous hydrogen chloride with eulphur

hexafluoride as scavenger in 3690 cc cell

Hel pressure Irradiation tine 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---

sunfOoe no

?armH 2

x7y gO NOLLYMWOs sO JLVY

bY

FIG. 22

---Page Break---

Recessary 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 systenatic and thorough investigation would have to

be carried out. The r

jults 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 ySeld 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 mechanisn was quite complex and would need a detailed

study, Before this study could be pursued further a public

.

cation appeared**) on thie reaction putting forward a

3.7 voSr RATE FFFecT

Three similar cells (fig. 9) without electrical connections, 11 containing break off seals, were sent to

chatk Ri

T (ALE.Csis) to be frradiated with a Gann,

cell, These cells vere filled with pure hydrogen chioride

---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---

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 vith a 200 Curie Co? source.

the nature of the experiment made it difficult

te 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 vas very Little difference in the scavenging at the higher dose rate.

3.8 EFFECT OF COATING THE CELL

?the ceil used here was coated with colloidal carbon in a nanner sinflar to that described by Pack et.

(37) | hese results compared with those from uncoated

celis 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 deno:

trate 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.

*

sured amounts of a mixture of hydrogen chloride

---Page Break---

uss stssLevot

29

' 08

s FD 00z Treo-4

? - tata

- eeree

- zeree

peonpgs ? (uyu/$yu>/setou)

PTORs Hg, wotee 8

19

Ts'o

were

aa

oTeK

ours,

o9'68

us'66

er8e

aay

Soros

sztos

scen

Soros

oes

Suton

(3x 82)

eanssead ToH

qr

Pa

tte9

treo

qte9

t199

treo

trea

para esop yary Aton a8 ouruoug yarn apruoty> ussoaphy 50 esehtorpEN

st sya,

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crag eto vere on ertt sets

erus8ta9 ante set sut snrts

org oore ort euot sete

peseooun poseoo

- wwe - o00t snrts

- aste - c66 sats

paongos(wpe/Suue/seton) Tag (eaye) Gn =)

proré bay pov ea § ston sua voraerreses sunetesd TOM

dupseos TT29 50 390550

ot suave

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- 93

and hydrogen bromide were firet irradiated in @ manner

sinilar to those already described. 5

11 arounts of

bromine were then added to observe its effect on the

above mixture.

on the assumption of the following competing reactions

we neath, +e

We wer toe Hl, + Br

Wg ey Ae mae + 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 te 100, From fig. 24, k,/k, can be evaluated using the previously

obtained value for ky/kyy to be 1.96 4 0.15 x 107, the

calculation gives the value ky/ky = 6.1 + 0.3 x 107%

which is net in age

ent with the rat{o 0.12 fer

thermal H atoms obtained by conventional gas kinetic

techniqui

(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 ce cell

Heh pressure Mole $ Irrad, tine ole & R x 101?

(eB He) HBr (mins) Bry (motes/entig/nin)

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 ¢ (fig. 11) were used. Th

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 Cro}

Hospital, Calgary. The voluses of the cells were all about 230 cc differing by only about 3 cc, Next, small anounts of bromine were added and the cells re-irradiated.

A treatment of the resuits (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 +

keue

0.9) x 107° for (H+ HBF) ig obtained, This provides

?

Gr + Bry)

further justification for referring to the scavenged species

as H? rather than Hy

---Page Break---

- oe

TABLE 18

a nadiolysis of hyéregen bromide containing bromine using

Xerays in cell of apprexinately 290 cc

hop pressure Irrad, tine Hole § Cell Rx Lol?

(em He) (eins) Bra (moles /entig/min)

ss. as - 8 2.97

55.08 as - B 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 sane

manner as the previous irradiations using sulphur

hexafluoride instead of bromine.

If the following competitions are assuned

e+ HBr aH + Bee

e+ srg sre?

then by treating the results similarly to the previous

section a value for

K(e + HBr) can be calculated.

Ke + ste)

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 40,3) x 107%, thie is within experimental error

of the value for and therefore it is not

Kir 4 uBe)

ee

(ie + Bry)

unreasonable to conclude that the i? 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 hyérogen bronide containing sulphur

hexaflucride using X-rays in cell of approximately 230 ce

Her pressure Irrad. tine Mole $ Celt ? Rx 1027

(om Ea) (mins) SF, (moles /eng/ain)

$5.77 20 - ? 2.97

55.77 as 027k 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 hyérogen bromide than

in hydrogen chloride.

