

THE γ -RADIOLYSIS OF AQUEOUS THALLIUM (111)
SOLUTIONS CONTAINING SIMPLE ORGANIC SOLUTES

by

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ABSTRACT

The radiation-induced chain reduction of Tl(III) and oxidation of 2-propanol in deaerated aqueous perchloric acid solution has been investigated. Tl(III) is reduced to Tl(I) and 2-propanol oxidized to acetone in yields which are stoichiometrically equivalent. $G(-Tl^{3+})$ and $G(\text{acetone})$ increase linearly with increasing alcohol concentration in the range $1 - 10 \times 10^{-2} M$, are independent of Tl^{3+} concentration in the range $1 - 4 \times 10^{-3} M$, and vary inversely with the square root of the dose rate in the range 1.6×10^{17} to 1.8×10^{19} $\text{ev. l}^{-1} \cdot \text{sec}^{-1}$.

These observations are consistent with a mechanism in which initiation is by hydrogen atom abstraction from the alcohol by the water-derived radicals H and OH. Propagation occurs via the sequence



For this latter reaction a rate constant of $3 \times 10^4 M^{-1} \text{sec}^{-1}$ is estimated. Termination is by the dismutation of Tl^{2+} species



The chain reaction is unaffected by the presence of Tl^+ but inhibited by oxygen and Fe^{2+} .

Methanol and ethanol are oxidized by similar mechanisms whereas t-butyl alcohol gives a much lower yield of Tl^{3+} reduction along with the alcohol fragmentation products acetone, methane and ethane.

Formic acid is oxidized to CO_2 and the Tl^{3+} reduced in a very high yield under γ -irradiation while with acetic acid the reaction is a non-chain process.

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1. INTRODUCTION

1.1 The Nature of the Experiment

A study has been conducted on the radiation-induced reduction of Tl^{3+} solutions containing several simple organic solutes in an aqueous perchloric acid medium. Alcohols such as methanol (Me OH), ethanol (Et OH) and 2-propanol (i - Pr OH) are oxidized by a chain mechanism as the Tl^{3+} is reduced to Tl^+ . A similar, but more rapid, reaction occurs with solutions of Tl^{3+} containing HCOOH. Reactions with other organic solutes, such as tertiary butyl alcohol (t - Bu OH), show little chain nature. The effects of Tl^+ and other inorganic solutes have also been examined.

A mechanism is proposed for the reactions in solutions containing the primary and secondary alcohols, accounting for the stoichiometry of the system as well as the concentration and dose rate dependencies. The differences between solutions of these alcohols and Tl^{3+} solutions containing other organic scavengers are also discussed.

This study developed out of an original intent to examine further the photochemistry of $Tl^{3+} - Tl^+$ reactions, previously investigated by Stranks and Yandell⁽¹⁾, with the addition of organic solutes. As a preliminary investigation an experiment using γ - irradiation was attempted with an aqueous Tl^{3+} solution containing i - PrOH. The discovery of a chain reaction led to the present research in an attempt to elucidate the mechanism.

1.2 Radiation Chemistry

Radiation chemistry deals with the chemical reactions caused by radiation both of an electromagnetic nature, such as x-rays or γ -rays,

and of a corpuscular nature, such as neutrons, α -particles, β -particles, protons and fission fragments. Until the advent of the "nuclear age" experimental work was seriously hampered since the sources of radiation were exceedingly weak and/or unreliable and most analytical procedures for the identification of resulting products, let alone intermediates, were unsatisfactory. Recent developments now enable one to classify radiation chemistry as an independent branch of chemistry.

In radiation chemical research it is desirable to know the nature of the interaction of the radiation with the absorber, the mode of formation and nature of resulting reactive intermediates, and how these intermediates react so as to yield the ultimate products.

Gamma-rays from Co^{60} , with an average energy of 1.25 MeV, are an important radiation source. In the physics of the interaction of γ -radiation and matter, described elsewhere^(2,3,4), the loss of energy occurs by three processes: photoelectric absorption, Compton scattering and pair production. The photoelectric effect, important at low photon energies and for materials of high atomic number, consists of absorption of the incident photon by an electron of the atom and the resulting release of an electron with energy $E = h\nu - E_c$, where $h\nu$ is the photon energy and E_c the binding energy of the ejected electron. In Compton scattering an elastic collision of a photon and electron in the medium results in electron ejection and scatter of the photon at reduced energy. The energy of this recoil electron is $E = h\nu - h\nu'$. The scattered photon, of energy $h\nu'$, may further interact in another process. Pair production, in which annihilation of the photon results in production of an electron and positron,

occurs only if the photon energy exceeds 1.02 MeV and is significant only above 10 MeV, thus being of no consequence for Co^{60} γ -rays.