9412. THE EFFECT OF AN APPLIED ELECTRICAL FEFLD OW THE

YeRADIOLYSIS 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 hyérogen bromide sep: ately, and soon as they were placed in the irradiator, the saturation fonizetion currents were obtained, This achieved by measuring ionization current with applied voltages in intervels of 500 volte at first and smaller intervals after 3000 volts. This took about 2 sinutes. ?The applied voitage required was then set and the radiolysis carried out for ¥ to 8 hours. At the end the ionization currents against voltage were rechecked.

After this the cells were analyzed for hydrogen to obtain

jon-pair yields.

The results are shown in tables 20 and 21. Plots

of (a) don pair yield of hydrogen against applied

vortage:

and (b) donization currents against appiied

voltages are denonstrated for hydrogen chloride and

hydrogen bromide in figs. 28 and 29 respectively.

---Page Break---

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Cw,

oztn

gntn

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TOR CusH)

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ot x setnoetou

prers %y

oz save

+ sot

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gr-ot

sap aor

ro

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1Br0

3303/09/4

preys pertddy

ostez

osrae

oprsz

osrsz

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section 1v

DISCUSSION OF THE HYDROGEN CHLORIDE RESULTS

N21 RADIOLYSIS OF PURE HYDROGEN CHLORIDE GAS

In the introductory section the sinilarity of nase spectronetric studies to radiation chenistry was pointed out. Therefore, in considering the possible fonic 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 HCI?, HeI**, ci*, ca** and H*(52), the approxi te relative abundance of the first four fons are estimated to be 100:11:10:3. The parent ion (itci") 4s predominant in the mass spectrum and should also be the predominant prisary ionic species formed in the radiolysis of gaseous hydrogen chloride:

Wer we neat +e @

Since the ionization potentials of Cl and

(12.96 and 19.60 ev respectivety)(52) are slightly higher

than that of the HCl molecule (22.74 ev)?°%), the ions

c1* and Ht should rapidly undergo the following charge

---Page Break---

= 110 -

transfer processes at high hydrogen chloride pry

cat + Hel?eer + Hert aus-0.22 ev @

BY ca ?en + wea? ? ane-0,86 ev a

The doubly charged Hc** and c1** fons,

Decause of the such larger values of second ionization

potentials (e.g. second I.?. of ci223.8 ev(52)), wourd be capable of fer more highly exothernic charge transfer processes with hydrogen chloride molecules. These processes (given below) may lead to excitation and dissociation of the product fon(S#),

catt + uem?ecat + cit tt aw -s.7 ev (uD

crt? s ncr?ecit cree ans 8.9 ev (5)

neat? + Hea?eE* + ca + Heat «e)

These reactions would obviously be Followed by reactions (2) and (3), The overall stoichionetry for the primary Jonization processes can therefore be represented as follows

(CL + x)Hea ?* Heat + e+ x + xen m

?The value of x would obviously depend on the fon distribution in the radiolysis and on the fraction of energetic charge transfers leading to dissociation. If it is assumed that every charge transfer of He1** and

cat? leads to dissociation, a value for x (0.26) can be

---Page Break---

<a

estimated using the ion distribution obtained in the mass spectral data,

Before con.

idering the possible reactions which the species Hcl", e, # and Cl can undergo, the results of the experinents with scavengers will be

discus:

4.2_ THE SCAVENGING EFFECTS oF CHLORINE, BROMINE AND SULPHUR HEXAFLUORIDE ON THE RADIOLYSIS OF GASEOUS HYDROGEN cHtorrp:

It is quite clear fron the results, that the three scavengers used, decrease appreciably the hydroge: 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 sone 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

Ho + Hel ey + cr)

H+ 8 ?» products other than Hy a)

ws ner ea, + cn ao)

---Page Break---

uM 4s ?e products other than H, ay

(S denotes seavenger)

Mow if the species H* is a thot! hydrogen atom reaction

(a2) wilt be unable te compete with reaction (20) at the scavenger concentrations used in these experinent.

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 kglkg

Padiolysis 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 colunne in table 22 permit a

comparison 6f the values of kg/kg obtained from radiolysis

and from conventional studies in which ¥* is a thermal

---Page Break---

hydrogen atom. The disagreement in the two sets of ratios indica!

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 St will not react with thermal H atone at the sulphur hexafluoride concentrations usedS®), st 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 Gj#

(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 inplie
that there is a source of thermal hydrogen atons whose

precursor

not the electron. A yield G, of 1.85 thermal
hydrogen atons per 100 eV can be calculated from the
difference in the G,. value obtained in the bromine and

sulphur hexafluoride results. The ke/kg ratios obtained

---Page Break---
=a

with chlorine and bromine as scavengers are really
Functions of keueuery/*cues) 84 ¥cegncry/*cessy? aRé ae
best treated as "complex" rate ratios.

Tt has been suggested?®®) that at high dos:

and high chlorine concentrations, the back reaction

Hy + cl?pHel + aay

with an activation energy of 5.48 keate/moie(®0), may cause a slight reduction in the observed hydrogen yield. With bromine, the analogous reaction

By + Br?pnBr +H as)

is lees Likely to occur since its activation energy is

19.7 keals/noie'®°),

Consequently, the differences in 6,# for these two scavengers may be ascribed to the effects of reaction (12).

The scavengers chlorine, bromine and sulphur

hexafluoride, and the hydrogen chloride molecules can

all react with electrons thus

e+ Heron + cr? (asad

e+ cl; eer + cam as)

e+ Bry ?eBe + Br as)

e+ srg esr.? an

The energy thresholds for the above electron capture

reactions are 0,65, 1.60, 0,00 and 0.00 ev?®2) respectively.

---Page Break---

Since the electrons would be expected to thernalize quite

rapidly, reaction (15) could hardly compete effectively

with reactions (1sacb) unless chlorine molecules vere present

in very high concentrations, The chlorine must therefore

be competing with the lic molecules for hydrogen atons which

are formed in reactions (14a) or (4B).

? + 2iic1 ?» electron-uc1 complex

HF cay csp)

A study of the effect of chlorine on the radiolysis of a nixture of Hel 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 sulphur 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 radfolytic yield. The results obtained here can therefore be used in ap empirical manner to correct those of Vandanne'®?), whose radiolyses were all carried out to a high percentage Gecomposition (>0,3%) relative to thie work (0.0u8), If

R is the dose rate in eV per unit volum

per unit time,

then the equation for the rate of formation of hydroge:

---Page Break---

= 11a -

eto 7 we eto F Thm sentra 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 Thm 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---

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

50.815). Assuming that the valu:

oF Kenes nery/Kenre 29)

(2.8 x 107%) ane of A for the a-particie radiolysis and yeradiolysis are the eane,

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:

Vandanme's reauite were corrected

using the above equation. Table 23 shows these

corrections and displays the close agreenent in hydrogen

yields between the a-particle and y-radiolysis of pure

hydrogen chloride.

The re:

ults 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 464 of the total yield of hydrogen molecules

---Page Break---

- ars

have thermal electrons as their precursors (2) about 22.3%

are formed fron "thermal" hydrogen atons (not originating

fron electrons) and (3) the remaining 31.78 originate fron

thot! hygrogen atoms.

4.9 THE EFFECT OF BROMINE ON A NIXTURE OF HYDROGEN CHLORIDE AND HYDROGEN BROMIDE,

with the value of 8 x 107% obtained in the liquid phase

(8 keais/moie(®?)) is greater than F,

cea)

(0.9 Keates

BeBe

mole! the gas phase ratio would be expected to be

larger if the sane species were involved. It is therefore

apparent that the bromine is not scavenging the sane

species in the Liquid and gas phase radiolysis. the

rate constant ratio for k, at 25°C is known

Heian! *HeBr,

264),

from conventional studies to be 0.12 + 0.0: thie

value has been made use of, by comparing it with that

obtained in the radiolysis of a mixture of hydrogen

---Page Break---

- ale =

chloride and hydrogen bromide containing varying percentages of bromine. A value of 6.1 x 107° has bi obtained for kyeyuse/Fucaue, Using the method outiined in section 3.9, This adds to the evidence already accumulated in establishing that the specietH* 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 bronine was independent of hydrogen chloride pressure, radiation cell volune, 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 te the pressure of

hydrogen chloride (P) and the square of the radius of

the irradiation ce11 (r?

i however the rate of homogeneous

combination of the same species should be proportional

to the dose rate (1), The value of IPr? (which should be

a measure of the heterogeneous process) varied in these

---Page Break---

75 01.7 x 1027 guring which

experiments from 1.3 x 10

the plateau remained the sane within experinental 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 ELperRIc FreLp 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 {on-recombination reactions.