These primary interactions of the photon and absorber lead to important chemical consequences only because of the effects produced by the resulting high energy electrons. Since the energy required to produce chemical change is only a few electron volts per molecule these fast electrons may alter several thousand molecules of the absorber as they lose their energy.

While the fast electrons may interact with the nuclei or inner electrons of the atoms present, the effect of such improbable interactions are generally swamped by the chemical changes due to the non-specific interactions of these, or slower electrons, with the outer electrons of atoms in the absorber. These outer electrons are either ejected from their atoms to leave positive ions or excited to higher energy levels. Secondary ejected electrons with sufficient energy may repeat a similar action. Other electrons with lower energy, but still in excess of about 100 eV, form a branch or "delta ray" on the primary track as they lose their energy by ionization. The remaining energy transfer, about half the total, is by ionization or excitation due to electrons with less than 100 eV energy. This occurs very close to the original area of ionization and the resulting small volume elements where the energy is dissipated are known as "spurs". Most of the total ionization is caused by these slow electrons in the widely scattered "spurs" along the primary fast electron track or along the δ -ray tracks. Eventually the energy of the electrons is less than the

lowest ionization potential in the medium and excitation alone occurs as the electrons are captured by molecules or positive ions. Magee⁽⁵⁾ has examined how this primary energy in the electron track is lost in more detail.

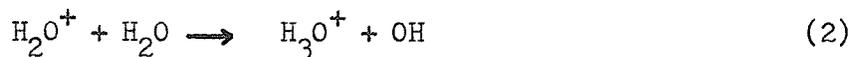
The nature of the ionized or excited intermediates and the ultimate consequences of their reactions with one another or other species present depends on the characteristics of the original absorber. Only the specific case of aqueous solutions, where water is the major absorber, will be examined further.

1.3 γ -Radiolysis of Aqueous Solutions

Co^{60} γ -rays interact with water or aqueous solutions essentially by Compton scattering. Since this is a non-specific interaction the primary species formed are mainly those derived from water since it forms the bulk of the material. The deposition of energy in the aqueous system initiates a number of consequences. In the spurs the original products will be ionized water molecules (H_2O^+), electrons (e^-) having energy in excess of thermal energy and excited water molecules (H_2O^*).

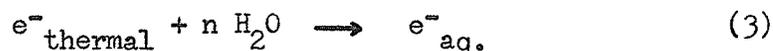


H_2O^+ undergoes a rapid ion-molecule reaction



Meanwhile, the secondary electrons lose their excess energy by collision with water molecules to form subexcited electrons which, when reduced to near thermal energy, may become solvated as the charged species orientates

the surrounding water molecules

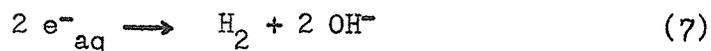


The excited water molecules present may dissociate or be deactivated



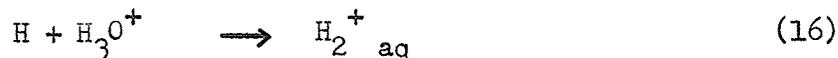
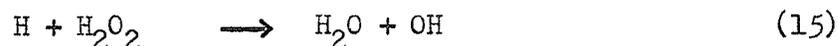
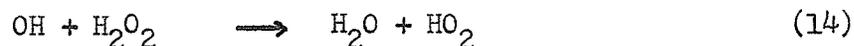
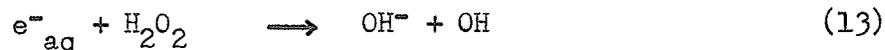
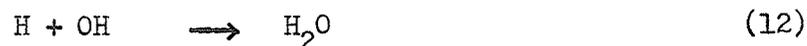
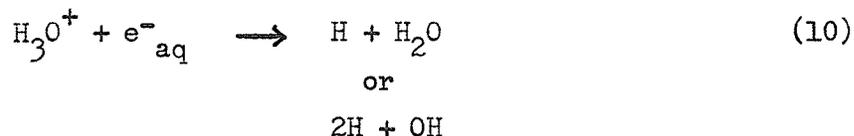
While the exact nature of this process is still unclear some recent reports do explain the suspected reactions⁽⁶⁾. Thus, in about 10^{-11} seconds there exist in the widely separated spurs (about 5000 Å)⁽⁷⁾ high concentrations⁽⁷⁾ of the primary products H_3O^+ , OH, $e^-_{\text{aq.}}$ and H.