In the absence of an electric field it would be expected that the HC1* fon would either undergo ion

recombination with the electron or gone other negative ion

thus

weit +e > Heat H+ 2 as)

neat + clten + 202 as)

oF else react with the neutral hydrogen chloride molecule as follows

nea* + He. ?> Her" + c2 (20)

Assuming an ion recombination coefficient of 107° cc/ion

---Page Break---

sec(®*) ang the rate of ion formation to de 1022 tons/ce

Jeec in these experiments, the steady state approximation

@

would give a concentration of 10° fons/ee and hence the

+ 3

calculated iifetine of the HCL? fon would be about 10

sec. For the fon molecule reaction (20) Schissier and

(65)

Stevenson?°*) have found the specific rate constant to

be 4 x 107° cc/molecule sec. At a hydrogen chloride

9

concentration of about 10° *nolecui:

Jee (in thie study)

the lifetine of the Hcl" fon is about 1072° sec. Hence the ion molecule reaction will undoubtedly be responsible for the removal of HiC1" ions, The H,C1* ion would be the principal positive ion collected at the cathode on application of an electric field.

The scavenger studies have denonetrated the importance of electrons as a precursor to hydrogen forsation in the radiolysis of hydrogen chloride. These electrons produced from the initial fonization process (2) should rapidly become thermalized ané eventually

Ateappear by any of the three Following proces:

ambipolar diffusion to the walls of the veesei, son-electron recombination (HjC1* + e) and attachment to a neutral hydrogen chloride molecule to form a negative ion.

?The first order decay constant for electron-

---Page Break---

- aa

fon loss by ambipolar aiffusion is given by D/A? where

D ie the anbipolar diffusion coefficient and A is a length

characteristic of the vessel geometry. A typical value

of D (0,09 en?/sec at 1 atm.)(%) and A (>tem) for the

syotem used, lead to D/A? = 70/P mm per sec. This gives

@ diffusional loss tine of at least 1 sec in this study.

The fon electron recombination has already

deen discussed where the estimated lifetine of the

electron for this process is about 107 sec,

The electrons will lose their energy initially

in reactions (21) and (22) viz:

e+ Hcr?>Et sci te an

e+ Her ?pHer* + ean scree (2)

and finally to rotational and vibrat{onal excitation of

Hed molecules. They may also be captured in one of the

following proces:

e+ uel 4 n+ cae (a)

© + HCL + He1?serectron-ier complex

cease ayy

(Hen)

Both reactions (21) and (23) have been observed in the

1oW 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

---Page Break---

(67), the ionization current of

and 14,5 eV respectively

cL? coming from the low energy resonance capture process

at its peak was at 1

t one order of magnitude greater

than that for the on pair formation reaction. The collection efficiencies for the C1? Jon coming from the

two reactions (21) and (23) should be the sane, and

therefore the cros:

ction 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 10728 en? at the

imum. Us

ng this and the data

for energy loss per collision with hydrogen chloride a:

summarized by Healey and Read(®®), i can be shown by the method of Magee and Burton(®®), nat only a small fraction (58) of the subexeitation 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(70) has obtained evidence that the

electrons disap:

1 in a termolecular reaction represented above as reaction (24). Ke estinates that the rate

32

constant of this reaction is approximately 2.1 x 107°

---Page Break---

cn®/molecule?sec, from which a mean lifetime for the electron would de of the order of 1078 sec, a

concentration of hydrogen chloride molecules of about 10*°

molecules/ce.

From the foregoing it can be concluded that
the ions H,C1* and C1?, and maybe electrons would be
collected at the electrodes on application of an electric
fieid.

At a field strength of 10 V/en/torr, the

effective electron energy in HCL
amy

timated at 0.14 eV

?This energy is puch lo

than the threshold energy

of reaction (22).

eter ?encl* +e oi scise (2s)

which requires an energy of at least 4.5 eV. This means

that a reduction of hydrogen yield caused by neutralization

of fons at the electrod

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

poth the MH,? end H,0° ions are heavily clustered, In view

of this, it would be expected that the H,C1° and C1? fone
would also be heavily clustered. Consequently, in the
absence of an electrical field, the occurrence of a non-

Aissociative combination, viz:

---Page Break---

1H

at +o,

"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 nixture of hydrogen chloride and sulphur hexafluoride. 99)

The application of an electrical field curing

the radiolysis shows no effect on the hydrogen yield in the

fon-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 H,C1" ion on being neutralized at the cathode forms hydrogen, Very Little is known about reactions taking place at electrodes in

seous 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

etions

The free radicals produced in the ionic ri and in the excitation process are mainly the H and CL

Fadicals, These radicals would be expected to react as

follows

He Her ?> Hy +0 en

Heer ?suer (2a)

Net pon, om (2s)

---Page Break---

che cl +s ?peipe x (30)

Reaction (27) has an activation energy of about 3 kcals/nole whereas the others (28), (25) and (30) would be expected to have zero activation energy; however, since the radicals # and C1 would be present in very low concentrations the reactions (28) and (29) would be unable to conpete with reaction (27), As the products hydrogen and chlorine build up during the radiolysis (e.g. at high doses) the back reactions

We caj?ener + cr can)

Hy + cl ?enea + (2)

can be expected to interfere with the hydrogen yield, Their activation energies are 3,0 keals/nole and 5.48

keals/nole, respectively.

In the stoichiometric equation

Ce Her > neat +e at + xen ?

an estinated 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 C1 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

---Page Break---

yield, this must be coming fron processes such as

ee 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 phenonenon.

4.7 PROPOSED MECHANISM ToR 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 compiex

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 agreenent with 3.8 obtained from the scavenger

studies. Assuming an x value of 0.26, reactions (1)

and (4) can account for up toa 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) ané

(21) become inportant

Heel, > Hers cr ae)

Weel + Here ay

---Page Break---

SECTION v

DISCUSSION OF HYDROCEN BROMIDE RESULTS

5.1 RADIOLYSIS OF PURE GASEOUS HYDROGEN BROMIDE

When pure gaseous hydrogen bromide ie 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 a1.(S28) on the radiolysis of this gas using X-rays. It appears fron the above result that X- and y-rays produce the sane effect

on HBr gas, This is to be expected since both of these rays are penetrating electronagnetic radiation only

aiffering in their energies.

Before a mechanism for the decomposition of the

gas is attempted, all the pertinent data will be reviewed.

?The mass spectral date 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 proc

es (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---

art? 4 npr par? ses Br anesteev (uy

(2nd T.P, of Bre19.2 ev'52))

These equations would lead to an overall stoichionetric 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 WEXATLUORIDE ON THE RADIOLYSTS OF GASEOUS HYDROGEN BROMIDE

In the radiolysis of gaseous hydrogen bromide, the scavengers bromine and sulphur hexafluoride reduce the hydrogen yield to about the sane 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 Hic radiolysis (Tables 22 and 24), {t 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

conpeting for the reactive species Hi

A kinetic analysis similar to that used for

the HCL scavenging results, assuning that the

scavenger and HPr conpete for the reactive species i?,

---Page Break---

gives the results shown in Table 24, From the last two

colunns 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

Bust therefore be scavenging electrons since both bromine

and sulphur hexafluoride are good electron scavengers having maximun capture cross sections at zero energy.

Table 24

Scavenger out Kuen! Ks

radiolysis # atom

Bromine 2.6 7.0 5.9x1079 0.12

Suiphur e

Hexafluorige 2,7 6.9 6ax20 pa

and t* represent the scavengeable and unscavengeable

species, respectively,

The scavenging resuits give a Gy, value of

2.7 which should be equai to G,. However, fron 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 cage of He.

---Page Break---

During thermalization the electrons may

interact with the HBr molecule as follows

e+ Bron? + ar te (6)

e+ Hor?snbr* +e en are om

e+ mar oH + are ro)

Finally, as in HCL, the three body process

© + 2ir ?> E1ectron-HBr complex «

ue °F ane)

Bay occur. The energies required for reactions (6) and

(7) are 19,8 ev and at least 3.75 ev, respectivery.

Reaction (6) has a threshold energy of 0.1 ev with a

Raximun oapture cross section occurring at 0.21 eV, and

Feaction (9) should take place with thermalized electrons.