These regions of high radical concentration expand, and at the same time radical-radical and radical-solute reactions take place. In aqueous solutions additional so called 'primary products', H_2 and H_2O_2 , are found to be produced in about 10^{-8} seconds. Other products, dependent on the concentration and reactivity of the solute and the state of expansion of the spurs, may also be produced. The most widely accepted theory of the origin of the molecular products H_2 and H_2O_2 is that they are formed by the following combination reactions of the diffusing radicals:



The majority of the molecular hydrogen is derived from e^-_{aq} , with smaller

amounts contributed by reactions involving H atoms.⁽⁸⁾ Although the kinetics of these reactions are extremely involved several authors^(2,7,8,9,10,11) have dealt with, at least in part, the production of these species as well as the other radical reactions which could occur.



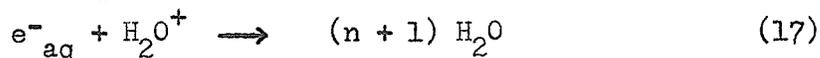
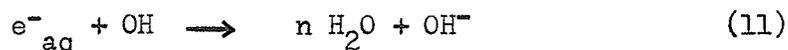
Thus after about 10^{-8} seconds there is an essentially homogenous solution containing e^-_{aq} , H, OH, H_2O_2 , H_2 and H_3O^+ .

These theoretical concepts have been developed as the radicals and molecules which were formed and their chemistry became known. The molecular products, H_2 and H_2O_2 , have been identified directly but the radicals, except for some recent spectral identifications, have been characterized only indirectly through the use of scavenger techniques. The detection of intermediates in water radiolysis is examined in more detail by Matheson⁽⁷⁾. The relative reaction rates of the radicals have been determined by introducing various solutes in various ratios and noting the amount of each reacting. In some cases absolute reaction rates may be

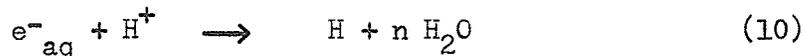
established using techniques such as pulse radiolysis or flash photolysis.

The yields of the primary reactions, normally quoted as G - values which specify the number of molecules, ions or radicals formed or removed for each 100 eV of energy absorbed by the system, can be determined from the extent of changes produced in the system if the detailed mechanism is known.

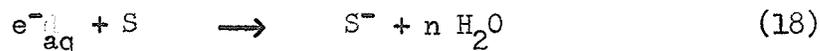
The primary yields in radiation chemistry of aqueous solutions are still subject to some controversy. As such, the choice of values must be based on particular studies. In his report, Hayon⁽¹²⁾, concludes that in the radiolysis of water yields of the oxidizing and reducing species, as well as the decomposition of water, increase as pH is lowered from that of a neutral solution. For the reducing radicals, $G(\text{red}) (G e_{\text{aq}}^- + G_{\text{H}})$ in dilute solutions increases from 2.85 at pH 7 to 3.7 at pH 0.5. The effect of acid is to reduce in the spurs the back reactions



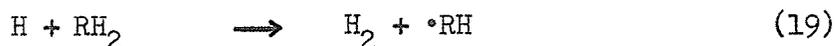
and consequently increase the yield by the reaction



If a solute scavenger is present, such as acetone for e_{aq}^- so that



and i-PrOH to react with H atoms according to



one can, by measuring H_2 , determine G_H in the solution since

$$G(H_2) = G_{H_2} + G_H + \frac{G e^-_{aq}}{1 + \frac{K_{18}[S]}{K_{10}[H^+]}}$$

Hayon⁽¹²⁾ concluded that $G_H = 0.55 \pm 0.05$ independent of pH in the range 0.6-7. Since it is known that an increase in [S] reduces $G(H_2)$ but not G_H a precursor of the H atom must be excited H_2O^* . However, in acid solutions most H is the product of the reaction of e^-_{aq} with H^+ in the spur



The yield of the primary oxidizing radical, OH, can be found by combinations of experimental results using various systems. In the presence of solutes which react with OH radicals the molecular yield of H_2O_2 is decreased, in a manner comparable to the case of decreased H_2 yield with solutes present which react with the reducing species. Therefore, the yields are dependent on the solutes present and their concentration. For example, Hayon⁽¹³⁾ reports that although the yields of radicals in a solution of Tl^+ are independent of the presence of oxygen there is a dependence of $G(\text{red})$ on solute concentration, increasing from about 2.9 to 3.5 as Tl_2SO_4 concentration changes from 1×10^{-3} to $3 \times 10^{-2}M$.

In aqueous solutions of about pH 0.5, similar to those employed in this laboratory, the yields of radical and molecular products of the γ -radiolysis are about:⁽¹⁴⁾

$$G(\text{red}) = G_H + G e^-_{aq} = 3.66 ,$$

$$G_{\text{OH}} = 2.97 \quad , \quad G_{\text{H}_2} = 0.40 \quad ,$$

$$G_{\text{H}_2\text{O}_2} = 0.76 \quad , \quad G(-\text{H}_2\text{O}) = 4.50$$

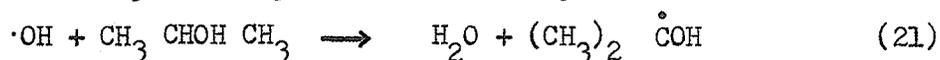
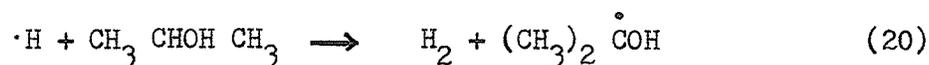
As mentioned, these values are subject to discussion⁽⁶⁾ and other values, although similar, have been quoted.⁽¹¹⁾

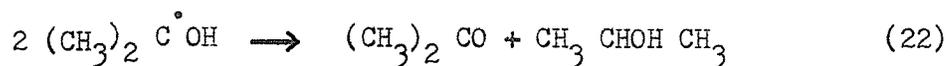
Excellent summaries of the events that take place in the radiolysis of liquid water, including the reactions and species present at various intervals of time, may be found in Spinks and Woods⁽²⁾ Table 8.3 and Matheson⁽⁷⁾ Table 1. A table outlining the various systems used for measuring molecular and radical yields in aqueous solutions is also presented in Table 8.7.⁽²⁾

1.4 Background to this Investigation

Although a system identical to the one investigated has not been reported a great deal of effort has gone into related studies. A number of chemists have investigated the γ -radiation chemistry of the simple organic solutes in aqueous solution. Knowledge of the effects of this radiation on these organic materials in solution may give insight into the nature of the products and reactivity of the radicals of importance to this study. The γ -radiolysis of Tl^{3+} and Tl^+ solutions has also been reported and this, plus the knowledge of the chemistry of thallium so far discovered, is also relevant to this report.

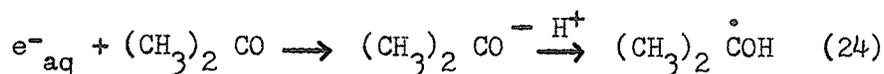
The main product formed when i-PrOH solutions are irradiated is acetone. The expected mechanism is:



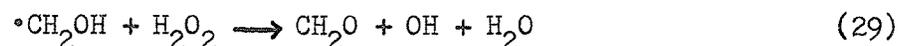
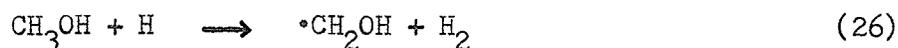
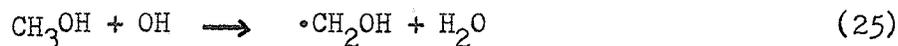


where the disproportionation reaction predominates⁽¹⁵⁾. The predominant radical produced by hydrogen abstraction, $(\text{CH}_3)_2 \overset{\cdot}{\text{C}}\text{OH}$, has been detected by E.S.R. techniques^(16,17), with a small amount of $\cdot\text{CH}_2 \text{CHOH CH}_3$ found to be formed by abstraction of β -hydrogens.⁽¹⁶⁾ Anbar and Meyerstein⁽¹⁸⁾ have estimated that the reactivity of the α -hydrogen in *i*-PrOH towards H atoms is higher than that of β -hydrogen by a factor of about 110 in neutral and acid solutions.