The cross section for electron capture by an HBr molecule

im reaction (8) is 15 times larger than that for the

corresponding reaction with llCl and also, capture occurs

at a much lower e

rey. It must therefore play a much

greater part in the HBr radiolysis than in the HeL

radiolysis, Reaction (6) gives fone which would be

measured in the ¥ value, but not be scavengeable by sf..

ence it nay contribute to the difference between 6,

fron the scavenger date and Gionseation (alculated

from W value for HBr).

---Page Break---

The rate constant ratio Kysupe/Fyeae, #8

2068)

and therefore at 6 mole & bromine concentration

only one third of all the thersal hydrogen atoms formed

in the systen would be scavenged by bronine, in addition

to the competition for electrons, therefore, depending

fon 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. tence the ?thermal? hydrogen atom yield cannot be large and nost of the hot hyérogen atoms must be reacting before beconing thernalized.

The H atoms resulting from the stoichionetric equation (7) of the previous section can contribute up to 1.6 6 units to the Gy yiewe.

5.9 APPLIED ELECTRICAL FIELD EFrECT

The effect of an applied eletric 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 yielé in the jon recombination regio:

however, as the field strength increases and before

secondary ionization sets in, the ion pair yield incre

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 stoichionetry of reaction (#) is the sane as reaction

(9), fe, one 11, molecule per electron. Reactfon (7) can

the observed effect since a constant appiied electric

Field would be expected to increase the average energy of

the electrons in the gas. A fraction of then may attain

the threshold energy of reaction (7).

5.4 PROPOSED MECHANTSH

The following mechanism has been put forward

by Hamill et a1. for the radiolytic decomposition of HBr using X-rays.

HBr ?onBr* +e Qo)

ef Br on 6 pee (a)

wart + be? en + opr an

out ea, + Be a2)

Bret +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

au

jocfative excitational process which may be depicted as

e+ Wor Sense? +e ent sore as)

Since their investigation the rate constant fer the fon

molecule reaction

---Page Break---

~ isn

MBr + HBr? ??& fi,Br? + oe as)
bas been measured by Schissler and Stevenson?®5) to be

4.7 107?

ce/nolecute 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 ie no change in the ion pair yield for either the production of hydrogen or the destruction of HBr molecules in the Son recombination region, reaction (16) below must be proposed as the ion recombination reaction.

nybe? + Bre Hor ae
For similar reasons to the HCi case, instead of reaction (16), reaction (27) would be expected.

2 Canpey * PF (anaes ??? (otnt2dBE an
With the above sodifications to Ham{il's echanien, the proposed mechaniem for the radiolytic decomposition of

gaseous hydrogen bromide should then be as follows.

Tonic reactions

HBr sur? +e ()

© + 2UBr?+ electron-iBr complex

Ky 8 @

CBr)

---Page Break---

= 138 -

e+ HBr eH + Bet fe)

Wer + nae? oe nytet + ar «a

Hyer? 4 okie ?= RP" Cyan (ed

. Br? + alr era w

HABE Cana) TPP Gmuagy > (mene HEE (®

Exeitation

e+ br our +e ete ree OH)

Radical reactions

Moe HBr My tee wo

H's war en, + ar a

Bre ares ear en 00

The scavengers would be conpeting with reactions (b) and

(©) for electrons, Reaction (h) followed by (J) is

responsible for the unseavenged hydrogen yield, The

energy to form an fon par in HBr ie 24.4 eV. The T.P.

of WBr 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 cannet be 3:2, thus accounting for the high

unscavengeable yield of hydrogen.

---Page Break---

APPENDIX T

: Consider the two competitions below

x

Wener ?Ls ys er

weer, ?2 4 wer scr

Let Gy. be the yield of He

then in the presence of the scavenger C1,

Cg = (aeons) ;

a),

¥, Haein, ely)

+ The reduction in Gy, represented as A6cy,)

is given by

(kG GD))

- (0-2

a 7 >

1 GP GeDen, GF Ie,

te (x (ea)

? ae)

iWin er, (er)

. (: « Kyrea \/

Rea

: actH,) =

---Page Break---

197 =

APPENDIX IT

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

vhere 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 tines x

Ws on,

Putting ne 2000

x 7H 3.8 (Her

wee wea POD rea)

(1g) + (Hig) = x ang assuming that (HC1) is constant,

the equation becom

a

ax + ex. +

Bexeuy f sare va}

---Page Break---

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 Ss dose,

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a

20.

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