Radiolysis of the major product, acetone, has been examined⁽¹⁹⁾. Since it is produced in relatively low concentrations and since the rate of abstraction for one of the methyl hydrogens is low ($k = 7.5 \times 10^3 \text{ M}^{-1} \text{ sec}^{-1}$)⁽¹⁸⁾ the solutions would be nearly unaffected by its presence. Although a commonly used electron scavenger, any back reaction which would diminish the yield is negligible below $\text{pH} \approx 3$.⁽²⁰⁾



Hart, Thomas and Gordon⁽²¹⁾ reported that the radiolysis products of aqueous MeOH are ethylene glycol, hydrogen and formaldehyde. In a similar experiment, Siberskaya and Pikaev⁽²²⁾ irradiated aqueous 0.4M H_2SO_4 solutions of 0.06M MeOH with Co^{60} γ -rays and found $G(\text{glycol}) = 2.5-2.7$, $G(\text{CH}_2\text{O}) = 0.55 - 1.1$ and $G(\text{H}_2\text{O}_2) = 0.06 - 0.4$ with increased yields for 0.01 M MeOH, in which case $G(\text{H}_2) = 4.05$. The reaction sequence suggested is:



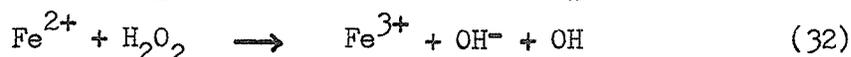
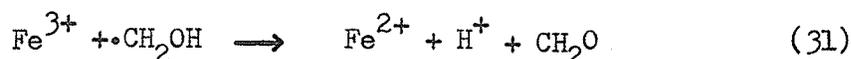
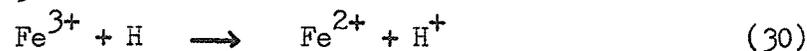
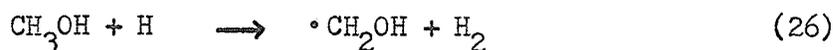
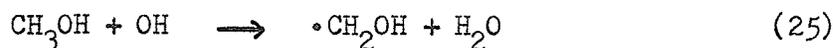
These hydrogen abstraction reactions have been investigated by Thomas⁽²³⁾ using pulse radiolysis and the rate constants estimated to be $4.7 \times 10^8 \text{ M}^{-1} \text{ sec}^{-1}$ and $1.9 \times 10^6 \text{ M}^{-1} \text{ sec}^{-1}$ for reactions (25) and (26) respectively.

Riesz and Burr,⁽²⁴⁾ studying the D atom reaction in irradiated D_2O , concluded that the abstraction took place predominantly at Carbon, as the equations imply. However, further investigation using 0.1M CD_3OH in deaerated water enabled them to determine $G(\text{HD}) = 3.3 \pm 0.1$ and $G(\text{H}_2) = 0.90 \pm 0.03$ over a wide pH range with dosage from 1 to 10×10^{20} ev/l. Since $G_{\text{H}_2} = 0.42$ abstraction from oxygen as well as carbon must occur. In this singular evidence for abstraction from the oxygen they calculate that the rate of hydrogen abstraction from oxygen compared to that from carbon is

$$\frac{K_o}{K_c} = \frac{G(\text{H}_2) - G_{\text{H}_2}}{G(\text{HD})} = 0.15 \pm 0.01$$

E.S.R. studies⁽¹⁶⁾ confirm the existence of the $\cdot\text{CH}_2\text{OH}$ radical produce by OH abstracting hydrogen. From investigations⁽²⁵⁾ of hydrogen abstraction by H atoms it also was concluded that the radical $\cdot\text{CH}_2\text{OH}$ resulted.

Baxendale and Hughes⁽²⁶⁾ found that in the x-irradiation of aqueous 0.02 - 1.0M MeOH solutions containing $0.5 - 5 \times 10^{-3} \text{M Fe}^{3+}$ or Cu^{2+} the only products were formaldehyde, hydrogen and Fe^{2+} or Cu^+ . Using the proposed mechanism



they accounted for the good oxidation reduction balance

$$2 G(\text{H}_2) + G(\text{Fe}^{2+}) = 2 G(\text{CH}_2\text{O})$$

where

$$G(\text{H}_2) = G_{\text{H}_2} + G_{\text{H}} = 3.97$$

$$G(\text{Fe}^{2+}) = G_{\text{OH}} + G_{\text{H}} = 6.13$$

$$G(\text{CH}_2\text{O}) = G_{\text{OH}} + G_{\text{H}_2\text{O}_2} + \alpha G_{\text{H}} = 6.71$$

for

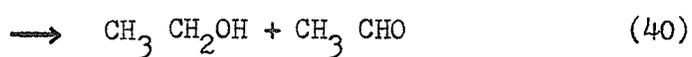
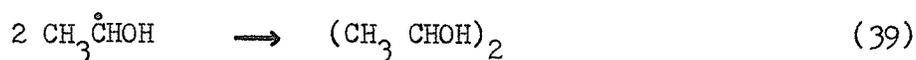
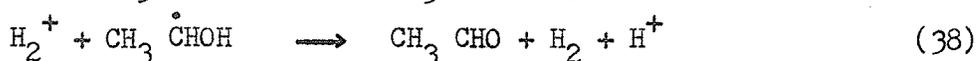
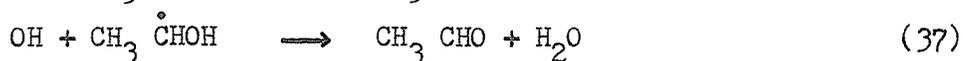
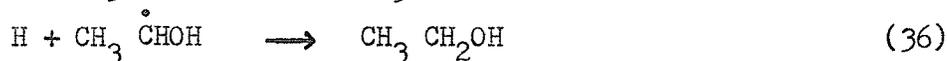
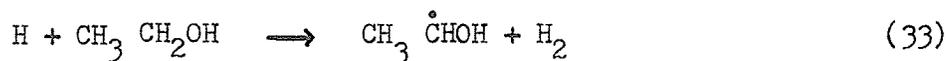
$$\alpha = \frac{K_{26} [\text{CH}_3\text{OH}]}{K_{30} [\text{Fe}^{3+}] + K_{26} [\text{CH}_3\text{OH}]} = 1$$

In another study⁽²⁵⁾ by introducing $1 \times 10^{-3} \text{M Pb}^{2+}$ into 0.1M MeOH it was determined that $G(\text{H}_2) = 1.02$ and $G(\text{CH}_2\text{O}) = 4.1$. This second study by Baxendale and his colleagues⁽²⁵⁾ further confirms the implication that in the presence of readily reducible metallic cations the only major oxidation product is CH_2O , contrasting the production of glycol as well as CH_2O reported for uncontaminated aqueous MeOH solutions^(21,22).

The effect of radiolysis of the formaldehyde formed, a process known to yield MeOH and HCOOH, would not be expected to interfere with the system in the presence of the much higher concentration of MeOH.

In the γ -irradiation of deaerated solutions of E t OH the products are confirmed to be H₂, acetaldehyde, butane-2,3-diol and H₂O₂.^(27,28,29,30)

In acid solutions the expected reaction sequence is:



The hydrogen abstraction predominates from α -position.^(24,30,31) The results of isotopic studies conducted by Lifshitz and Stein⁽³¹⁾ confirmed that although the α -position in E t OH is attacked preferentially by H and OH there is β -position attack as well, but no attack on the hydroxylic hydrogen. The selectivity of abstraction is in the order of the bond strengths.

The major organic product is the diol. According to Seddon and Allen⁽³²⁾ the disproportionation reaction to form the aldehyde and alcohol occurs in about 30% of the biradical reactions. Dorfman and Taub^(28,29) drew similar conclusions listing $2k_{39} = 8.8 \pm 2.1 \times 10^8 \text{ M}^{-1} \text{ sec}^{-1}$ and

$2k_{40} = 2.2 \pm 0.5 \times 10^8 \text{ M}^{-1} \text{ sec}^{-1}$. As the pH is lowered the yields of aldehyde and H_2 increase. This can be explained by the inclusion of H_2^+ in the proposed mechanism. (30)

Thus it can be seen that for primary and secondary alcohols the reactions are similar when the solutions are irradiated. Formation of the organic radical by hydrogen abstraction is by the same mechanism for each but the reactivity increases from MeOH, EtOH to i-PrOH. (23)

In the absence of α -hydrogens, as with t-BuOH, radical reactions are much slower and the β -hydrogen is attacked. The main radical formed is $\cdot\text{CH}_2\text{C}(\text{CH}_3)_2\text{OH}$ (16,17). It has been noticed (31), as well, that the total hydrogen yield is much lower for t-BuOH than for EtOH. This could be explained if the H radicals, formed by the radiolysis of water, attacked the carbon-oxygen bond, which is weaker for t-BuOH, and thus produced t-Bu $^\circ$ radicals and H_2O . Any chain reaction involved in the oxidation of primary or secondary alcohols is no longer likely to be a chain process for this tertiary alcohol. (33)

Organic compounds other than the alcohols have been investigated. Hart (34) investigated the γ -ray induced oxidation of dilute HCOOH in air free aqueous solutions. Equimolar amounts of H_2 and CO_2 were produced, independent of dose rate and formic acid concentration from 0.001 to 0.01 M and linearly dependent on total dose absorbed. The mechanism is believed to be:

