Steady-State γ-Radiolysis of Aqueous 2-Butanone (MEK) and Its Effect on Aqueous Iodine Volatility in Containment.

by

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Abstract

Iodine-131 has been recognized as one of the most hazardous fission products present in the used fuel of a nuclear power reactor. In the event of a loss-of-coolant accident (LOCA) in a water cooled reactor, a break in the primary cooling circuit followed by fuel failure could release a significant fraction of the core inventory of radioactive iodine into containment. Non-volatile aqueous iodide may be converted into volatile I_2 and subsequently released into the environment. This process has been shown to be affected by the radiolytic breakdown of dissolved organic compounds that may be present in containment. In this study, the effect of a model organic compound, 2-butanone (methylethylketone, MEK), on iodine chemistry was investigated.

In this work, MEK was γ-irradiated in aqueous solutions and the formation of decay products were followed by a various analytical methods (HPLC, GC, GC/MS and MS) to establish a decay profile. For aerated solutions, MEK degradation produced products, of continually decreasing size. In contrast, in non-aerated solutions where hydroxyl radical was not scavenged evidence of dimerization was observed.

Under aerated conditions the main pathway for radiolysis is the abstraction of a hydrogen atom by hydroxyl radical attack to give MEK radical which undergoes reaction with dissolved oxygen, producing an organic peroxide. This species recombines to form a tetroxide intermediate that subsequently dissociates to form carbonyl compounds.

Based on this understanding and literature data, a hypothetical decay pathway for the breakdown of MEK under aerated conditions was postulated and used to create a computer model of MEK decay. The predictions of this model showed good agreement with the experimental data observed for pH evolution, MEK degradation, product formation and decay.

A preliminary study of the effects of iodide on the decay of aqueous MEK as also conducted. This work revealed that methyl iodide was formed for all except reducing conditions and supports the idea that methyl iodide is formed by a reaction with iodine (I_2).

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Introduction

1.1 The Importance of Iodine-131

The CANDU® (CANada Deuterium Uranium) nuclear reactor system uses natural uranium oxide fuel and deuterium oxide (heavy water) moderator and coolant to generate electrical energy from the heat generated by nuclear fission. During this process, energy is released into the heavy water coolant when the ^{235}U atom decays, yielding fast neutrons and a variety of fission products.

The CANDU power reactor consists of primary and secondary heat transfer circuits. The primary circuit, which contains the heavy water coolant and fuel at about 300°C, transfers heat to the secondary circuit, which contains the steam generators that drive the turbine generator to produce electricity.

In the event of a loss-of-coolant accident (LOCA) in a CANDU® nuclear reactor, a break in the primary cooling circuit followed by fuel failure could release some fraction of the core inventory of fission products into the reactor containment building. This radioactive material will collect on the floor of the containment building and be mixed with water from the safety spray systems that will activate in the event of such an accident [1]. Under these conditions hydrogen gas may be formed by the radiolysis of water. To prevent the possibility of an explosion, controlled venting of the containment building may be required. Therefore, in the event of such an accident, it is important to have the ability to predict the amounts of the most hazardous radionuclides expected in the containment atmosphere as a function of time.

Iodine-131 is recognized as the most hazardous radionuclide present in used nuclear fuel because of its large inventory, its ability to form volatile species and the fact that it is easily absorbed by living organisms and incorporated into the food chain [2]. Radioactive iodine that has been ingested into the human body is concentrated in the thyroid gland, increasing the risk of thyroid cancer [3,4]. Therefore, to minimize this risk, it is important to be able to mitigate the volatility of iodine in containment

Evidence obtained in experiments as well as thermodynamic calculations, suggests that in the event of most LOCA reactor accidents, iodine will be initially released into containment in a reduced form, as cesium iodide (CsI), which will easily dissolve into the large amounts for water present. Radioactive iodine in the form of iodide (I^-) is not considered a major hazard, as it is non-volatile [5,6,7,8, 9, 10].

The chemistry of aqueous iodine species under containment LOCA conditions has been studied for many years. This chemistry has been shown to be very complex, and strongly dependent on solution conditions such as pH, dissolved oxygen concentration and the presence of ionizing radiation. Under these conditions, there are a number of processes that can oxidize the non-volatile iodide (I^-) into volatile molecular iodine (I_2) [1]. The subsequent aqueous chemistry of I_2 is also complex; it can undergo further oxidation to form non-volatile iodine oxides or be converted back to iodide by a variety of thermal and radiolytic processes [11]. Understanding the overall chemistry of these iodine systems is essential to determine the optimal conditions within containment after an accident, so that the potential release of radioactive iodine to the environment is minimized. Furthermore, the effects on these processes of other solutes, such as organic compounds, present in the containment building, must be considered in any realistic study of iodine behavior [11].

It has been shown that aliphatic organic compounds in aqueous solutions can have a large effect on many solution parameters that may indirectly or directly affect iodine chemistry and its speciation. Possible sources of organic compounds inside a reactor containment building are paints, wire insulation and lubricating compounds. For example, the paint used in containment typically contains, 2-butanone (Methyl ethyl ketone, MEK), methyl isobutyl ketone, ethanol and toluene [12]. The effect of these species on iodine chemistry in containment during accident scenarios have recently become an area of much interest in reactor safety chemistry [11].

Sump solution conditions have also been shown to be affected by the radiolysis of aliphatic species dissolved in solution. The reaction of the radiation-induced degradation species of these organic compounds with dissolved oxygen has been shown to produce aliphatic acids. This results in both the lowering of solution pH and the dissolved oxygen concentration in solution, with both conditions promoting the formation of volatile iodine species. Also, reactions of organic species with iodine (I_2) can produce volatile iodoalkanes under these containment conditions [11,13].

In this study, the radiolytic degradation of a model organic compound MEK in aqueous solution under simulated LOCA reactor accident conditions was investigated. A mechanistic breakdown pathway was derived from literature data and used to construct a computer model for the breakdown of MEK under aqueous containment conditions. The predicted pathway created by this model was then compared to the experimental data to evaluate the important parameters in this process. Based on this understanding, scoping studies into the breakdown of MEK in the presence of iodide were performed.

1.2 Radiation Dosimetry

Determining the amount of energy absorbed by a sample from radiation is essential for any quantitative study of radiation chemistry. The ionizing radiation energy absorbed per unit mass of an irradiated material is termed the absorbed dose. This value is dependent on radiation intensity as well as the composition of the specific irradiated material. One common way of determining this value is through the use of dosimeters to determine the dose provided by a particular radiation source. For liquid samples, a useful dosimeter is the Fricke dosimeter, which involves the radiation-induced oxidation of ferrous ion ferris ion at low pH in the presence of oxygen [14]. The initial solution consists of an air-saturated 1×10^{-3} M ferrous sulfate, 1×10^{-3} M sodium chloride in 0.4 M sulfuric acid solution.

Since, the presence of organic impurities affects the yield of the dosimeter, only high purity reagents and water must be used and all containers must be carefully cleaned.

The absorbed dose is determined by placing the dosimeter solution in a radiation field for a measured period of time and measuring the yield of ferric ion produced. To minimize any wall effects the container used should be at least 1 cm in diameter for γ-radiation. The average absorbed dose (D_D) is calculated using the equation

$$D_D = (2.77\,\Delta A / l)\ Gy$$

in which ΔA is the difference between the absorbance of the irradiated and non-irradiated Fricke solutions at 340 nm, measured immediately after irradiation, and l is the optical path length used when determining the absorbance measured in meters.

Oxygen is consumed during the irradiation of the Fricke solution and when all the oxygen is exhausted the solution will no longer correctly respond. Typically the absorbed dose is kept between 30 and 350 Gy for γ-radiation. The Fricke dosimeter response is linear over this range for air-saturated solutions. This range can be increased if the solution is purged with pure oxygen just prior to irradiation [14].

1.3 Water Radiolysis

In dilute aqueous solutions, γ-radiation is absorbed by water molecules which break down to give various reactive species that will readily attack any dissolved organic compounds. The affected organic compounds will continue to break down providing further reactive species. Therefore, to understand the effects of radiolysis on dissolved species in dilute aqueous solution, a thorough understanding of the initial water radiolysis process is necessary.

The absorption of radiation energy by water forms tracks of excited and ionized species. The number of ionized and excited species inside a solution is dependent on the total amount of energy absorbed, while the local concentrations of these species along the particle tracks are a function of the rate at which this energy is absorbed. To describe the rate of energy deposition provided by a moving particle the term linear energy transfer (LET) is used.

As the energy is deposited into the water, "packets" of secondary electrons are formed along the track, with a distribution of sizes and energies. These packets of secondary electrons can be divided into different groups according to their energy; relatively low energy packets have a short range in water and any secondary ionization and excitation will occur close to the original track to give spurs (<100 eV) or blobs (100 to 500 eV) of excited and ionized species. Secondary electrons with higher energies form additional tracks which branch from the primary track. Lower energy tracks are known as short tracks (500 to 5000 eV) while high energy tracks are called branch tracks (>5000 eV).

The term spur is often generically used to describe both spurs (as defined previously) and blobs. For γ-radiation it has been calculated that spurs occur at intervals of about 1 μm and have an initial diameter of 2 nm. Spurs persist for a short time after formation but disappear as the newly formed species diffuse apart. Fast reactions, such as ion neutralization and the fragmentation of excited ions and molecules to give radicals, occur before the spurs expand and dissipate.

The primary reactions in the tracks caused by the radiolysis of liquid water at room temperature have been shown to be [15,16]:

Note: The symbol → refers to the absorbtion of γ radiation by a water molecule.

$H_2O \rightarrow H_2O^+, e^-, H_2O^*$ (1-1)

$H_2O^+ + H_2O \rightarrow H_3O^+ + {\bullet}OH$ (1-2)

$H_2O^* \rightarrow H_2O$ (1-3)

$H_2O^* \rightarrow [H{\bullet} + {\bullet}OH] \rightarrow H_2O$ (1-4)

$e^- \rightarrow e_{aq}^-$ (1-5)

Hydrated Electron Reactions:

$2\,e_{aq}^- + 2\,H_2O \rightarrow 2\,OH^- + 2\,H_2$ $k = 5.5 \times 10^9\ dm^3\ mol^{-1}\ s^{-1}$ (1-6)

$e_{aq}^- + H_2O \rightleftharpoons \bullet H + OH^-$ $k_f = 19\ dm^3\ mol^{-1}\ s^{-1}$, $k_b = 2.2 \times 10^7\ dm^3\ mol^{-1}\ s^{-1}$ (1-7)

$e_{aq}^- + \bullet H + H_2O \rightarrow OH^- + H_2$ $k = 2.5 \times 10^{10}\ dm^3\ mol^{-1}\ s^{-1}$ (1-8)

$e_{aq}^- + H^+ \rightarrow \bullet H$ $k = 2.3 \times 10^{10}\ dm^3\ mol^{-1}\ s^{-1}$ (1-9)

$e_{aq}^- + \bullet OH \rightarrow OH^-$ $k = 3.0 \times 10^{10}\ dm^3\ mol^{-1}\ s^{-1}$ (1-10)

$e_{aq}^- + H_2O_2 \rightarrow \bullet OH + OH^-$ $k = 1.1 \times 10^{10}\ dm^3\ mol^{-1}\ s^{-1}$ (1-11)

$e_{aq}^- + HO_2^- \rightarrow \bullet O^- + OH^-$ $k = 3.5 \times 10^{9}\ dm^3\ mol^{-1}\ s^{-1}$ (1-12)

$e_{aq}^- + \bullet O^- + H_2O \rightarrow 2\ OH^-$ $k = 2.2 \times 10^{10}\ dm^3\ mol^{-1}\ s^{-1}$ (1-13)

$e_{aq}^- + O_2\bullet^- + H_2O \rightarrow \bullet OH + HO_2^-$ $k = 1.3 \times 10^{10}\ dm^3\ mol^{-1}\ s^{-1}$ (1-14)

$e_{aq}^- + O_2 \rightarrow O_2\bullet^-$ $k = 1.9 \times 10^{10}\ dm^3\ mol^{-1}\ s^{-1}$ (1-15)

$\bullet$H Atom Reactions:

$\bullet H + \bullet OH \rightarrow H_2O$ $k = 7.0 \times 10^{9}\ dm^3\ mol^{-1}\ s^{-1}$ (1-16)

$\bullet H + \bullet H \rightarrow H_2$ $k = 7.75 \times 10^{9}\ dm^3\ mol^{-1}\ s^{-1}$ (1-17)

$\bullet H + H_2O \rightarrow H_2 + \bullet OH$ $k = 10\ dm^3\ mol^{-1}\ s^{-1}$ (1-18)

$\bullet H + \bullet HO_2 \rightarrow H_2O_2$ $k = 10^{9}\ dm^3\ mol^{-1}\ s^{-1}$ (1-19)

$\bullet H + H_2O_2 \rightarrow H_2O + \bullet OH$ $k = 9.0 \times 10^{7}\ dm^3\ mol^{-1}\ s^{-1}$ (1-20)

$\bullet H + O_2 \rightarrow \bullet HO_2$ $k = 2.1 \times 10^{10}\ dm^3\ mol^{-1}\ s^{-1}$ (1-21)

$\bullet H + O_2\bullet^- \rightarrow HO_2^-$ $k = 2.0 \times 10^{10}\ dm^3\ mol^{-1}\ s^{-1}$ (1-22)

$\bullet$OH Atom Reactions:

$2\ \bullet OH \rightarrow H_2O_2$ $k = 5.5 \times 10^{9}\ dm^3\ mol^{-1}\ s^{-1}$ (1-23)

$\bullet OH + H_2O_2 \rightarrow \bullet HO_2 + H_2O$ $k = 2.7 \times 10^{7}\ dm^3\ mol^{-1}\ s^{-1}$ (1-24)

$\bullet OH + H_2 \rightarrow \bullet H + H_2O$ $k = 4.2 \times 10^{7}\ dm^3\ mol^{-1}\ s^{-1}$ (1-25)

$\bullet OH + \bullet HO_2 \rightarrow O_2 + H_2O$ $k = 6.0 \times 10^{9}\ dm^3\ mol^{-1}\ s^{-1}$ (1-26)

$$\bullet OH + OH^- \rightleftharpoons \bullet O^- + H_2O \quad k_f = 1.2 \times 10^{10}\ dm^3\ mol^{-1}\ s^{-1},\ k_b = 1.7 \times 10^6\ dm^3\ mol^{-1}\ s^{-1} \tag{1-27}$$

$$\bullet OH + HO_2^- \rightarrow \bullet HO_2 + OH^- \quad k = 7.5 \times 10^9\ dm^3\ mol^{-1}\ s^{-1} \tag{1-28}$$

$$\bullet OH + \bullet O_2^- \rightarrow O_2 + OH^- \quad k = 8.0 \times 10^9\ dm^3\ mol^{-1}\ s^{-1} \tag{1-29}$$

$$H^+ + \bullet O_2^- \rightleftharpoons \bullet HO_2 \quad k_f = 4.5 \times 10^{10}\ dm^3\ mol^{-1}\ s^{-1},\ k_b = 6.75 \times 10^5\ s^{-1} \tag{1-30}$$

$$H^+ + HO_2^- \rightleftharpoons H_2O_2 \quad k_f = 2.0 \times 10^{10}\ dm^3\ mol^{-1}\ s^{-1},\ k_b = 3.56 \times 10^{-2}\ s^{-1} \tag{1-31}$$

$\bullet O^-$ Reactions:

$$\bullet O^- + \bullet OH \rightarrow HO_2^- \quad k = 2.0 \times 10^{10}\ dm^3\ mol^{-1}\ s^{-1} \tag{1-32}$$

$$\bullet O^- + H_2O_2 \rightarrow \bullet O_2^- + H_2O \quad k = 2.0 \times 10^8\ dm^3\ mol^{-1}\ s^{-1} \tag{1-33}$$

$$\bullet O^- + H_2 \rightarrow \bullet H + OH^- \quad k = 8.0 \times 10^7\ dm^3\ mol^{-1}\ s^{-1} \tag{1-34}$$

$$\bullet O^- + HO_2^- \rightarrow OH^- + \bullet O_2^- \quad k = 4.0 \times 10^8\ dm^3\ mol^{-1}\ s^{-1} \tag{1-35}$$

$$\bullet O^- + \bullet O_2^- + H_2O \rightarrow 2\ OH^- + O_2 \quad k = 6.0 \times 10^8\ dm^3\ mol^{-1}\ s^{-1} \tag{1-36}$$

$$\bullet O^- + O_2 \rightleftharpoons \bullet O_3^- \quad k_f = 3.6 \times 10^9\ dm^3\ mol^{-1}\ s^{-1},\ k_b = 3.0 \times 10^2\ s^{-1} \tag{1-37}$$

$$\bullet O^- + \bullet O^- \rightarrow O_2^{2-} \quad k = 1.0 \times 10^9\ dm^3\ mol^{-1}\ s^{-1} \tag{1-38}$$

$$\bullet O_3^- + H_2O_2 \rightarrow \bullet O_2^- + O_2 + H_2O \quad k = 1.6 \times 10^6\ dm^3\ mol^{-1}\ s^{-1} \tag{1-39}$$

$$\bullet O_3^- + H_2 \rightarrow O_2 + \bullet H + OH^- \quad k = 2.5 \times 10^5\ dm^3\ mol^{-1}\ s^{-1} \tag{1-40}$$

$$\bullet HO_2 + \bullet O_2^- \rightarrow O_2 + HO_2^- \quad k = 8.9 \times 10^7\ dm^3\ mol^{-1}\ s^{-1} \tag{1-41}$$

$$2\ \bullet HO_2 \rightarrow H_2O_2 + O_2 \quad k = 2.0 \times 10^6\ dm^3\ mol^{-1}\ s^{-1} \tag{1-42}$$

$$H_2O_2 \rightarrow 2\ \bullet OH \quad k = 2.3 \times 10^{-7}\ s^{-1} \tag{1-43}$$

In liquid water, all charged species at thermal energies become hydrated within 10^{-11} s. Excitation energy is lost rapidly in liquids which allows excited molecules to return to their ground state, preventing dissociation by collision processes.

The properties of water ensure that virtually all electrons formed become hydrated, while positive ions react to form radicals before diffusing from the track or spur. For regions of high radical concentrations, reactions between radicals inside the spur are favored, these intra-spur reactions give molecular products such as hydrogen, oxygen and hydrogen peroxide. Spurs and tracks diffuse with time to give a homogeneous distribution of radical and molecular species throughout the solution.

The most abundant and reactive species produced during this process are hydrogen atoms, hydroxyl radicals, solvated electrons, hydrogen peroxide and other species as given by equation 1-44 [14].

$$4.2\ H_2O \rightarrow 2.7\ e_{aq}^- + 0.6\ \bullet H + 2.7\ \bullet OH + 0.6\ H_2O_2 + 2.7\ H^+ + 0.03\ HO_2\bullet + 0.4\ H_2 \qquad (1\text{-}44)$$

The coefficients listed in Equation 1-44 are G-values, and represent the number of the particular species created per 100 eV absorbed for neutral solutions approximately 1 µsec after irradiation. Hydroxyl radicals behave as oxidizing species, electrons as reducing species, and hydrogen peroxide and hydrogen atom can behave as either.

The relative yields of these primary species are greatly affected by solution parameters. Under acidic conditions, protons scavenge electrons to give atomic hydrogen (H•). Thus solutions of low pH values can be used to study the effects of hydroxy radical and atomic hydrogen in solution. Under basic conditions the effects of solvated electrons and hydroxyl radicals can be determined, since atomic hydrogen reacts rapidly with hydroxide anion to give solvated electrons and water [14,16,17]. The addition of MEK has a large effect on the fate of reactive species formed by the radiolysis of water, as even at low concentrations organic species scavenge virtually all of the reactive species produced by water radiolysis.

In this study, MEK was chosen as a model organic compound because it has many of the characteristics of common organic species found in paints used in containment (Figure 1-1). Another advantage of using MEK is that its relatively simple structure allows better quantitative analysis of the thermal and radiolytic degradation processes.

It should also be noted that MEK cannot be used as a model for the radiolysis of some organic molecules expected within containment. For example, long-chain aliphatic ketones undergo β-scission due to reaction with solvated electron, while MEK does not. This process will be discussed later.

1.4 Effects of Radiolysis on Iodine Speciation

Because iodine (I_2) is very volatile, one means of containing radioactive iodine is to maintain conditions that promote the formation of the non-volatile and soluble species such as iodide (I^-).

Many radiolytic reactions of iodine species in water have been discussed in the literature[11,18,19]. The most significant of these, from a volatility perspective are the reactions of iodine species with hydroxyl radicals, solvated electrons and superoxide ions. Equations 1-45 through 1-47 show the oxidation of iodide by hydroxyl radical to produce I_3^- which exists in equilibrium with I_2,

$$I^- + \bullet OH \rightarrow \bullet I + OH^- \quad (1\text{-}45)$$

$$I^- + \bullet I \rightleftharpoons \bullet I_2^- \quad (1\text{-}46)$$

$$2 \bullet I_2^- \rightarrow I^- + I_3^- \quad (1\text{-}47)$$

$$I_3^- \rightleftharpoons I^- + I_2 \quad (1\text{-}48)$$

Iodine can also be reduced back to iodide by reaction with solvated electrons.

$$I_2 + e_{aq}^- \rightarrow \bullet I_2^- \quad (1\text{-}49)$$

$$\bullet I_2^- + e_{aq}^- \rightarrow 2\, I^- \quad (1\text{-}50)$$

In aqueous solution iodine also undergoes thermal hydrolysis as described in Equations 1-51 and 1-52.

$$I_2 + H_2O \rightleftharpoons HOI + I^- + H^+ \quad (1\text{-}51)$$

$$I_2 + OH^- \rightleftharpoons OI^- + I^- + H^+ \quad (1\text{-}52)$$

Under containment conditions, hypoiodous acid (HOI/OI$^-$) is formed, which subsequently disproportionates (Equation 1-53) to form IO_2^- that further reacts with HOI to give water soluble, non-volatile, iodate (IO_3^-)(Equation 1-54).

$$HOI + HOI \rightarrow IO_2^- + I^- + 2H^+ \qquad (1\text{-}53)$$

$$HOI + IO_2^- \rightarrow IO_3^- + I^- + H^+ \qquad (1\text{-}54)$$

Hydrogen peroxide reduces iodine to give iodide, but can also oxidize iodide back to iodine [16,20,21].

$$I_2 + H_2O_2 + H_2O \rightarrow 2\, I^- + 2\, H_3O^+ + O_2 \qquad (1\text{-}55)$$

$$2\, H^+ + 2I^- + H_2O_2 \rightarrow I_2 + 2\, H_2O \qquad (1\text{-}56)$$

In aerated solution, the concentration of oxygen will effectively scavenge all of the formed solvated electrons and hydrogen atoms (Equations 1-15 and 1-21) to form superoxide anion and its conjugate acid, the perhydroxyl radical. These species also play an important role in the reduction of iodine [22,23].

$$O_2^- + H_3O^+ \rightleftharpoons HO_2 + H_2O \qquad pKa = 4.8 \qquad (1\text{-}57)$$

$$I_2 + O_2^- \rightleftharpoons I_2^- + O_2 \qquad (1\text{-}58)$$

$$I_2 + HO_2 \rightleftharpoons H^+ + I_2^- + O_2 \tag{1-59}$$

1.5 Radiolysis of Aqueous Organic Species

For dissolved organic compounds the initial reaction of the directly formed water radiolysis species proceed by abstraction and addition reactions. Aliphatic and aromatic compounds react differently toward hydroxyl radicals. Generally, aromatic compounds react by hydroxylation of the ring to give •OH adducts [24,25], while aliphatic compounds react by hydrogen abstraction to give radicals and water. Solvated electrons react with aromatic and aliphatic compounds by addition to any unsaturated bonds. For aromatic and aliphatic a ketones, the reaction is a very selective addition to the carbonyl group followed by protonation, forming ketyl radicals [24]. An aromatic compound without ketone group, such as benzene, reacts with solvated electron by addition to the ring giving a radical anion species that hydrates to give a cyclohexadienyl radical with a delocalized unpaired electron [26].

1.5.1 Reactions of Hydroxyl Radical/Hydrogen atoms

Hydrogen atoms and hydroxyl radicals will abstract hydrogen from aliphatic compounds in solution, forming organic radicals and molecular hydrogen (H_2) or water respectively [14,27].

$RH + \bullet OH \text{ (or } \bullet H) \rightarrow R\bullet + H_2O \text{ (or } H_2)$ (1-59)

These radicals will react via disproportionation, polymerization, or in aerated solutions by the addition of dissolved oxygen to give organic peroxides.

$2\ \bullet CH_2OH \rightarrow (CH_2OH)_2$ (1-60)

$2\ \bullet CH_2OH \rightarrow CH_3OH + HCHO$ (1-61)

$\bullet R + O_2 \rightarrow RO_2\bullet$ (1-62)

In aerated solutions, the dominant pathway is the reaction of dissolved oxygen [14]. This reaction is very rapid, occurring at near diffusion controlled rates. One important effect of this process is to prevent the organic radical from undergoing repair, by extracting a hydrogen atom from another molecule, to give the parent compound. This peroxidation process is known as the oxygen effect.

A survey of the literature showed that the breakdown reactions of peroxyacetone radicals has been fully elucidated in aerated solutions, with decay occurring by self-termination reactions [28]. This bimolecular reaction forms a short-lived, unstable tetroxide intermediate that decays by many different pathways including dissociation back to the constituent organo peroxy radicals [28].

$2\ \bullet O_2CH_2COCH_3 \rightleftharpoons [CH_3COCH_2\text{-}O_4\text{-}CH_2COCH_3] \rightarrow \text{products}$ (1-63)

The breakdown of the aceto-tetroxide intermediate was shown to have the following pathways. In the most important reaction about half of the reaction proceeds by a concerted reaction to give hydrogen peroxide and methylglyoxal.

$$[CH_3COCH_2\text{-}O_4\text{-}CH_2COCH_3] \rightarrow 2\,CH_3COCHO + H_2O_2 \quad (1\text{-}64)$$

The second most important pathway, occurring for slightly more than one quarter of these intermediates, proceeds via the Russell reaction [29] giving methylglyoxal, hydroxy-2-propanone and oxygen.

$$[CH_3COCH_2\text{-}O_4\text{-}CH_2COCH_3] \rightarrow CH_3COCH_2OH + CH_3COCHO + O_2 \quad (1\text{-}65)$$

The third pathway, accounting for about one eighth of the reaction, proceeds by a concerted process giving formaldehyde, oxygen and acetyl radicals.

$$[CH_3COCH_2\text{-}O_4\text{-}CH_2COCH_3] \rightarrow 2\,CH_2O + 2\,CH_3C\bullet O + O_2 \quad (1\text{-}66)$$

A fourth process that also accounts for about one eighth of the reaction, proceeds by a two step radical process where the intermediate eliminates molecular oxygen to give two alkoxide radicals that also decay to give formaldehyde and an acetyl radical (Equation 1-68).

$$[CH_3COCH_2\text{-}O_4\text{-}CH_2COCH_3] \rightarrow 2\ \bullet O\text{-}CH_2COCH_3 + O_2 \qquad (1\text{-}67)$$

$$\bullet O\text{-}CH_2COCH_3 \rightarrow CH_2O + CH_3C\bullet O \qquad (1\text{-}68)$$

This later pathway is important as a potential decay mechanism for MEK peroxy radicals.

1.5.2 Reactions with Solvated Electron

Solvated electrons are very reactive towards carbonyl compounds. The primary product of the its reaction with ketone is a strongly basic negative ion known as a ketyl radical. For ketones, the reactivity decreases as the electron-withdrawing ability of the substituent groups increases. This effect correlates with the observation that groups with higher electron-withdrawing capacity cause the C=O bond to shorten, which increases the electron density in the π orbital, resulting in a decreased tendency for the bond to accommodate another electron.

The ketyl radical exists in an equilibrium [24,30]

$$R_1(C{=}O)R_2 + e^- \rightarrow R_1(C\text{-}O\bullet^-)R_2 \qquad (1\text{-}69)$$

$$R_1(C\text{-}O\bullet^-)R_2 + H^+ \rightleftharpoons R_1(\bullet COH)R_2 \qquad (1\text{-}70)$$

where the protonated form can undergo disproportionation into the parent ketone and the corresponding alcohol [14].

$$2(R_1(\bullet COH)R_2) \rightarrow R_1(C{=}O)R_2 + R_1CH(OH)R_2 \qquad (1\text{-}71)$$

For ketones with three or more carbons on either side of the carbonyl group a process known as β-scission can cause the molecule to cleave between the carbons α- and β- to the carbonyl carbon. As the aliphatic chain gets larger this pathway becomes more important because the free radical generated is more stable [31].

$$R_1\text{-}(\bullet COH)\text{-}CH_2\text{-}CH_2\text{-}CH_2\text{-}R_2 \rightarrow R_1\text{-}(COH){=}CH_2 + \bullet CH_2\text{-}CH_2\text{-}R_2 \qquad (1\text{-}72)$$

$$R_1\text{-}(COH){=}CH_2 \rightleftharpoons R_1\text{-}CO\text{-}CH_3 \qquad (1\text{-}73)$$

In aerated aqueous solutions, oxygen present at a concentration of 250 μM is sufficient to scavenge 99.8 % of the hydrated electrons relative to their reaction with a 1×10^{-3} M organic solute (Reaction 1-15).

$$RH + e_{aq}^{-} \rightarrow \text{Product} \qquad k \approx 1\times10^{7}\ dm^{3}\ mol^{-1}\ s^{-1} \qquad (1\text{-}75)$$

Also, any ketyl radical that is formed will react very rapidly with dissolved oxygen to give peroxy compounds.

$$R_1C\bullet OHR_2 + O_2 \rightarrow R_1C(OO\bullet)OHR_2 \qquad (1\text{-}76)$$

This α-hydroxyalkylperoxyl radical decays in a first order reaction to give the original ketone and $HO_2\bullet$ [32].

1.6 Potential Effects of MEK on Aqueous Iodine Speciation

The presence of organic impurities in solution may shift the equilibrium between I^- and I_2 by altering solution pH, as well as by changing the concentrations of reactive species such as hydroxyl radical and the solvated electron that are available for reaction with iodine species in solution [11].

As stated previously, the reaction of hydroxyl radicals with MEK gives organic peroxides in aerated solution. These species will breakdown by a series of self-termination reactions to give organic acids as major products. The effect of this is to lower the pH of the solution, thereby influencing both the hydrolysis of iodine (I_2) (Equation 1-51) and its reduction by peroxide (Equation 1-55), and superoxide (Equations 1-58 and 1-59), which are inversely dependent on acid concentration [11].

Organic radicals can also react with molecular iodine in solution to give low molecular weight organic iodides. These species are volatile and therefore also need to have their formation processes characterized for a full understanding of the total iodine chemistry in containment.

1.7 Purpose

The purpose of this study is to develop an understanding of the degradation mechanisms involved in the γ-radiolysis of aqueous MEK, in order to allow the effects of organic impurities on overall iodine volatility under reactor LOCA conditions to be evaluated.

Experimental

2.1 Sample Preparation

Glass irradiation vessels of volumes 25 and 50 mL were constructed for use in this study. Each irradiation vessel had a single neck with a stopcock and threaded top to allow for the inclusion of a septum. To safeguard solution purity, irradiation vessels were washed and rinsed in distilled water and baked at 500 °C to remove organic films from the surface prior to use. Syringe needles were passed through the septum and stopcock into the main vessel for vessel purging and sample addition. This arrangement provided a means to add purged solutions to the irradiation vessel without room air contamination.

The water used for all of the solutions in this study was distilled and filtered with a Millipore Milli-Q water purification system. Stock MEK solutions were made up in a 250 mL mixing vessel with a removable septum. Purified water was adjusted to pH 10.0 and added to the mixing vessel. Two syringe needles were placed into the mixing vessel through the septum and the solution was purged for approximately 20 minutes. Any reagents that were required to control solution conditions (i.e. radical scavengers) were added (see Table 2-1). Finally MEK was added to give a concentration of 1.00×10^{-3} M. The solution was then mixed for at least 30 minutes.

Each empty irradiation vessel was purged of air for 2 minutes. To prevent the introduction of air during the removal of solution from the mixing

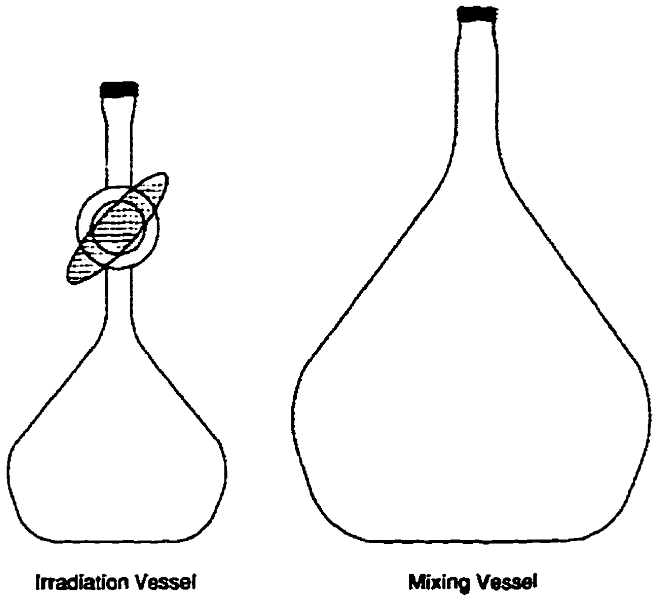

Figure 2-1 - Irradiation vessels

vessel, purge gas was added to displace the volume of the sample removed. The sample liquid was added to each irradiation vessel, the stop cock was closed and the septum was removed. For aerated solutions 50 mL vessels were used with 5 mL liquid samples. For all the other series, 25 mL irradiation vessels were filled to capacity. Samples were then irradiated and analyzed as described below.

2.2 Irradiation Conditions and Dosimetry

Samples were irradiated in one of two Model 220 Gammacell ^{60}Co irradiators at dose rates that were determined by Fricke dosimetry. The actual dose rates for specific runs were calculated according to the run date to correct for the decay of the ^{60}Co source.

Trials were carried out with added radical scavengers, to elucidate the behavior of individual water radiolysis species formed during irradiation. A method of isolating the effect of hydroxyl radicals is to saturate a solution with nitrous oxide (N_2O) prior to irradiation. Nitrous oxide rapidly converts solvated electrons to hydroxyl radicals in solution by the following reaction [33].

$$e_{aq}^- + N_2O \rightarrow \bullet OH + N_2 + OH^- \qquad k = 9.1\times10^9\ dm^3\ mol^{-1}\ s^{-1} \qquad (2\text{-}1)$$

Hydrogen atoms are not scavenged by nitrous oxide; however, they react with aliphatic compounds in a similar fashion as hydroxyl radicals, typically by abstracting a hydrogen atom from the carbon backbone.

To isolate the reaction of solvated electrons, t-butyl alcohol (t-butanol) was added to the reaction system. Hydroxyl radicals are scavenged by t-butanol according to reaction (2-2). Since oxygen is a strong scavenger of hydrated electrons, it must also be purged from solution.

$$\bullet OH + (CH_3)_3COH \rightarrow (CH_3)_2(CH_2\bullet)COH + H_2O \qquad (2\text{-}2)$$

Under these conditions hydrogen atoms will also be scavenged but at a lower rate: for 0.5 M t-butanol, approximately 30% of the hydrogen atoms will react with MEK.

However, since the yield of hydrogen atoms is only 10% of that of hydroxyl radical, only 3% of the overall MEK decay will occur by this pathway.

The pH of the solution also affects the yield of primary species available for reaction. Under acidic conditions, $pH < 3$, protons quickly scavenge electrons to form hydrogen atoms.

$$H^+ + e^-_{aq} \rightarrow \bullet H \qquad (2\text{-}3)$$

Under basic conditions hydrogen atoms are scavenged by hydroxide as shown in equation 2-4 to give hydrated electrons.

$$\bullet H + OH^- \rightarrow e^-_{aq} + H_2O \qquad (2\text{-}4)$$

Also in more basic solutions, the dissociation of hydrogen peroxide, hydroxyl radicals and HO_2 occurs [14].

$$HO_2 \rightleftharpoons H^+ + O_2^- \qquad pKa = 4.8 \qquad (2\text{-}5)$$

$$H_2O_2 \rightleftharpoons H^+ + HO_2^- \qquad pKa = 11.6 \qquad (2\text{-}6)$$

$$\bullet OH \rightleftharpoons H^+ + O^- \qquad pKa = 11.9 \qquad (2\text{-}7)$$

2.3 High Performance Liquid Chromatography (HPLC) Analysis of Carbonyl Compounds

Analysis of reactant and products containing carbonyl groups was performed by high performance liquid chromatography (HPLC) of their 2,4-dinitrophenylhydrazine (DNPH) derivatives (Figure 2-2). A DNPH-stock solution was made by mixing 0.4 g of DNPH with 15 mL of a solution of acetonitrile, water, sulfuric acid in a proportion of of 2:5:2 by volume. Trace carbonyl contaminants were removed from the DNPH solution by extraction with carbon tetrachloride. This extraction involved the addition of 2 mL of carbon tetrachloride to 15 mL of DNPH solution, shaking for 5 minutes followed by centrifugation at 2000 rpm for 5 minutes. The organic layer was removed and discarded. Blank samples of purified water were analyzed as described below to verify water and reagent purity.

One mL of the irradiated MEK sample was derivatized using 50 µl of the DNPH solution [34]. After leaving the mixture 16 hours 3 mL of acetonitrile was added to each sample to dissolve any formed DNPH-carbonyl precipitate. These samples were then analyzed using HPLC.

The HPLC system consisted of two Waters 510 pumps, a Waters WISP 712 autosampler, a Waters 490E programmable multiwavelength length detector interfaced through a Waters System Interface Module (SIM) to a Compaq computer running the Waters baseline chromatography software. A programmed gradient with acetonitrile and water at pH 2.6 was run through a 15 cm reverse phase 5 nm Supelco

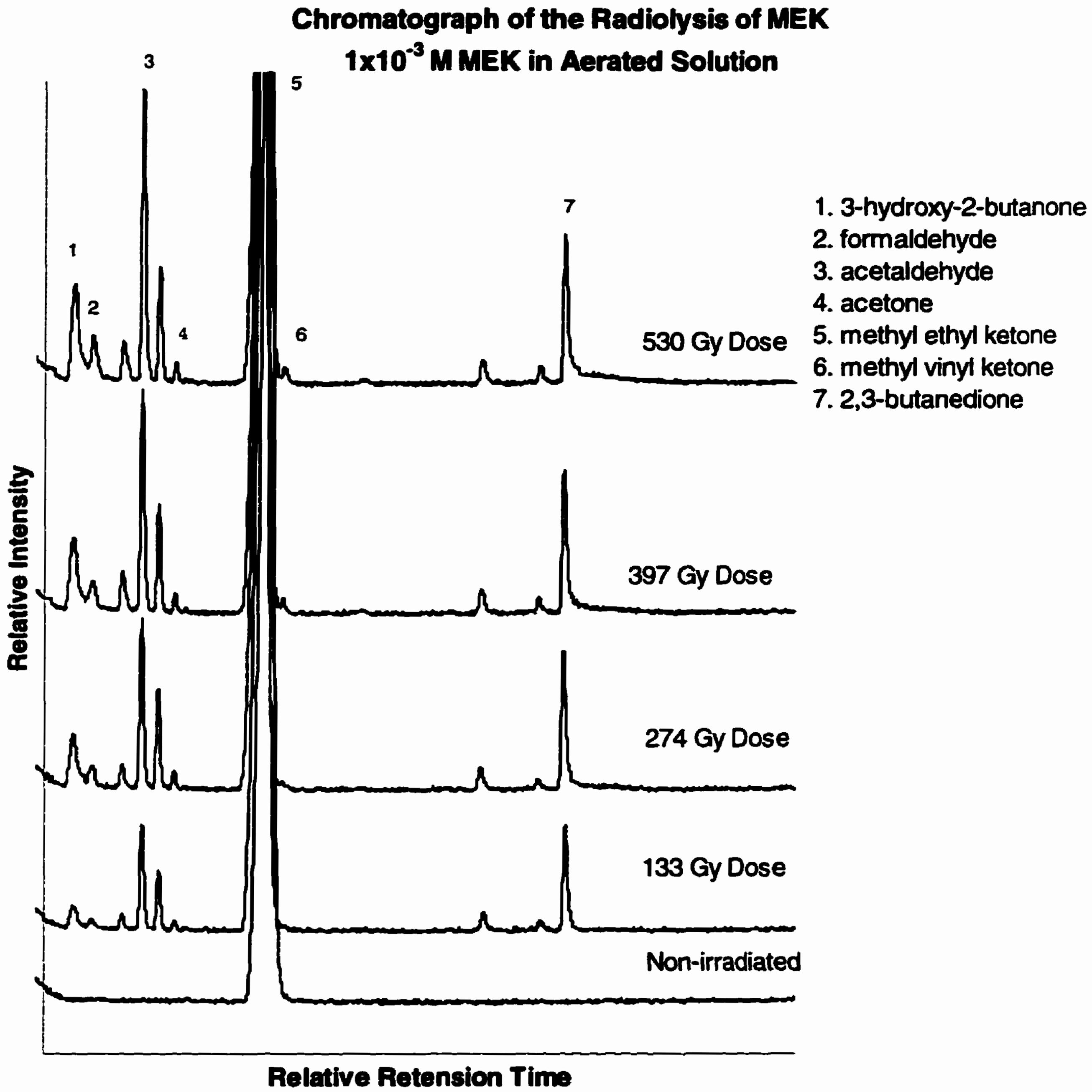

Figure 2-2 - HPLC analysis of 2,4 Dinitrophenylhydrazine (DNPH) derivatives of carbonyl compounds during the gamma radiolysis of aerated aqueous MEK solutions.

C_{18} model Supelcosil LC-18-DB column. Components were detected at 370 nm [34]. Standard solutions made up from pure compounds, and derivatized using the DNPH solution were used to determine detector response and elution times for analyzed compounds.

2.4 Gas Chromatography

Gas chromatography was used to analyze methyl iodide in irradiated solutions containing iodide. Samples not containing nitrous oxide were directly analyzed by a model 3700 Varian Gas Chromatography using a Ni-63 electron capture detector, interfaced to an IBM compatible PC. Samples with nitrous oxide were extracted with iso-octane, with a 1:10 volume ratio of sample to iso-octane, before analysis.

2.5 Ion Chromatography for Detection of Organic Acids

The analysis of organic acids was performed using a Waters 7.8 x 300 mm IC-Pak ion-exclusion column and a Waters 431 conductivity detector, utilizing 1 mM nitric acid mobile phase with an isocratic (mobile phase with a constant solvent composition) flow rate of 1.0 mL/minute delivered by a Waters Model 510 HPLC Pump. A 50 µL sample was injected directly onto the column, with data collected and integrated on a Waters Model 740 Data Module. Standard solutions of formic and acetic acids were used to calibrate this analysis.

2.6 Gas Space Analysis by Mass Spectroscopy

After sample irradiation the gas spaces above the aerated solutions were analyzed for hydrogen, nitrogen, carbon dioxide and oxygen using a VG 8-80 magnetic sector mass spectrometer. Irradiation vials were fitted with screw caps and stop cocks that connected to the instrument. Vacuum was applied to the cell and the quality of the seal tested. If the seal was acceptable the stopcock was opened, drawing the gas space into the instrument. The instrument was calibrated using mixtures prepared by Canadian Liquid Air. The software used to calculate concentrations of individual components was the VG Process Soft software provided with the instrument.

2.7 Gas Chromatography / Mass Spectrometry

Gas chromatography/mass spectrometry (GC/MS) was used to identify MEK dimers formed in solution during irradiation. This analysis was performed on a Hewlett Packard 5972 series Mass Selective Detector connected to a Hewlet Packard 5890 series Gas Chromatograph with a 25 m methylsiloxane column. The injection port temperature was 200 °C and the column temperature was initially set at 35 °C. This temperature was maintained for 3 minutes after sample injection then raised to 275 °C at the rate of 10 °C/minute.

Large volumes (500 mL) of argon and nitrous oxide-purged 1×10^{-3} M MEK solutions were irradiated to an absorbed dose of ~2000 Gy. The samples were split into two 250 mL aliquots and each extracted with 5 mL of dichloromethane to provide duplicate samples. The organic layer was removed and 1 µL from each aliquot was directly injected onto the column using a glass syringe.

2.8 Summary of Experimental Work

In order to investigate MEK degradation, experiments were conducted under a variety of conditions (Table 2-1). As explained previously, each series of experiments provided a different insight into the mechanism of the decay of MEK. Since only 8 individual samples could be irradiated and analyzed in a single experiment, a large number of experiments were performed for each series. Separate vessels were used for each dose to provide better control of sample conditions during the irradiation and prevent possible contamination during sampling. In each series, experiments were carried out until the decay of MEK, and of any products, was complete. For most experiments, total irradiation times ranged up to 48 hours in the gammacell, depending on the total dose required. All samples were run in duplicate and all results reported.

A typical experiment began by making up a sample solution as described in section 2.1. Samples were irradiated in the Gammacell to the desired dose then removed and their contents analyzed as follows:

- For aerated samples without iodide, the gas space was analyzed immediately by mass spectroscopy as described in section 2.6. Liquid samples were removed from the irradiation vials and analyzed for carbonyl compounds as described in section 2.3. Subsequently organic acids were analyzed by ion chromatography, as described in section 2.5.

- For aerated samples with iodide, liquid samples were removed from the irradiation vials and analyzed for carbonyl compounds. Methyl iodide was determined by gas chromatography as described in section 2.4.
- For non-aerated solutions without iodide, liquid samples were removed from the irradiation vials and analyzed for carbonyl compounds and organic acids.
- For non-aerated solutions with iodide, liquid samples were removed from the irradiation vials and analyzed for carbonyl compounds and methyl iodide. Nitrous oxide-purged solutions containing iodide were extracted with iso-octane before analysis since nitrous oxide is so strongly detected by the electron capture detector that no other peaks could be observed.
- For aerated solutions of 3-hydroxy-2-butanone, liquid samples were removed from the irradiation vials and analyzed for carbonyl compounds.
- For aerated solutions of acetaldehyde, liquid samples were removed from the irradiation vials and analyzed for carbonyl compounds and organic acids.

All standards were made up on the same day as the run was performed and were analyzed just before or after samples were analyzed.

2.9 Computer Modeling

Modeling of solution kinetics was carried out using a computer program called FACSIMILE [i] which solves coupled differential equations encountered in scientific and

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[i] FACSMILE Version 3.0 - AEA Technologies, Harwell Laboratory, Oxfordshire, UK, OX11 0RA.

engineering problems. One feature of this program is its ability to solve a series of chemical equations using variables to represent the concentrations of chemical species in solution. A special high-level programing language is used to express the chemical equations and initial concentrations of chemical species to the program. Upon successful completion of a program run, a temporal profile of the concentrations of chemical species is given.

TABLE 2-1 - SOLUTION CONDITIONS

Series #	Starting Solute	Iodide Conc. (M)	Purge Gas	Radical Scavenger
1	MEK	--	Air	--
2	MEK	--	Argon	--
3	MEK	--	Nitrous Oxide	Nitrous Oxide
4	MEK	--	Argon	t-Butanol
5	MEK	5.0×10^{-4}	Argon	t-Butanol
6	MEK	5.0×10^{-4}	Argon	--
7	MEK	5.0×10^{-4}	Air	--
8	MEK	5.0×10^{-4}	Nitrous Oxide	Nitrous Oxide

Starting concentration of MEK: 1.0×10^{-3} M
Starting pH 10.0

Results and Discussion

In this chapter the mechanism for the radiolytic degradation of aqueous MEK is studied. The emphasis of this mechanism is on the aerated condition, since this is the situation expected in containment during a LOCA in a nuclear reactor. The methodology used was first to devise a qualitative degradation mechanism based on the results of analogous systems reported in the literature. This mechanism was then compared to the experimental results collected in this study. Based on this comparison, a quantitative computer model was devised for the overall degradation process, utilizing literature rate constants and mechanisms. The predictions of this quantitative model were then compared to experimental results obtained for the evolution of solution pH as a function of absorbed dose. This parameter was chosen because of its importance to iodine volatility under LOCA conditions. A preliminary study was also performed to investigate how the presence of iodide affects the decay of aqueous MEK.

In the next two sections the qualitative degradation mechanism for the decay of MEK under LOCA conditions is constructed. The reactions of hydroxyl radical and hydrogen atoms are first discussed followed by the possible reactions of the hydrated electron.

3.1 Reaction of MEK with Hydroxyl Radical and Hydrogen Atom

Hydrogen atoms and hydroxyl radicals will abstract hydrogen from MEK in solution, forming MEK radicals and molecular hydrogen (H_2) or water respectively [27,35].

$$\bullet H + CH_3CH_2COCH_3 \rightarrow CH_3C\bullet HCOCH_3 + H_2 \qquad (3\text{-}1)$$

$$\bullet OH + CH_3CH_2COCH_3 \rightarrow CH_3C\bullet HCOCH_3 + H_2O \qquad (3\text{-}2)$$

In non-aerated solutions these radicals will react via disproportionation or polymerization, to give methyl vinyl ketone and MEK dimer respectively.

$$2\ CH_3C\bullet HCOCH_3 \rightarrow CH_3CH_2COCH_3 + CH_2{=}CHCOCH_3 \qquad (3\text{-}3)$$

$$2\ CH_3C\bullet HCOCH_3 \rightarrow CH_3COCH(CH_3)CH(CH_3)COCH_3 \qquad (3\text{-}4)$$

In aerated solutions, expected in containment under LOCA conditions, the dominant pathway is the reaction of MEK radicals with dissolved oxygen [14]. This reaction is very rapid, occurring at near diffusion controlled rates.

$$CH_3C\bullet HCOCH_3 + O_2 \rightarrow CH_3CH(O_2\bullet)COCH_3 \qquad (3\text{-}5)$$

The breakdown of peroxy carbonyl radicals have been studied previously and have been well elucidated [28,36,37]. From these results an analogous mechanism for the decay of peroxy MEK radicals was surmised. The bimolecular reaction of two peroxy MEK radicals is expected to form a short-lived, unstable tetroxide intermediate, which quickly decays giving various products [28,36,37].

$$2\ CH_3COCH_2(CH_3)\text{-}O_2\bullet \rightarrow [CH_3COCH_2(CH_3)\text{-}O_4\text{-}CH(CH_3)COCH_3] \rightarrow \text{Products} \qquad (3\text{-}6)$$

Using the breakdown of the acetone tetroxide intermediate as a model for the decay of the MEK tetroxide intermediate the following mechanism was constructed. In the most important pathway about half of the tetroxide intermediate decays by a concerted reaction to give hydrogen peroxide and 2,3-butanedione [28].

$$[CH_3COCH_2(CH_3)\text{-}O_4\text{-}CH(CH_3)COCH_3] \rightarrow 2\ CH_3COCOCH_3 + H_2O_2 \qquad (3\text{-}7)$$

The second most important pathway, occurring for slightly more than one quarter of the intermediate, proceeds via the Russell reaction [29] giving 2,3-butanedione, 3-hydroxy-2-butanone and molecular oxygen.

$$[CH_3COCH_2(CH_3)\text{-}O_4\text{-}CH(CH_3)COCH_3] \rightarrow CH_3CH(OH)COCH_3 + CH_3COCOCH_3 + O_2 \qquad (3\text{-}8)$$

The third pathway, accounting for about one eighth of the reaction, proceeds by another concerted process to give acetaldehyde, the acetyl radical and molecular oxygen.

$$[CH_3COCH_2(CH_3)\text{-}O_4\text{-}CH(CH_3)COCH_3] \rightarrow 2\,CH_3CHO + 2\,CH_3C{\bullet}HO + O_2 \qquad (3\text{-}9)$$

A fourth process, which accounts for about one eighth of the reaction, proceeds by a two step radical process where the intermediate eliminates molecular oxygen, to give the MEK alkoxide radical (Equation 3-10), which can subsequently abstract hydrogen atoms from aliphatic hydrocarbons in solution, to give 3-hydroxy-2-butanone and organic radicals.

$$[CH_3COCH_2(CH_3)\text{-}O_4\text{-}CH(CH_3)COCH_3] \rightarrow 2\,CH_3COCH_2(CH_3)O{\bullet} + O_2 \qquad (3\text{-}10)$$

The abstraction of hydrogen atoms from 2,3-butanedione, again by hydroxyl radicals and hydrogen atoms, gives radicals that also react with dissolved oxygen to form peroxyl radicals, and which again decay by an analogous tetroxide mechanism (reaction 3-14 to 3-19).

This pathway occurs in competition with reaction of 2,3-butanedione with hydrogen peroxide (reaction 3-11) [32,38], which forms the α-hydroxide hydroperoxy radical, and decays *via* a first order reaction to give acetic anhydride and ultimately forms acetic acid [38].

$$CH_3COCOCH_3 + H_2O_2 \rightleftharpoons CH_3COC(OH)(O_2H)CH_3 \tag{3-11}$$

$$CH_3COC(OH)(O_2H)CH_3 \rightarrow CH_3CH_2(O)\text{-}O\text{-}(O)CH_2CH_3 \tag{3-12}$$

$$CH_3CH_2(O)\text{-}O\text{-}(O)CH_2CH_3 + H_2O \rightarrow 2\ CH_3COOH \tag{3-13}$$

$$CH_3COCOCH_3 + {}^\bullet OH \rightarrow CH_3COCO^\bullet CH_2 + H_2O \tag{3-14}$$

$$CH_3COCOCH_3 + {}^\bullet H \rightarrow CH_3COCO^\bullet CH_2 + H_2 \tag{3-15}$$

$$2\ CH_3COCOCH_2O_2^\bullet \rightarrow [\text{tetroxide intermediate}] \tag{3-16}$$

$$[\text{tetroxide intermediate}] \rightarrow 2\ HCO + 2\ CH_3CHO + 2\ CO + O_2 \tag{3-17}$$

$$[\text{tetroxide intermediate}] \rightarrow 2\ HCO + 2\ CO + 2\ CH_3^\bullet CO + H_2O_2 \tag{3-18}$$

The breakdown of 3-hydroxy-2-butanone proceeds by hydrogen abstraction, followed by reaction with dissolved oxygen giving an α-hydroxyalkylperoxyl radical which will decay in a first-order reaction to eliminate $HO_2^\bullet$ and 2,3-butanedione [32].

$$CH_3CH(OH)COCH_3 + {}^\bullet OH \rightarrow CH_3^\bullet C(OH)COCH_3 + H_2O \tag{3-19}$$

$$CH_3CH(OH)COCH_3 + {}^\bullet H \rightarrow CH_3^\bullet C(OH)COCH_3 + H_2 \tag{3-20}$$

$$CH_3^\bullet C(OH)COCH_3 + O_2 \rightarrow CH_3C(O_2^\bullet)(OH)COCH_3 \tag{3-21}$$

$$CH_3C(O_2^\bullet)(OH)COCH_3 \rightarrow CH_3COCOCH_3 + HO_2^\bullet \tag{3-22}$$

The formation of a tetroxide species will compete with the previous first-order reaction; however, since this reaction is second order it is likely to be a relatively minor pathway under these low concentration conditions.

$$2\ CH_3C(O_2\bullet)(OH)COCH_3 \rightarrow \text{[tetroxide intermediate]} \rightarrow \text{Products} \qquad (3\text{-}23)$$

This mechanism implies that acetic acid is a major product of the radiolytic decay of aqueous aerated 2,3-butanedione. Acetic acid decays by hydroxyl radical abstraction of a hydrogen atom from the methyl group [39,40], followed by the addition of oxygen to give the peroxy acetic acid (and acetate) radicals. The decay mechanism of peroxy acetate radicals have been shown to occur by self-termination reactions, through the formation of a tetroxide intermediate, similar to those discussed previously. According to this mechanism, glyoxylate, hydroxylacetate, formaldehyde, hydrogen peroxide, carbon dioxide, oxygen, hydroxide and O_2^- are products formed by this decay [37]. Hydroxyl radicals and hydrogen atoms will also abstract hydrogen atoms from glyoxylic acid and hydroxy acetic acid [41] and their anions [42,43]. These radicals will react with oxygen to again form organic peroxyl radicals that decay by a tetroxide intermediate mechanism [16, 37,39-51].

$$CH_3CO_2^- + \bullet OH \rightarrow \bullet CH_2CO_2^- + H_2O \qquad (3\text{-}24)$$

$CH_3CO_2^- + \bullet H \rightarrow \bullet CH_2CO_2^- + H_2$ (3-25)

$\bullet CH_2CO_2^- + O_2 \rightarrow \bullet O_2CH_2CO_2^-$ (3-26)

$2\,\bullet O_2CH_2CO_2^- \rightarrow$ [tetroxide intermediate] (3-27)

[tetroxide intermediate] $\rightarrow CHOCO_2^- + CH_2OHCO_2^- + O_2$ (3-28)

[tetroxide intermediate] $\rightarrow 2\,CHOCO_2^- + H_2O_2$ (3-29)

[tetroxide intermediate] $\rightarrow 2\,HCHO + 2\,CO_2 + H_2O_2 + 2\,OH^-$ (3-30)

[tetroxide intermediate] $\rightarrow 2\,CHOCO_2^- + O_2^- + H_2O$ (3-31)

3.2 Reaction of MEK with Solvated Electron

Solvated electrons are very reactive towards MEK. The primary product of its reaction with MEK is the ketyl radical. The ketyl radical exists in an equilibrium [24,30]

$CH_3(C{=}O)CH_2CH_3 + e^- \rightarrow CH_3(\bullet CO^-)CH_2CH_3$ (3-32)

$CH_3(\bullet CO^-)CH_2CH_3 + H^+ \rightleftharpoons CH_3(\bullet COH)CH_2CH_3$ (3-33)

where the protonated form can undergo disproportionation into the parent ketone and the corresponding alcohol [14].

$2(CH_3(\bullet COH)CH_2CH_3) \rightarrow CH_3(C{=}O)CH_2CH_3 + CH_3CH(OH)CH_2CH_3$ (3-34)

However in 1×10^{-3} M MEK aerated aqueous solutions, oxygen is present at 250 µM, which is sufficient to scavenge 99.8 % of the hydrated electrons to give the relatively unreactive $O_2^{\bullet-}$ anion (reaction 1-15). Hydrogen atoms are also scavenged by dissolved oxygen to form hydroperoxy radicals (reaction 1-21).

The ketyl radical that is formed will react very rapidly with dissolved oxygen to give MEK α-hydroxyalkylperoxyl radicals.

$$CH3(\bullet COH)CH_2CH_3 + O_2 \rightarrow CH_3C(OO\bullet)OHCH_2CH_3 \qquad (3\text{-}35)$$

This α-hydroxyalkylperoxyl radical will decay in a first-order reaction to give the MEK and $HO_2\bullet$ [32].

The pathways just described provide a possible general pathway for the radiolysis of aerated aqueous MEK. Based in this information, it is expected that in aerated solutions radiolytic decay will initially occur by hydrogen abstraction from hydroxyl radical attack on MEK and its radiolysis products to form organic radicals that will react with dissolved oxygen to give organic peroxide species. These will subsequently decay by a self termination mechanism to form a variety of oxidized species. The pathway developed in the previous section suggests that 3-hydroxy-2-butanone, 2,3-butanedione and acetic acid are the main products of the decay of aqueous aerated MEK. These species will also decay as the radiolysis continues. In ensuing sections the predictions of this mechanism will be compared to experimental results obtained in this study.

3.3 Radiolysis of MEK Solutions Without Iodide

To establish the validity of the qualitative MEK degradation mechanism detailed in sections 3.1 and 3.2, experiments involving the radiolysis of MEK under different limiting conditions were performed to isolate particular pathways in the decay mechanism. Both the decay of MEK and the formation of radiolysis products were measured for all systems.

3.3.1 Argon-Saturated Solutions

In this series of experiments, oxygen was removed from solution by purging with argon, which prevented the oxygen from scavenging of hydrogen atoms and hydrated electrons, to form relatively inert HO_2/O_2^- species.

The decay of MEK observed experimentally (Figure 3-1a) gave a calculated initial loss G-value of -2.8. The concentration profiles of carbonyl compounds and organic acids are shown in Figures 3-1a and 3-1b. The major observation in these experiments was that the concentration of oxidation products such as 3-hydroxy-2-butanone and acetic acid were as much as ten times lower than those found under aerated conditions (Figures 3-4a and 3-4b).

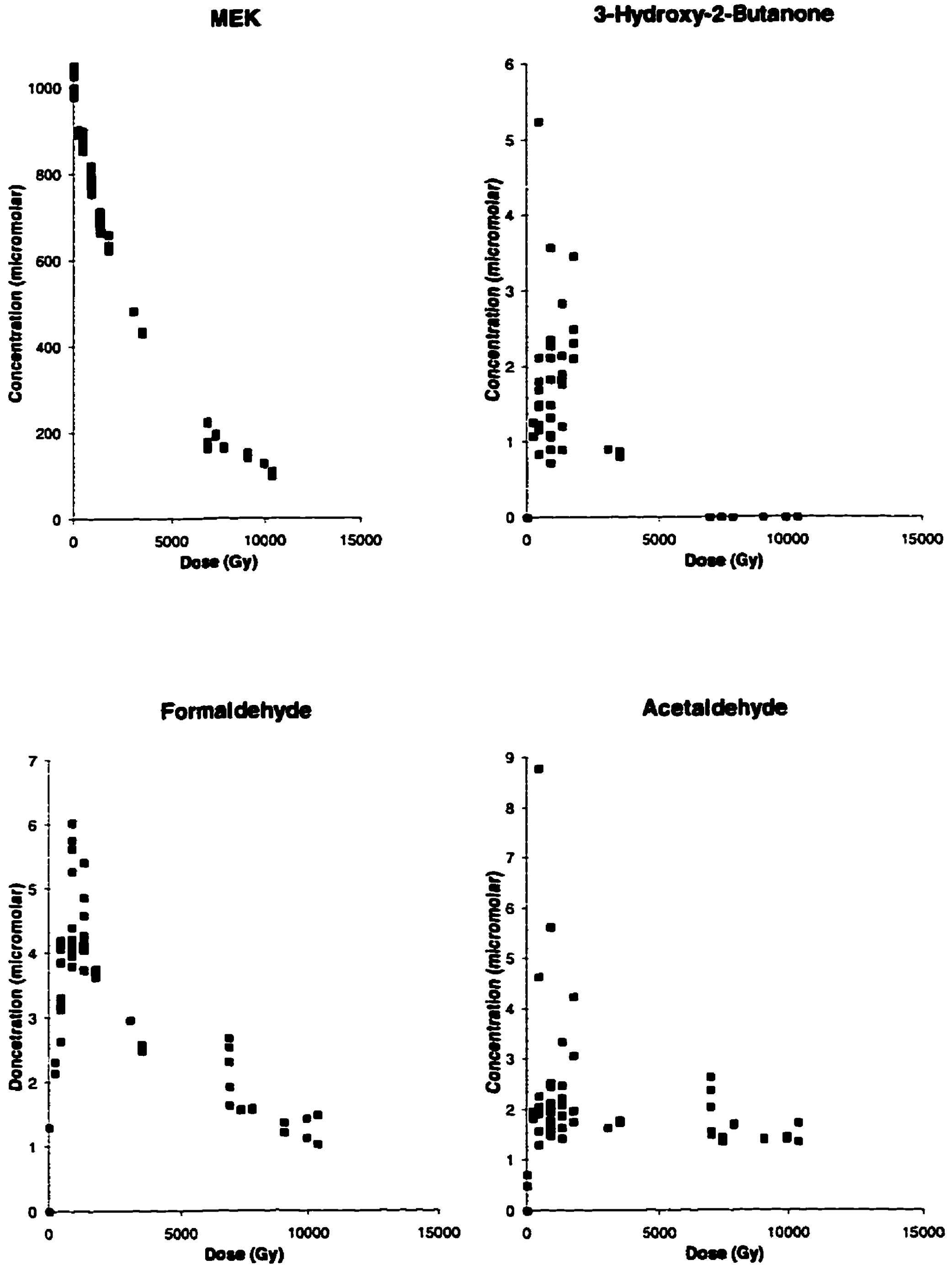


Figure 3-1a - Product analysis for the radiolysis of argon-purged 1x10-3 M MEK solutions. The decay of MEK gave an initial loss G-value of -2.8. The concentration of 3-hydroxy-2-butanone, formaldehyde and acetaldehyde were very low as compared to the irradiation of air-purged solutions.

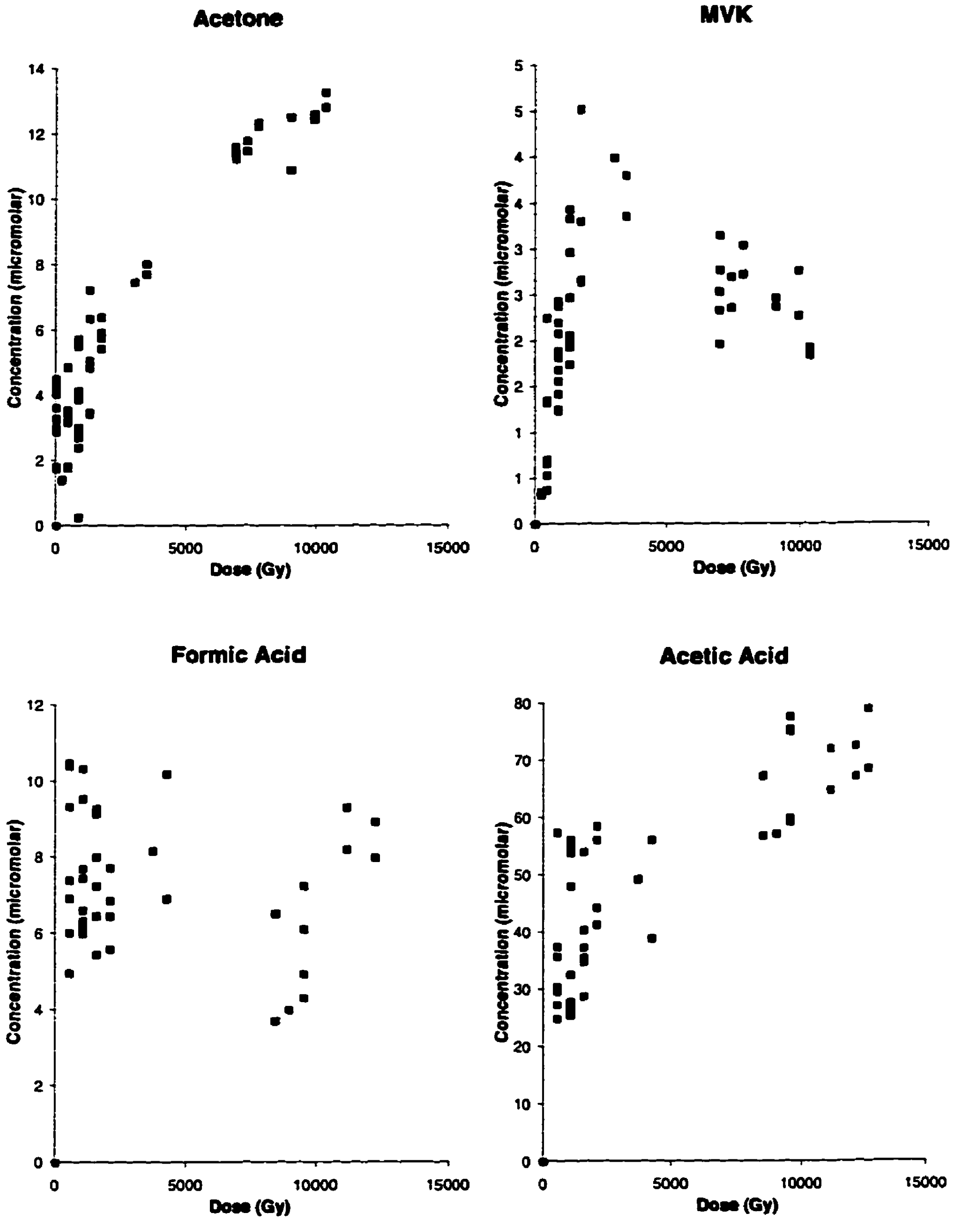


Figure 3-1b - - Product analysis for the radiolysis of argon-purged 1x10-3 M MEK solutions. The concentration of organic acids were very low under these conditions.

For the argon-saturated system, the radical product of hydroxyl radical hydrogen abstraction from MEK cannot decay by reaction with dissolved oxygen. Other pathways such as dimerization, or reactions that reform MEK, become prevalent. Initial evidence for the formation of MEK dimers was obtained from additional chromatogram peaks observed in the carbonyl analysis of non-aerated solutions at longer times, which were not present under aerated conditions.

An ESR study has experimentally established that the hydrogen on the third carbon of MEK is most likely to be removed by reaction with hydroxyl radicals or hydrogen atoms [52]. From this radical, dimerization would produce 3,4-dimethyl-2,5-hexanedione. This species has been isolated previously where MEK radicals were produced chemically by the breakdown of diacetyl peroxide in pure MEK [53].

GC/MS was used to corroborate the formation of MEK dimer under these conditions. After irradiation, a 500 mL argon-purged solution of 1×10^{-3} M MEK was extracted with two fractions using 5 mL of methylene chloride. This solution was concentrated by evaporation and 1 µL of the resulting solution analyzed. The resulting chromatogram gave four peaks whose mass spectra had a parent ion peak at M/E 142, the expected molecular weight of the MEK dimer (Figure 3.1c). Exact mass GC/MS analysis was performed on the same sample, with the most prevalent peak in the chromatogram giving a mass spectrum with a parent ion peak at M/E 142.099. The calculated exact mass M/E for $C_8H_{14}O_2$ is 142.0994.

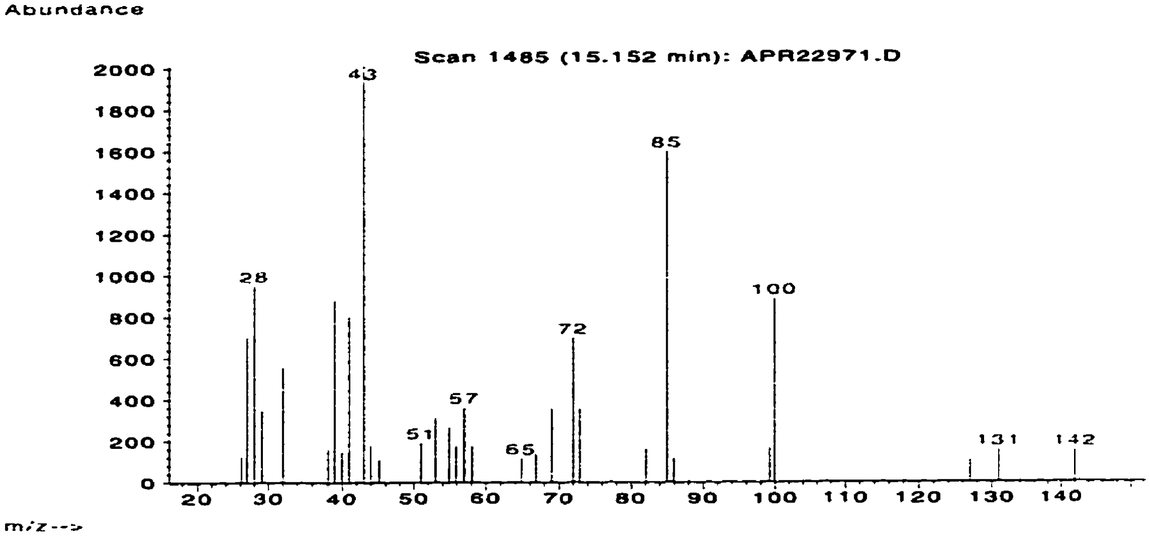


Figure 3-1c - GC/MS of possible MEK dimer formed by γ-radiolysis of argon-purged $1x10^{-3}$ M MEK aqueous solution.

3.3.2 Nitrous Oxide-Saturated Solutions

Figure 3-2a shows the decrease in MEK concentration during the irradiation of a nitrous oxide-purged aqueous MEK solution. As explained previously, the purpose of nitrous oxide saturation was to isolate the effects of hydroxyl radical. An initial G-value loss of -5.6 was calculated for the this decay, double than that determined for the argon-purged solution. This value agrees well with the expected G-value, since for γ-radiolysis the rate of production of hydrated electrons is equal to that of hydroxyl radical, and in saturated nitrous oxide solutions hydrated electrons are quantitatively converted into hydroxyl radicals (Reaction 2-1). The time profile of the analyzed carbonyl compounds is shown in Figures 3-2a and 3-2b. Acetic acid and 3-hydroxy-2-butanone were observed at levels only slightly higher than seen for argon-purged solutions.

As only hydroxyl radicals and hydrogen atoms were available to react with MEK, the initial step in the reaction mechanism is the removal of a hydrogen atom from MEK to yield an MEK radical, and water or molecular hydrogen respectively. The MEK radical can then undergo reaction to yield further products, or abstract a hydrogen atom from a product species with weakly bond hydrogen to reform MEK.

The higher concentration of hydroxyl radicals in solution will increase the yield of MEK radical formed, thus increasing the amount of dimer formed. As expected, the size of the analogous chromatogram peaks at longer retention times were larger for nitrous oxide-purged solutions than for argon solutions for

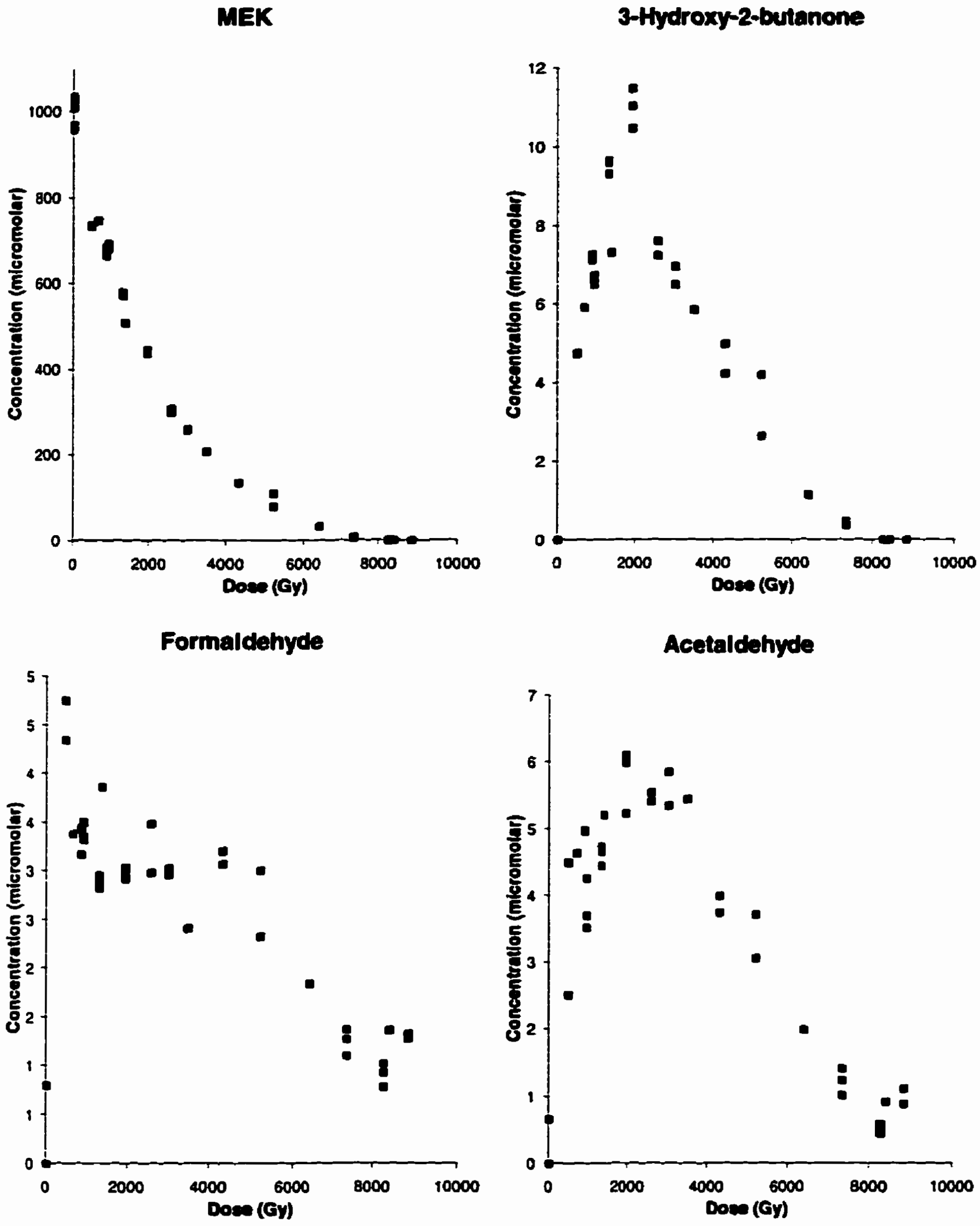


Figure 3-2a - Product analysis for the radiolysis of nitrous oxide-purged $1x10^{-3}$ M MEK solutions. The decay of MEK gave an initial loss G-value of -5.6. Oxidation products were found to have lower concentrations then for the irradiation of air-purged solutions.

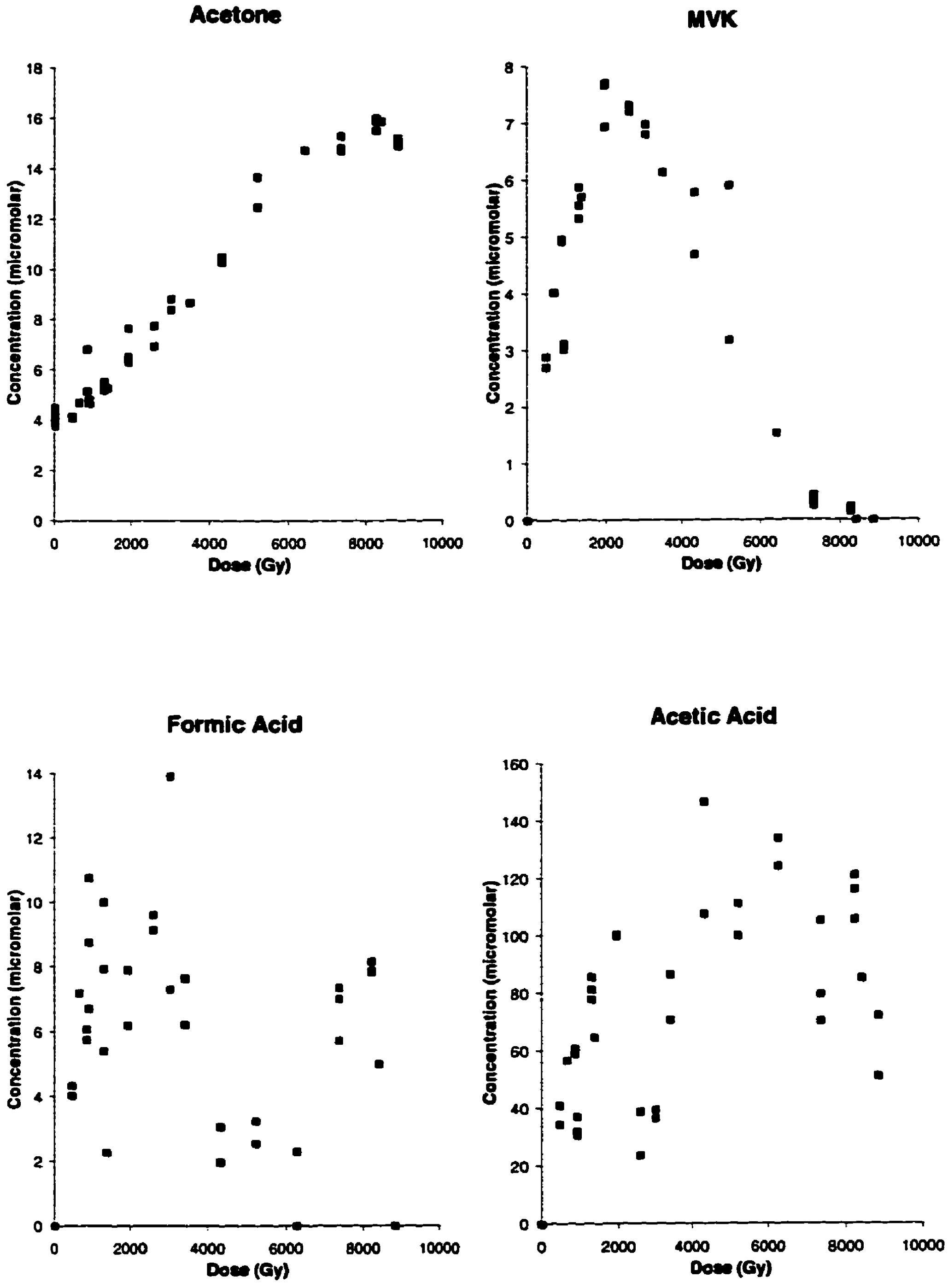


Figure 3-2b - Product analysis for the radiolysis of nitrous oxide-purged 1x10^{-3} M MEK solutions.

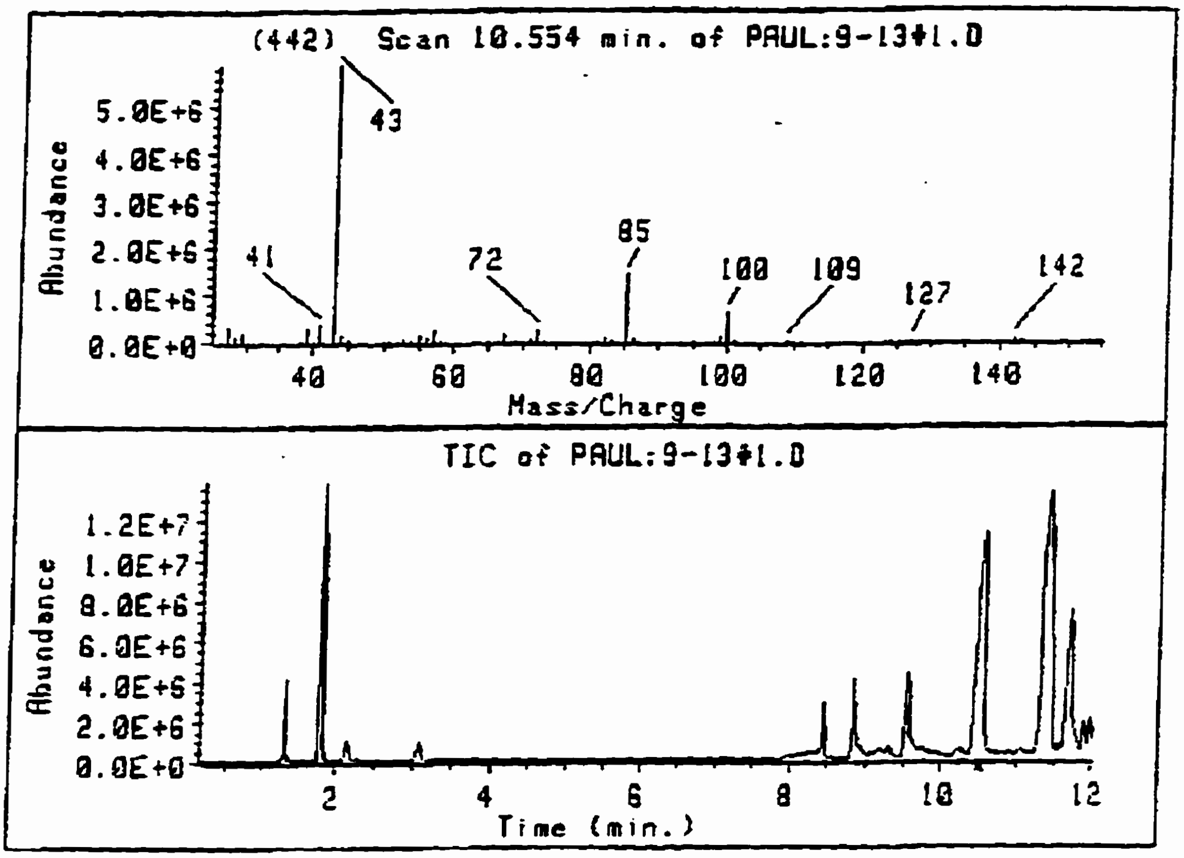


Figure 3-2c - GC/MS of possible MEK dimer formed by the γ-radiolysis of nitrous oxide-purged 1×10^{-3} M MEK aqueous solutions.

the same absorbed dose. GC/MS results have also shown species with molecular ions at M/E 142 with fragmentation patterns consistent with an MEK dimer (Figure 3-2c).

3.3.3 0.5 M t-Butanol Solutions

The addition of t-butanol scavenges hydroxyl radicals and hydrogen atoms, allowing the study of only the effect of solvated electron in the radiolytic decay of MEK (Figure 3-3a). Solutions were also purged with argon to remove oxygen. Under these conditions the formation of oxidation products were greatly decreased (Figures 3-3a and 3-3b), and no formation of 3-hydroxy-2-butanone was observed. However, a significant formation of acetone was seen. It was determined that this occurred from the radiolytically-induced decay of the t-butanol, not MEK. The MEK decay was calculated to have an initial G-value loss of 1.4, which is considerably lower than that observed for the argon or nitrous oxide solutions.

For the non-aerated conditions considered to this point, the formation of oxidized products were minimized while argon and nitrous oxide-purged solutions gave evidence of dimerization. The next solution condition that was studied was the aerated solution. Under these conditions the presence of dissolved oxygen in solution dominates the decay mechanism of the MEK in solution giving many oxidized product.

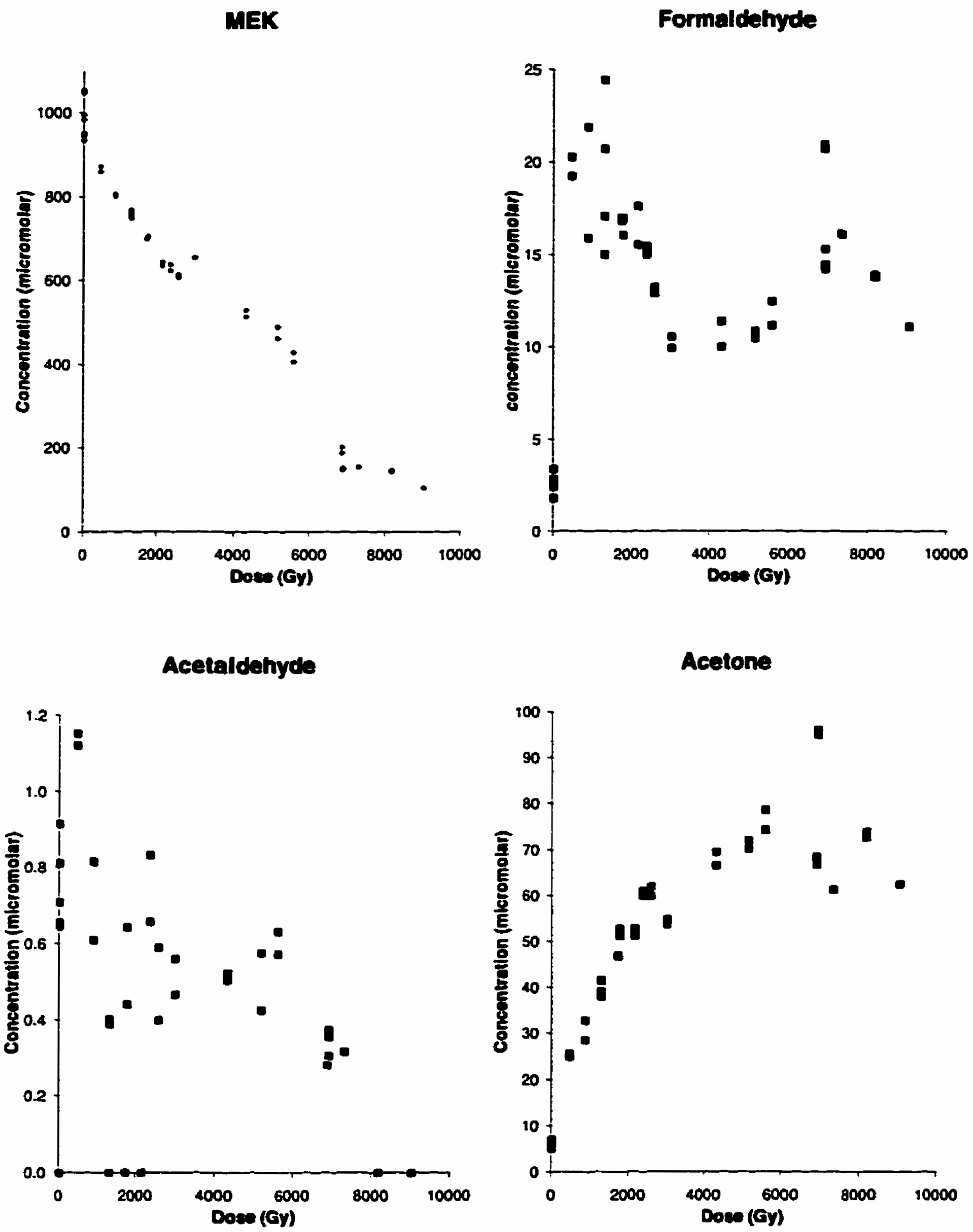


Figure 3-3a - Product analysis for the γ-radiolysis of 0.5 M t-butanol, argon-purged $1x10^{-3}$ M MEK solutions. The decay of MEK gave an initial loss G-value of -1.4. Acetone production was found to be due to the decay of t-butanol.

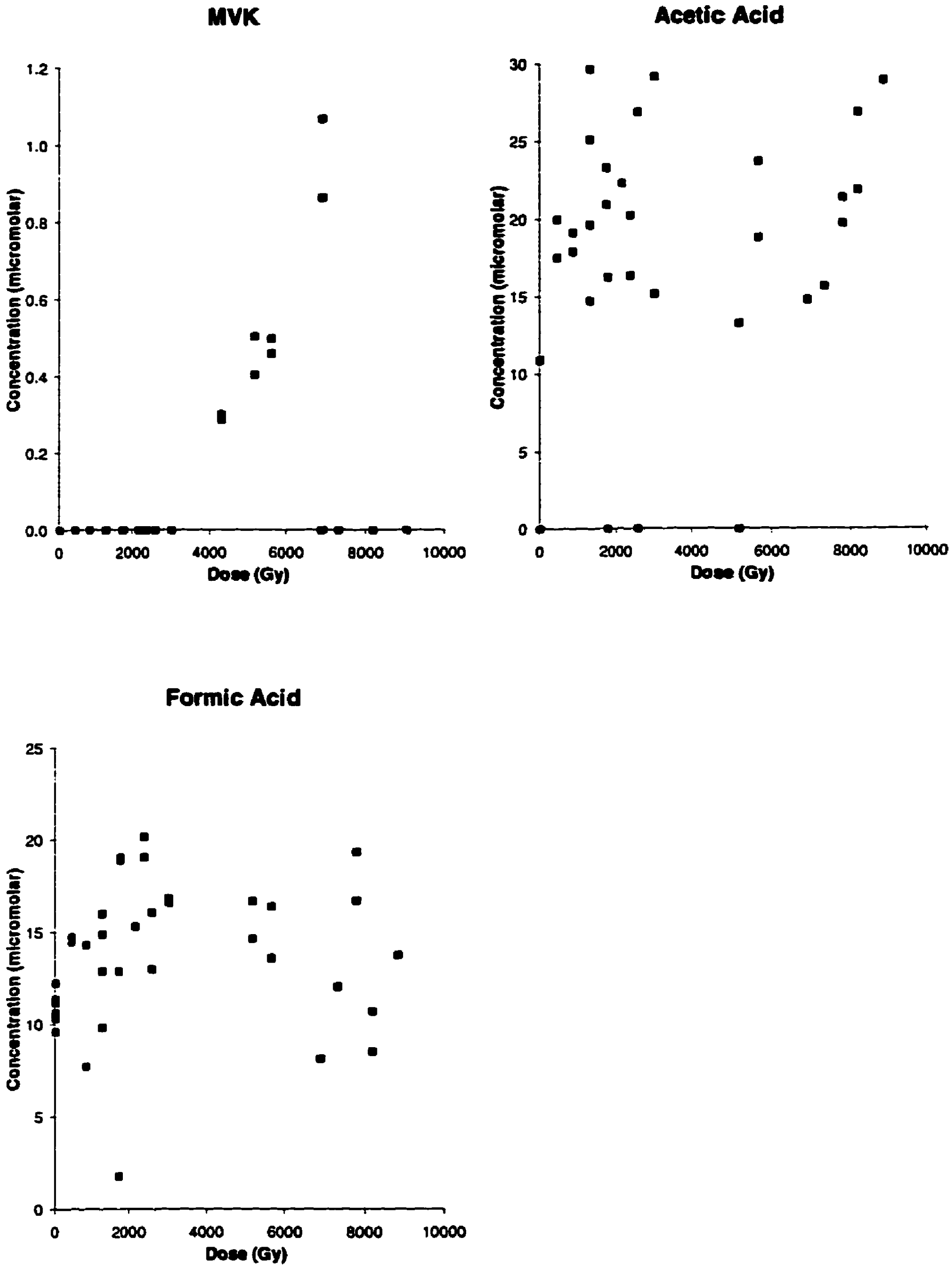


Figure 3-3b - Product analysis for the γ-radiolysis of 0.5 M t-butanol, argon-purged 1×10^{-3} M MEK solutions.

3.3.4 Aerated Solutions

In aerated solutions, as expected in containment under LOCA conditions, the concentration of MEK was seen to decrease with increasing dose, producing a variety of oxidized products, most notably acetic acid and 2,3-butanedione, as predicted. Smaller amounts of 3-hydroxy-2-butanone, acetaldehyde and formaldehyde, were also obtained, as shown in Figure 3-4a and 3-4b.

The initial slope shown in Figure 3-4a indicates that the breakdown of aerated MEK starts as a pseudo-first order process, with an initial G-value calculated to be -2.9. This value agrees well with the assumption that dissolved oxygen scavenges all the hydrogen atom and hydrated electrons from solution leaving only hydroxyl radicals (G value = 2.7) to react with MEK.

In the standard carbonyl compound/HPLC analysis of these irradiated solutions some samples yielded a precipitate that could not be fully dissolved in acetonitrile. This additional derivative was also shown to have very low solubility in carbon tetrachloride, dimethylsulfoxide, methanol, tetrahydrofuran, hexane or methanol. By subjecting standard carbonyl compounds to this procedure, it was observed that the 2,3-butanedione derivative also displayed the same behavior. Both species were found to dissolve sufficiently in acetonitrile to allow detection by HPLC, and showed similar highly tailed peaks for both compounds. Aliquots of the 2,3-butanedione derivative and the derivative of the unknown compound were also collected, purified and analyzed by IR spectroscopy. The spectra, given in Figure 3-4d, confirm that the insoluble compound is the 2,3-butanedione-DNPH derivative.

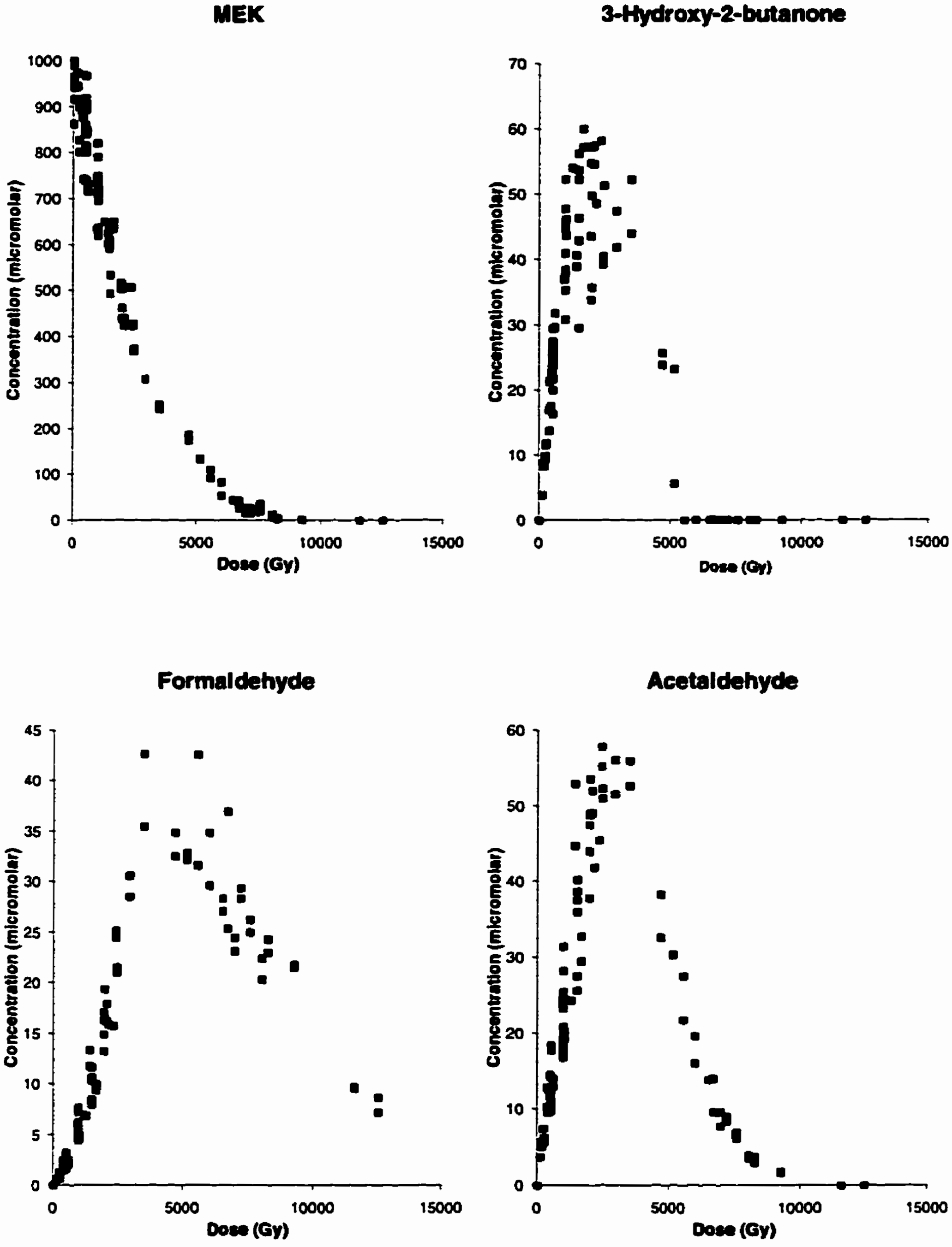


Figure 3-4a - Product analysis for the radiolysis of air-purged 1x10^{-3} M MEK solutions. The decay of MEK gave an initial loss G-value of -2.9. An initial G-value for the formation of 3-hydroxy-2-butanone of 0.6 was observed.

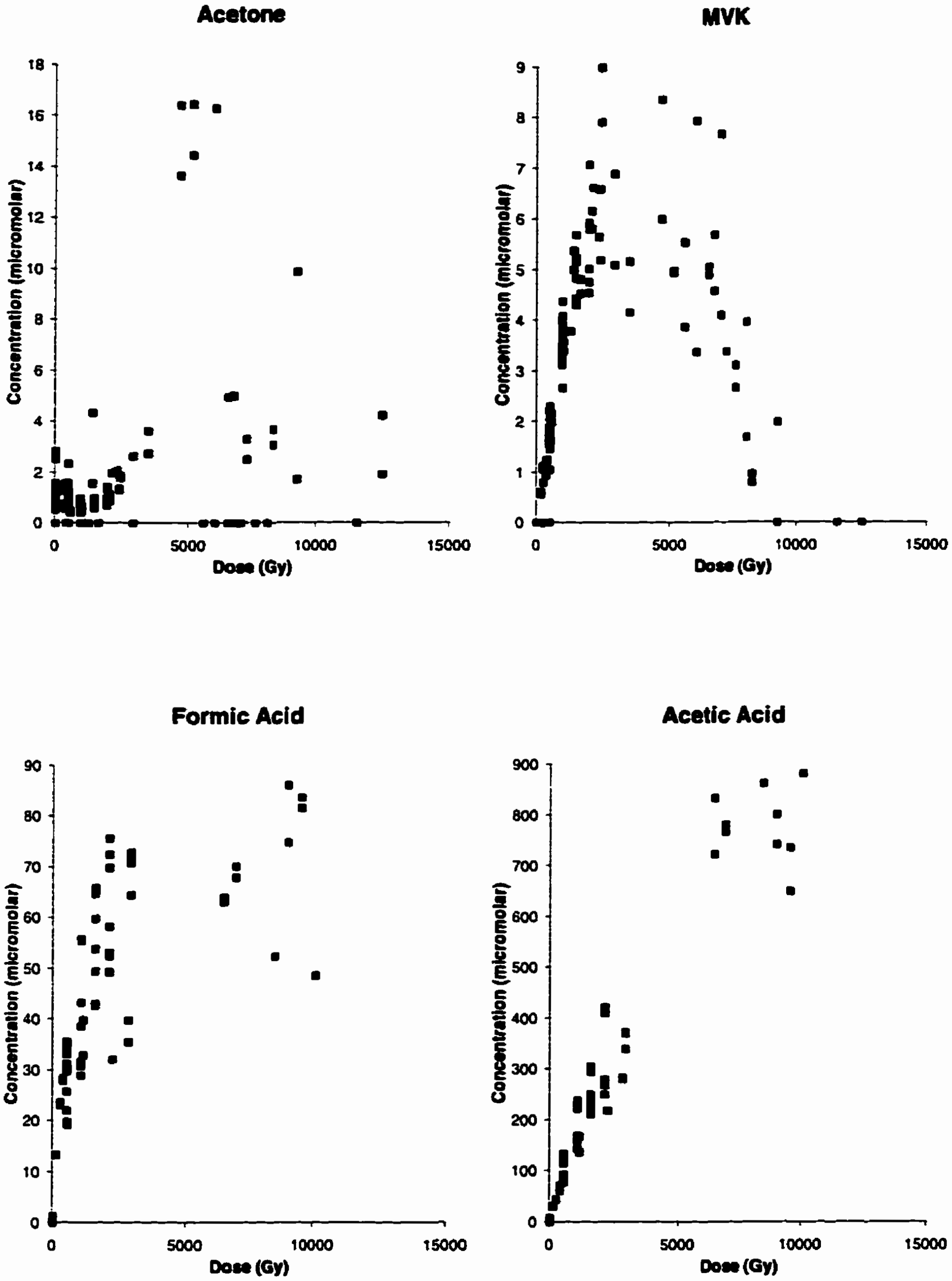
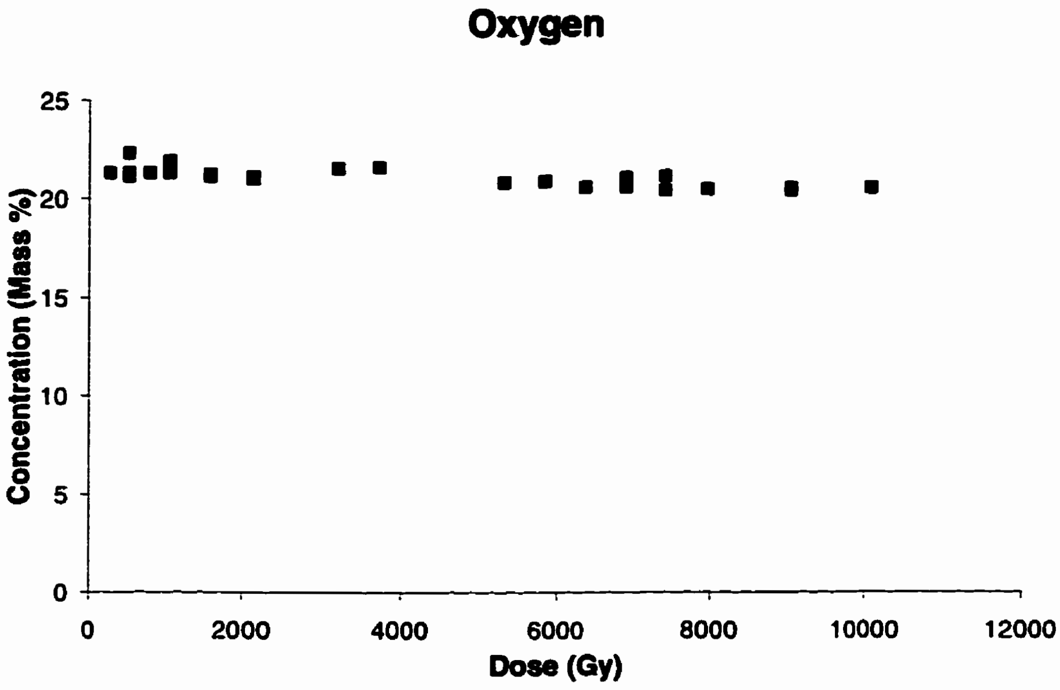


Figure 3-4b - Product analysis for the γ-radiolysis of air-purged 1x10^{-3} M MEK solutions. Acetic acid was observed as the major decay product observed under aerated concditions with a G-value of 1.7.



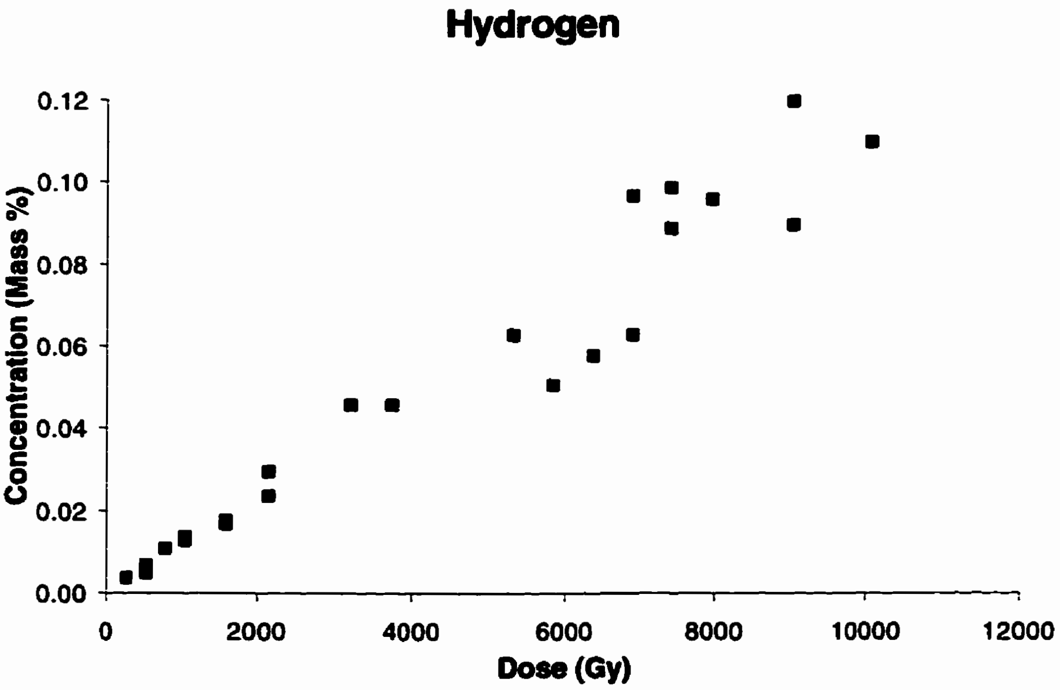


Figure 3-4c - Gas space analysis for the γ-radiolysis of air-purged $1x10^{-3}$ M MEK solutions. The concentration of oxygen in the gas phase decreases only slightly over the course of the irradiation. While the hydrogen is observed to be formed linearly throughout the entire irradiation.

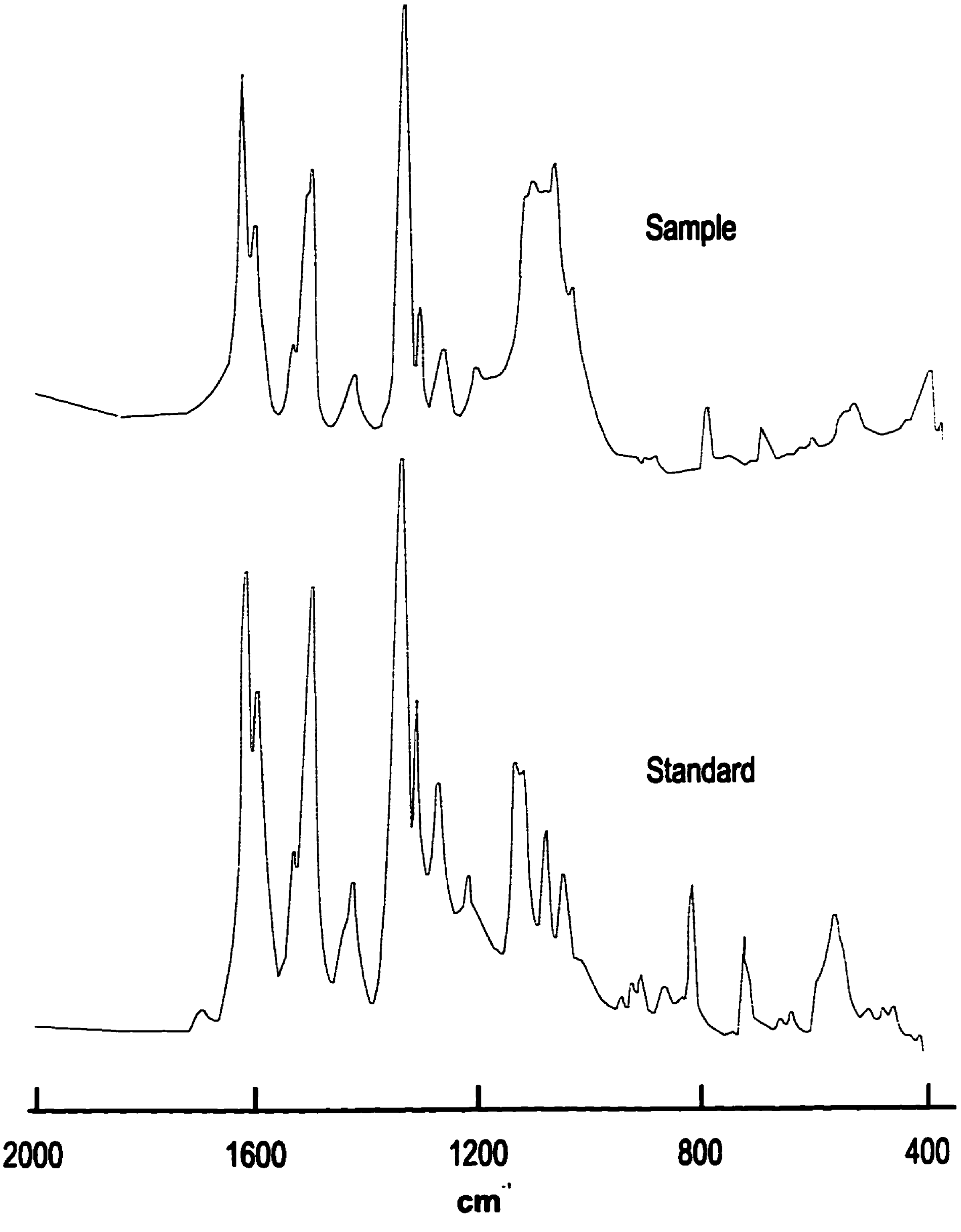


Figure 3-4d - FTIR spectra of DNPH derivative of 2,3-butanedione standard and the non-soluble derivative product species formed in the radiolysis of aerated aqueous MEK solutions

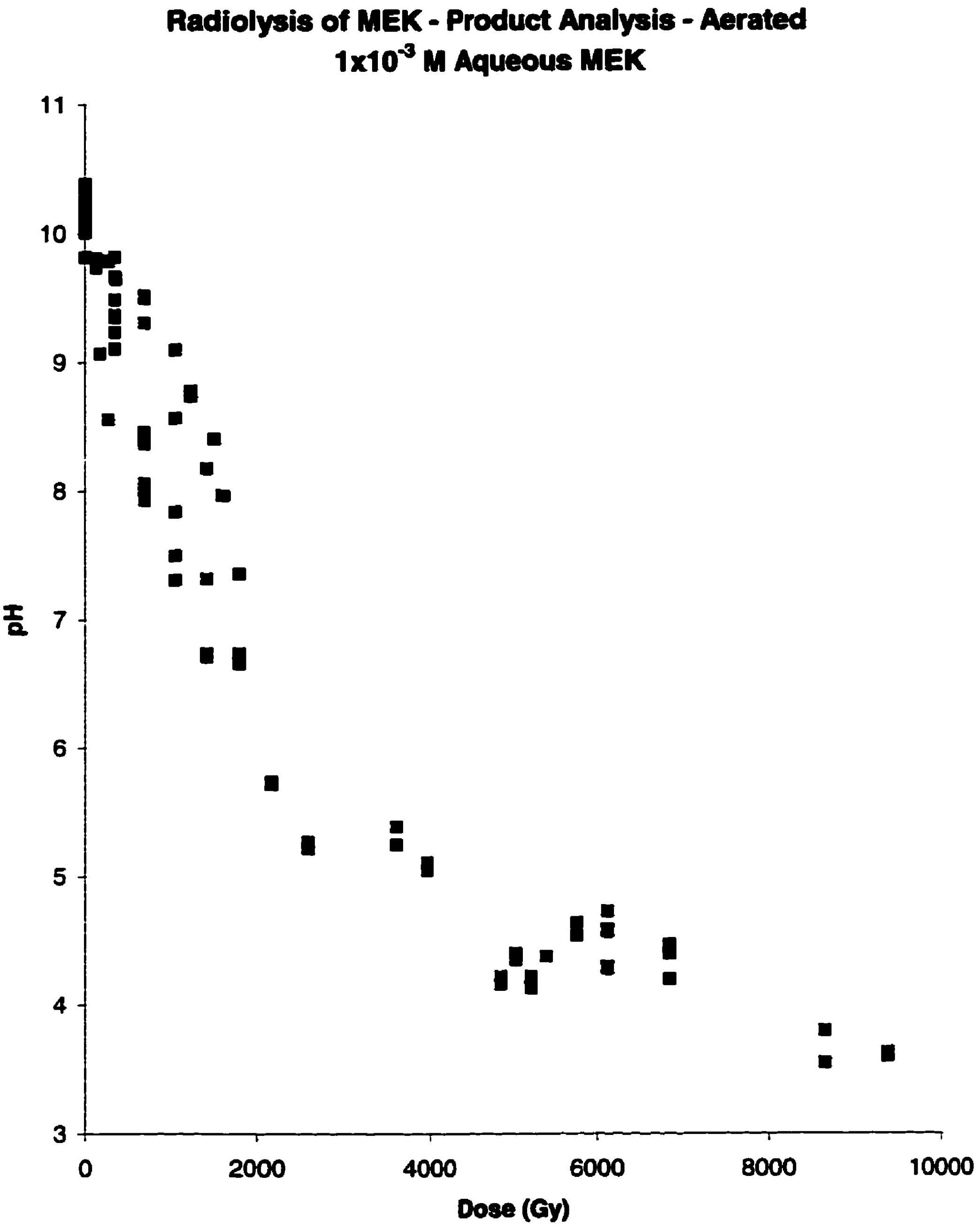


Figure 3-4e - As the irradiation continues the pH of solution decreases to below 4.

From the data in Figure 3-4a, it can be seen that the concentration of 3-hydroxy-2-butanone rises to a maximum at a dose of approximately 2000 Gy, with an initial G-value of 0.6, and then decreases as the irradiation continues.

The formation of 2,3-butanedione and 3-hydroxy-2-butanone is followed by the formation of acetaldehyde, acetic acid, and formaldehyde with minor amounts of methyl vinyl ketone (MVK) and acetone. Acetic acid is by far the most abundant radiolytic product (initial G-value 1.7) that was quantified in this study (Figure 3-4b). Products such as formaldehyde were detected later in the degradation process. These results indicate that as the breakdown proceeds, products of progressively lower molecular weight are created in aerated systems, opposite to dimerization pathways noted for non-aerated solutions. It should also be noted that the DNPH analysis for carbonyls provided some smaller peaks in the HPLC chromatogram, which were not identified.

Previous studies have show that one of the important effects on iodine volatility in a containment building after a LOCA in a nuclear reactor is the resultant pH of the solution [11]. The effect of radiolysis on the pH of an aqueous MEK solution on the pH of solution is shown in Figure 3-4e; there is a consistent pH decrease with increasing dose. From the dose profile it can be seen that there are two regions of buffering. This buffering is believed due to bicarbonate that is formed in basic solution from dissolved carbon dioxide under aerated conditions. Carbon dioxide is also a major product in the breakdown of MEK.

The results of these data support the qualitative mechanism presented in section 3.1.

3.4 The Radiolysis of Aqueous MEK Model

Using the general pathways developed in this chapter and the results of the literature searches, a quantitative degradation computer model was constructed for aqueous aerated MEK solutions with a starting pH of 10.0. This model incorporated published reactions and rate constants and consisted of the following sections:

3.4.1 Water Radiolysis Model

For dilute solutions of organic compounds that would be relevant to those expected in containment following a LOCA, it is unlikely that radiation will interact directly with dissolved organic compounds. Instead, the radiolytic breakdown of water produces a variety of transient species that can react with dissolved organic compounds. The model used in this study is based on the reaction set of Boyd et al. [15] with modified G-values and rate constants of Buxton et. al. [16] as detailed in the introduction.

3.4.2 MEK Radiolysis Model

The initial reactions in the breakdown of MEK are assumed to be caused by the reactions of hydroxyl radical, hydrated electron and hydrogen atom (reactions 3-36 to 3-38). As discussed above, the most important reaction for the initial MEK breakdown under aerated conditions is reaction 3-38. The rate constants for these reactions have been independently determined [27,35].

$$\bullet H + CH_3CH_2COCH_3 \rightarrow CH_3C\bullet HCOCH_3 + H_2 \qquad k = 3.82 \times 10^{7}\ dm^3\ mol^{-1}\ s^{-1} \qquad (3\text{-}36)$$

$$e_{aq}^- + CH_3CH_2COCH_3 \rightarrow CH_3CH_2C\bullet(OH)CH_3 + OH^- \qquad k = 4.90 \times 10^{9}\ dm^3\ mol^{-1}\ s^{-1} \qquad (3\text{-}37)$$

$$\bullet OH + CH_3CH_2COCH_3 \rightarrow CH_3C\bullet HCOCH_3 + H_2O \qquad k = 7.30 \times 10^{8}\ dm^3\ mol^{-1}\ s^{-1} \qquad (3\text{-}38)$$

In aerated solutions, the subsequent dominant pathway is expected to be the reaction of dissolved oxygen with MEK radical to yield organo peroxyl radicals (reaction 3-39) with minor contributions from disproportionation and dimerization.

$$CH_3C\bullet HCOCH_3 + O_2 \rightarrow CH_3CH(O_2\bullet)COCH_3 \qquad k = 3.1 \times 10^{9}\ dm^3\ mol^{-1}\ s^{-1} \qquad (3\text{-}39)$$

$$2\ CH_3C\bullet HCOCH_3 \rightarrow CH_3CH_2COCH_3 + CH_2{=}CHCOCH_3 \qquad k = 3.50 \times 10^{8}\ dm^3\ mol^{-1}\ s^{-1} \qquad (3\text{-}40)$$

$$2\ CH_3C\bullet HCOCH_3 \rightarrow CH_3COCH(CH_3)CH(CH_3)COCH_3 \qquad k = 3.50 \times 10^{8}\ dm^3\ mol^{-1}\ s^{-1} \qquad (3\text{-}41)$$

$$CH_2{=}CHCOCH_3 + \bullet OH \rightarrow CH_3CH(OH)COCH_3 \qquad k = 8.50 \times 10^{9}\ dm^3\ mol^{-1}\ s^{-1} \qquad (3\text{-}42)$$

The peroxyl radical of MEK, being the major product, will decay by the self-termination reactions detailed previously.

$$2\,CH_3COCH_2(CH_3)\text{-}O_2\bullet \rightarrow [CH_3COCH_2(CH_3)\text{-}O_4\text{-}CH(CH_3)COCH_3] \qquad (3\text{-}43)$$

By analogy to the acetone system studied by Zegota [28], the MEK tetroxide intermediate ($[CH_3COCH_2(CH_3)\text{-}O_4\text{-}CH(CH_3)COCH3]$ or [TI]) will follow four major decay pathways.

$$2\,CH_3COCH_2(CH_3)\text{-}O_2\bullet \rightarrow [TI] \rightarrow 2\,CH_3COCOCH_3 + H_2O_2$$

$$k = 4.00 \times 10^8\ dm^3\ mol^{-1}\ s^{-1} \qquad (3\text{-}44)$$

$$2\,CH_3COCH_2(CH_3)\text{-}O_2\bullet \rightarrow [TI] \rightarrow CH_3CH(OH)COCH_3 + CH_3COCOCH_3 + O_2$$

$$k = 2.00 \times 10^8\ dm^3\ mol^{-1}\ s^{-1} \qquad (3\text{-}45)$$

$$2\,CH_3COCH_2(CH_3)\text{-}O_2\bullet \rightarrow [TI] \rightarrow 2\,CH_3CHO + 2\,CH_3(\bullet C{=}O) + O_2$$

$$k = 1.60 \times 10^8\ dm^3\ mol^{-1}\ s^{-1} \qquad (3\text{-}46)$$

$$2\,CH_3COCH_2(CH_3)\text{-}O_2\bullet \rightarrow [TI] \rightarrow 2\,CH_3COCH_2(CH_3)O\bullet + O_2$$

$$k = 4.00 \times 10^7\ dm^3\ mol^{-1}\ s^{-1} \qquad (3\text{-}47)$$

This latter radical is easily able to abstract a hydrogen atom from any aliphatic hydrocarbon present, to give 3-hydroxy-2-butanone and another organic radical.

Since 2,3-butanedione and acetic acid are the most abundant species in solution, it is likely that abstraction will occur from one of these compounds.

The abstraction of hydrogen atoms from the 2,3-butanedione, by hydroxyl radicals and hydrogen atoms, again gives radicals that will react with dissolved oxygen, and undergo analogous breakdown reactions. This pathway for the breakdown of 2,3-butanedione occurs in competition with the established pathway with hydrogen peroxide (reactions 3-63 to 3-69) [32,38]. The reactions incorporated in the model that describe these events are [28,32,38,44,54,55]:

$$CH_3CH(O\bullet)COCH_3 + CH_3CH_2COCH_3 \rightarrow CH_3CH(OH)COCH_3 + CH_3C\bullet HCOCH_3$$

$k = 1.0 \times 10^6\ dm^3\ mol^{-1}\ s^{-1}$ (3-48)

$$CH_3CH(O\bullet)COCH_3 + CH_3COOH \rightarrow CH_3CH(OH)COCH_3 + \bullet CH_2COOH$$

$k = 1.0 \times 10^6\ dm^3\ mol^{-1}\ s^{-1}$ (3-49)

$$CH_3CH(O\bullet)COCH_3 + CH_3COO^- \rightarrow CH_3CH(OH)COCH_3 + \bullet CH_2COO^-$$

$k = 1.0 \times 10^6\ dm^3\ mol^{-1}\ s^{-1}$ (3-50)

$$CH_3CH(O\bullet)COCH_3 + CH_3COCOCH_3 \rightarrow \bullet CH_2COCOCH_3 + CH_3CH(OH)COCH_3$$

$k = 1.0 \times 10^6\ dm^3\ mol^{-1}\ s^{-1}$ (3-51)

$$CH_3COCOCH_3 + \bullet OH \rightarrow CH_3COCO\bullet CH_2 + H_2O$$

$k = 1.70 \times 10^8\ dm^3\ mol^{-1}\ s^{-1}$ (3-52)

$$CH_3COCOCH_3 + \bullet H \rightarrow CH_3COCO\bullet CH_2 + H_2$$

$k = 4.30 \times 10^6\ dm^3\ mol^{-1}\ s^{-1}$ (3-53)

$$CH_3CH(OH)COCH_3 + {\bullet}OH \rightarrow CH_3{\bullet}C(OH)COCH_3 + H_2O$$

$$k = 1.20 \times 10^{9}\ dm^{3}\ mol^{-1}\ s^{-1} \qquad (3\text{-}54)$$

$$CH_3CH(OH)COCH_3 + {\bullet}H \rightarrow CH_3{\bullet}C(OH)COCH_3 + H_2$$

$$k = 1.00 \times 10^{6}\ dm^{3}\ mol^{-1}\ s^{-1} \qquad (3\text{-}55)$$

$$CH_3{\bullet}C(OH)COCH_3 + O_2 \rightarrow CH_3C(O_2{\bullet})(OH)COCH_3$$

$$k = 1.00 \times 10^{9}\ dm^{3}\ mol^{-1}\ s^{-1} \qquad (3\text{-}56)$$

$$CH_3COCO{\bullet}CH_2 + O_2 \rightarrow CH_3COCOCH_2O_2{\bullet}$$

$$k = 1.00 \times 10^{9}\ dm^{3}\ mol^{-1}\ s^{-1} \qquad (3\text{-}57)$$

$$CH_3COCOCH_3 + e_{aq}^{-} \rightarrow CH_3COCO{\bullet}^{-}CH_3$$

$$k = 9.90 \times 10^{9}\ dm^{3}\ mol^{-1}\ s^{-1} \qquad (3\text{-}58)$$

$$CH_3COCO{\bullet}^{-}CH_3 + {\bullet}OH \rightarrow CH_3COCOCH_3 + OH^{-}$$

$$k = 1.00 \times 10^{9}\ dm^{3}\ mol^{-1}\ s^{-1} \qquad (3\text{-}59)$$

$$CH_3COCOCH_3 + H_2O \rightleftharpoons CH_3COC(OH)_2CH_3$$

$$k_f = 6.79 \times 10^{-2}\ dm^{3}\ mol^{-1}\ s^{-1},\ k_b = 2.67 \times 10^{-2}\ s^{-1} \qquad (3\text{-}60)$$

$$CH_3COC(OH)_2CH_3 + {\bullet}OH \rightarrow CH_3COCO{\bullet}CH_2 + H_2O$$

$$k = 1.70 \times 10^{8}\ dm^{3}\ mol^{-1}\ s^{-1} \qquad (3\text{-}61)$$

$$CH_3COCOCH_3 + CH_3COOOH \rightarrow 3\ CH_3COOH$$

$$k = 1.00 \times 10^{2}\ dm^{3}\ mol^{-1}\ s^{-1} \qquad (3\text{-}62)$$

Reaction of 2,3-butanedione with hydrogen peroxide forms the α-hydroxide hydroperoxy radical, which reacts via a first-order reaction to give acetic anhydride, which in water subsequently reacts to form acetic acid [38]. The reactions incorporated into the model to describe this are given below.

$CH_3COCOCH_3 + H_2O_2 \rightleftharpoons CH_3COC(OH)(O_2H)CH_3$

$k_f = 5.94 \times 10^{-1}\ dm^3\ mol^{-1}\ s^{-1},\ k_b = 5.24 \times 10^{-3}\ s^{-1}$ (3-63)

$CH_3COC(OH)(O_2H)CH_3 \rightarrow CH_3CH_2(O){-}O{-}(O)CH_2CH_3$

$k = 4.36 \times 10^{-2}\ dm^3\ mol^{-1}\ s^{-1}$ (3-64)

$CH_3CH_2(O){-}O{-}(O)CH_2CH_3 + H_2O \rightarrow 2\ CH_3COOH$

$k = 1.44 \times 10^{-2}\ dm^3\ mol^{-1}\ s^{-1}$ (3-65)

$CH_3C(O_2\bullet)(OH)COCH_3 \rightarrow CH_3COCOCH_3 + HO_2\bullet$

$k = 9.6 \times 10^{-2}\ dm^3\ mol^{-1}\ s^{-1}$ (3-66)

$2\ CH_3C(O_2\bullet)(OH)COCH_3 \rightarrow 2\ CH_3CHO + 2\ CH_3COOH$

$k = 1.0 \times 10^{8}\ dm^3\ mol^{-1}\ s^{-1}$ (3-67)

$2\ CH_3COCOCH_2O_2\bullet \rightarrow 2\ H\bullet CO + 2\ CH_3CHO + 2\ CO + O_2$

$k = 2.0 \times 10^{8}\ dm^3\ mol^{-1}\ s^{-1}$ (3-68)

$2\ CH_3COCOCH_2O_2\bullet \rightarrow 2\ H\bullet CO + 2\ CO + 2\ CH_3\bullet CO + H_2O_2$

$k = 1.0 \times 10^{8}\ dm^3\ mol^{-1}\ s^{-1}$ (3-69)

With this model for the reactions of the primary species, the further radiolytic degradation of the formed products were then determined, and likewise incorporated. The following sections detail the rate constants found in the literature, as well as the degradation mechanisms for the major products identified.

3.4.3 Acetaldehyde Reactions

Aldehydes are characterized by having a weakly bound hydrogen atom on their aldehydic carbon atom. This weak bond allows abstraction of this hydrogen by radicals that normally cannot break carbon-hydrogen bonds [14,45]. The acetyl radical generally reacts with oxygen to give the acetylperoxide radical. This radical then undergoes self-termination and β-scission-type reactions to form carbon dioxide, methyl radical and oxygen [36]. It is important to note that both the acetyl radical and acetaldehyde exist in equilibrium with hydrated forms in aqueous solution. This hydrate also loses hydrogen atoms via abstraction of hydroxyl radicals and hydrogen atoms and can also react with dissolved oxygen to give hydrated acetylperoxide radicals. This radical decays differently than the acetylperoxide radical to give acetate, protons and oxygen [36]. The reactions describing these processes [14,16,28,36] that were incorporated into the model are given below.

$CH_3{\bullet}CO \rightarrow {\bullet}CH_3 + CO$ $k = 1.00 \times 10^1\ s^{-1}$ (3-70)

$CH_3CHO + {\bullet}OH \rightarrow CH_3{\bullet}CO + H_2O$ $k = 3.60 \times 10^9\ dm^3\ mol^{-1}\ s^{-1}$ (3-71)

$CH_3CHO + CH_3{\bullet}CHCOCH_3 \rightarrow CH_3CH_2COCH_3 + CH_3{\bullet}CO$
$k = 1.00 \times 10^5\ dm^3\ mol^{-1}\ s^{-1}$ (3-72)

${\bullet}CH_3 + CH_3CHO \rightarrow CH_3{\bullet}CO + CH_4$ $k = 1.00 \times 10^7\ dm^3\ mol^{-1}\ s^{-1}$ (3-73)

$CH_3{\bullet}CO + O_2 \rightarrow CH_3CO_3{\bullet}$ $k = 5.00 \times 10^9\ dm^3\ mol^{-1}\ s^{-1}$ (3-74)

$2\ CH_3CO_3{\bullet} \rightarrow O_2 + 2\ CO_2 + 2\ {\bullet}CH_3$ $k = 1.00 \times 10^7\ dm^3\ mol^{-1}\ s^{-1}$ (3-75)

$CH_3CO_3{\bullet} + O_2{\bullet}^- \rightarrow CH_3CO_3^- + O_2$ $k = 1.00 \times 10^9\ dm^3\ mol^{-1}\ s^{-1}$ (3-76)

$CH_3{\bullet}CO + {\bullet}OH \rightarrow CH_3COOH$ $k = 1.00 \times 10^9\ dm^3\ mol^{-1}\ s^{-1}$ (3-77)

$CH_3CHO + H_2O \rightleftharpoons CH_3CH(OH)_2$

$k_f = 9.0 \times 10^{-3}\ dm^3\ mol^{-1}\ s^{-1},\ k_b = 7.2 \times 10^{-3}\ s^{-1}$ (3-78)

$CH_3CH(OH)_2 + {\bullet}OH \rightarrow {\bullet}CH_2CH(OH)_2 + H_2O$

$k = 1.20 \times 10^{9}\ dm^3\ mol^{-1}\ s^{-1}$ (3-79)

${\bullet}CH_2CH(OH)_2 + O_2 \rightarrow {\bullet}O_2CH_2CH(OH)_2$ $k = 1.00 \times 10^{9}\ dm^3\ mol^{-1}\ s^{-1}$ (3-80)

${\bullet}O_2CH_2CH(OH)_2 \rightarrow 2\ H^+ + CH_3CO_2^- + O_2$

$k = 1.00 \times 10^{8}\ dm^3\ mol^{-1}\ s^{-1}$ (3-81)

$CH_3{\bullet}CO + H_2O \rightleftharpoons CH_2{\bullet}CH(OH)_2$

$k_f = 2.0 \times 10^{4}\ dm^3\ mol^{-1}\ s^{-1},\ k_b = 3.00 \times 10^{4}\ s^{-1}$ (3-82)

$CH_3CHO + {\bullet}H \rightarrow CH_3{\bullet}CO + H_2$ $k = 3.10 \times 10^{7}\ dm^3\ mol^{-1}\ s^{-1}$ (3-83)

$2\ CH_3{\bullet}CO \rightarrow CH_3COCOCH_3$ $k = 1.00 \times 10^{9}\ dm^3\ mol^{-1}\ s^{-1}$ (3-84)

$CH_3CHO + {\bullet}HO_2 \rightarrow CH_3{\bullet}CO + H_2O_2$ $k = 1.00 \times 10^{3}\ dm^3\ mol^{-1}\ s^{-1}$ (3-85)

3.4.4 Acetic Acid Reactions

During radiolysis MEK undergoes an oxidation process to give 2,3-butanedione, which subsequently degrades to give acetic acid as a major product. Hydroxyl radical abstracts a hydrogen atom from the methyl group of both the protonated and deprotonated forms of acetic acid [39,40]. This process is followed by the addition of oxygen to give the peroxy acetic acid (or acetate) radical [37]. Consistent with the higher molecular weight peroxy radicals, these radicals decay by self-termination reactions. Protonated radicals give glyoxylic acid and hydroxyacetic acid, while de-protonated radicals give glyoxylate, hydroxylacetate, formaldehyde, hydrogen peroxide, carbon dioxide, oxygen, hydroxide and O_2^- [37]. Hydroxyl radicals and hydrogen atoms can also abstract a hydrogen atom from glyoxylic acid and hydroxyacetic acid [41] and their deprotonated forms [42,43]. These radicals react with oxygen and undergo reactions similar to those described previously, continuing until they have been converted into carbon dioxide and formic acid. The reactions describing these events that have been incorporated into the model are given below [16,37,39-51].

$CH_3CO_2H \rightleftharpoons CH_3CO_2^- + H^+$

$k_f = 1.75 \times 10^5\ s^{-1}$, $k_b = 1.00 \times 10^{10}\ dm^3\ mol^{-1}\ s^{-1}$ (3-86)

$CH_3CO_2^- + {\bullet}OH \rightarrow {\bullet}CH_2CO_2^- + H_2O$ $k = 1.00 \times 10^8\ dm^3\ mol^{-1}\ s^{-1}$ (3-87)

$CH_3CO_2H + {\bullet}OH \rightarrow {\bullet}CH_2CO_2H + H_2O$ $k = 2.30 \times 10^7\ dm^3\ mol^{-1}\ s^{-1}$ (3-88)

${\bullet}CH_2CO_2H \rightleftharpoons CH_2CO_2^- + H^+$

$k_f = 3.16 \times 10^5\ s^{-1}$, $k_b = 1.00 \times 10^{10}\ dm^3\ mol^{-1}\ s^{-1}$ (3-89)

$CH_3CO_2^- + {\bullet}H \rightarrow {\bullet}CH_2CO_2^- + H_2$ $k = 3.50 \times 10^6\ dm^3\ mol^{-1}\ s^{-1}$ (3-90)

$CH_3CO_2H + {\bullet}H \rightarrow {\bullet}CH_2CO_2H + H_2$ $k = 7.70 \times 10^6\ dm^3\ mol^{-1}\ s^{-1}$ (3-91)

${\bullet}CH_2CO_2H + O_2 \rightarrow {\bullet}O_2CH_2CO_2H$ $k = 1.00 \times 10^{10}\ dm^3\ mol^{-1}\ s^{-1}$ (3-92)

${\bullet}CH_2CO_2^- + O_2 \rightarrow {\bullet}O_2CH_2CO_2^-$ $k = 1.70 \times 10^9\ dm^3\ mol^{-1}\ s^{-1}$ (3-93)

$2\,{\bullet}O_2CH_2CO_2H \rightarrow CH_2OHCO_2H + CHOCO_2H$

$k = 1.00 \times 10^7\ dm^3\ mol^{-1}\ s^{-1}$ (3-94)

$CH_3CO_2H + e_{aq}^- \rightarrow CH_3{\bullet}CO + OH^-$ $k = 2.20 \times 10^8\ dm^3\ mol^{-1}\ s^{-1}$ (3-95)

$2\,{\bullet}O_2CH_2CO_2^- \rightarrow CHOCO_2^- + CH_2OHCO_2^- + O_2$

$k = 1.75 \times 10^7\ dm^3\ mol^{-1}\ s^{-1}$ (3-96)

$2\,{\bullet}O_2CH_2CO_2^- \rightarrow 2\ CHOCO_2^- + H_2O_2$ $k = 1.75 \times 10^7\ dm^3\ mol^{-1}\ s^{-1}$ (3-97)

$2\,{\bullet}O_2CH_2CO_2^- \rightarrow 2\ HCHO + 2\ CO_2 + H_2O_2 + 2\ OH^-$

$k = 1.75 \times 10^{7}\ \mathrm{dm^{3}\ mol^{-1}\ s^{-1}}$ (3-98)

$2\ {\bullet}O_2CH_2CO_2^- \rightarrow 2\ CHOCO_2^- + O_2^-$ $k = 7.00 \times 10^{6}\ \mathrm{dm^{3}\ mol^{-1}\ s^{-1}}$ (3-99)

${\bullet}O_2CH_2CO_2^- + O_2^- \rightarrow HO_2CH_2CO_2^-k$ $k = 1.00 \times 10^{7}\ \mathrm{dm^{3}\ mol^{-1}\ s^{-1}}$ (3-100)

$CH_2OHCO_2H \rightleftharpoons CH_2OHCO_2^- + H^+$

$k_f = 1.48 \times 10^{6}\ \mathrm{s^{-1}}$, $k_b = 1.00 \times 10^{10}\ \mathrm{dm^{3}\ mol^{-1}\ s^{-1}}$ (3-101)

$CHOCO_2H \rightleftharpoons CHOCO_2^- + H^+$

$k_f = 1.48 \times 10^{6}\ \mathrm{s^{-1}}$, $k_b = 1.00 \times 10^{10}\ \mathrm{dm^{3}\ mol^{-1}\ s^{-1}}$ (3-102)

$CH_2OHCO_2^- + {\bullet}OH \rightarrow {\bullet}CHOHCO_2^- + H_2O$

$k = 1.20 \times 10^{9}\ \mathrm{dm^{3}\ mol^{-1}\ s^{-1}}$ (3-103)

${\bullet}CHOHCO_2^- + O_2 \rightarrow {\bullet}O_2CHOHCO_2^-$ $k = 1.80 \times 10^{9}\ \mathrm{dm^{3}\ mol^{-1}\ s^{-1}}$ (3-104)

$CH_2OHCO_2H + {\bullet}OH \rightarrow {\bullet}CHOHCO_2H + H_2O$

$k = 5.40 \times 10^{8}\ \mathrm{dm^{3}\ mol^{-1}\ s^{-1}}$ (3-105)

${\bullet}CHOHCO_2H + O_2 \rightarrow {\bullet}O_2CHOHCO_2H$ $k = 1.00 \times 10^{9}\ \mathrm{dm^{3}\ mol^{-1}\ s^{-1}}$ (3-106)

$CHOCO_2^- + {\bullet}OH \rightarrow {\bullet}COCO_2^- + H_2O$ $k = 1.00 \times 10^{9}\ \mathrm{dm^{3}\ mol^{-1}\ s^{-1}}$ (3-107)

$CHOCO_2H + {\bullet}OH \rightarrow {\bullet}COCO_2H + H_2O$ $k = 1.00 \times 10^{9}\ \mathrm{dm^{3}\ mol^{-1}\ s^{-1}}$ (3-108)

${\bullet}COCO_2^- + O_2 \rightarrow {\bullet}O_2COCO_2^-$ $k = 1.00 \times 10^{9}\ \mathrm{dm^{3}\ mol^{-1}\ s^{-1}}$ (3-109)

${\bullet}COCO_2H + O_2 \rightarrow {\bullet}O_2COCO_2H$ $k = 1.00 \times 10^{9}\ \mathrm{dm^{3}\ mol^{-1}\ s^{-1}}$ (3-110)

$2\ {\bullet}O_2COCO_2H \rightarrow 2\ CO_2 + 2\ {\bullet}CO_2H + 2\ O_2$

$k = 1.00 \times 10^{9}\ \mathrm{dm^{3}\ mol^{-1}\ s^{-1}}$ (3-111)

$$2\,\bullet O_2COCO_2^- \rightarrow 2\,CO_2 + 2\,\bullet CO_2^- + O_2 \qquad k = 1.00 \times 10^9\ dm^3\ mol^{-1}\ s^{-1} \tag{3-112}$$

$$2\,\bullet O_2CHOHCO_2^- \rightarrow O_2 + 2\,HCO_2H + 2\,\bullet CO_2^-$$

$$k = 1.00 \times 10^9\ dm^3\ mol^{-1}\ s^{-1} \tag{3-113}$$

$$2\,\bullet O_2CHOHCO_2^- \rightarrow O_2 + 2\,HCO_2H + 2\,\bullet CO_2H$$

$$k = 1.00 \times 10^9\ dm^3\ mol^{-1}\ s^{-1} \tag{3-114}$$

$$(CH_2CO_2H)_2 \rightleftharpoons HO_2CCH_2CH_2CO_2^- + H^+$$

$$k_f = 6.92 \times 10^5\ s^{-1} \quad k_b = 1.00 \times 10^{10}\ dm^3\ mol^{-1}\ s^{-1} \tag{3-115}$$

$$HO_2CCH_2CH_2CO_2^- \rightleftharpoons {}^-O_2CCH_2CH_2CO_2^- + H^+$$

$$k_f = 2.45 \times 10^4\ s^{-1} \quad k_b = 1.00 \times 10^{10}\ dm^3\ mol^{-1}\ s^{-1} \tag{3-116}$$

$$CHOCO_2H + \bullet H \rightarrow CO + \bullet CO_2H + H_2 \qquad k = 2.20 \times 10^7\ dm^3\ mol^{-1}\ s^{-1} \tag{3-117}$$

$$CHOCO_2H + CH_3\bullet CHCOCH_3 \rightarrow CH_3CH_2COCH_3 + CO + \bullet CO_2H$$

$$k = 1.00 \times 10^3\ dm^3\ mol^{-1}\ s^{-1} \tag{3-118}$$

$$CH_3CO_2H + e_{aq}^- \rightarrow CH_3CO_2^- + \bullet H \qquad k = 2.20 \times 10^8\ dm^3\ mol^{-1}\ s^{-1} \tag{3-119}$$

$$CH_3CO_2H + e_{aq}^- \rightarrow CH_3\bullet CO + OH^- \qquad k = 1.00 \times 10^9\ dm^3\ mol^{-1}\ s^{-1} \tag{3-120}$$

3.4.5 Formaldehyde and Formic Acid Reactions

Formic acid and formate both react with hydroxyl radical and hydrogen atom via abstraction reactions to give the carboxyl radical and carboxyl radical anion respectively. The solvated electron reacts with formic acid by two separate pathways, to give the formyl radical and hydroxide or formate and a hydrogen atom. The breakdown of formaldehyde also gives a formyl radical via hydrogen abstraction by hydrogen atom or hydroxyl radical. The formyl radical may further decompose via reaction with dissolved oxygen by processes similar to those discussed previously.

The reactions included in this model for the radiolysis of these two species are given in Tables 6 and 7 [14,16,45,56,57].

$$HCO_2H + {\bullet}OH \rightarrow {\bullet}CO_2H + H_2O \qquad k = 1.30 \times 10^{8}\ dm^{3}\ mol^{-1}\ s^{-1} \qquad (3\text{-}121)$$

$$HCO_2H + e_{aq}^{-} \rightarrow H{\bullet}CO + OH^{-} \qquad k = 1.50 \times 10^{8}\ dm^{3}\ mol^{-1}\ s^{-1} \qquad (3\text{-}122)$$

$$HCO_2H + e_{aq}^{-} \rightarrow HCO_2^{-} + {\bullet}H \qquad k = 1.90 \times 10^{8}\ dm^{3}\ mol^{-1}\ s^{-1} \qquad (3\text{-}123)$$

$$HCO_2H + {\bullet}H \rightarrow {\bullet}CO_2H + H_2 \qquad k = 4.40 \times 10^{5}\ dm^{3}\ mol^{-1}\ s^{-1} \qquad (3\text{-}124)$$

$${\bullet}CO_2H + O_2 \rightarrow CO_2 + HO_2{\bullet} \qquad k = 2.40 \times 10^{9}\ dm^{3}\ mol^{-1}\ s^{-1} \qquad (3\text{-}125)$$

$${\bullet}CO_2H + H_2O_2 \rightarrow CO_2 + {\bullet}OH + H_2O \qquad k = 1.00 \times 10^{9}\ dm^{3}\ mol^{-1}\ s^{-1} \qquad (3\text{-}126)$$

$$2\ {\bullet}CO_2H \rightarrow HCO_2H + CO_2 \qquad k = 1.00 \times 10^{9}\ dm^{3}\ mol^{-1}\ s^{-1} \qquad (3\text{-}127)$$

$${\bullet}CO_2H + HCO_2H \rightarrow H{\bullet}CO + CO_2 + H_2O \qquad k = 1.00 \times 10^{9}\ dm^{3}\ mol^{-1}\ s^{-1} \qquad (3\text{-}128)$$

$${\bullet}CO_2H + H{\bullet}CO \rightarrow {\bullet}CH_2OH + CO_2 \qquad k = 1.00 \times 10^{9}\ dm^{3}\ mol^{-1}\ s^{-1} \qquad (3\text{-}129)$$

$${\bullet}CH_2OH + HCO_2H \rightarrow CH_3OH + {\bullet}CO_2H \qquad k = 1.00 \times 10^{6}\ dm^{3}\ mol^{-1}\ s^{-1} \qquad (3\text{-}130)$$

$$HCO_2^{-} + {\bullet}OH \rightarrow {\bullet}CO_2^{-} + H_2O \qquad k = 3.20 \times 10^{9}\ dm^{3}\ mol^{-1}\ s^{-1} \qquad (3\text{-}131)$$

$$HCO_2^{-} + {\bullet}H \rightarrow H_2 + {\bullet}CO_2^{-} \qquad k = 2.10 \times 10^{8}\ dm^{3}\ mol^{-1}\ s^{-1} \qquad (3\text{-}132)$$

$$HCO_2^{-} + e_{aq}^{-} \rightarrow H{\bullet}CO + 2\ OH^{-} \qquad k = 1.00 \times 10^{6}\ dm^{3}\ mol^{-1}\ s^{-1} \qquad (3\text{-}133)$$

$$HCO_2H \rightleftharpoons HCO_2^{-} + COOH$$

$$k_f = 1.75 \times 10^{5}\ s^{-1},\ k_b = 1.00 \times 10^{10}\ dm^{3}\ mol^{-1}\ s^{-1} \qquad (3\text{-}134)$$

$$H{\bullet}CO + HCO_2H \rightarrow HCHO + H^{+} \qquad k = 1.00 \times 10^{7}\ dm^{3}\ mol^{-1}\ s^{-1} \qquad (3\text{-}135)$$

$HCHO + \bullet OH \rightarrow H\bullet CO + H_2O$ $k = 1.00 \times 10^9\ dm^3\ mol^{-1}\ s^{-1}$ (3-136)

$HCHO + \bullet H \rightarrow H\bullet CO + H_2$ $k = 5.00 \times 10^6\ dm^3\ mol^{-1}\ s^{-1}$ (3-137)

$HCHO + e_{aq}^- \rightarrow \bullet CH_2OH + OH^-$ $k = 1.00 \times 10^7\ dm^3\ mol^{-1}\ s^{-1}$ (3-138)

$H\bullet CO + O_2 \rightarrow \bullet O_2HCO$ $k = 7.70 \times 10^8\ dm^3\ mol^{-1}\ s^{-1}$ (3-139)

$H\bullet CO + O_2 \rightarrow CO_2 + \bullet OH$ $k = 4.50 \times 10^9\ dm^3\ mol^{-1}\ s^{-1}$ (3-140)

$\bullet O_2HCO + HO_2\bullet \rightarrow HCO_2H + H_2O_2 + O_2$ $k = 1.00 \times 10^3\ dm^3\ mol^{-1}\ s^{-1}$ (3-141)

$2\ H\bullet CO \rightarrow HCHO + HCO_2H$ $k = 3.00 \times 10^8\ dm^3\ mol^{-1}\ s^{-1}$ (3-142)

$\bullet CH_2OH + HCHO \rightarrow CH_3OH + H\bullet CO$ $k = 3.40 \times 10^3\ dm^3\ mol^{-1}\ s^{-1}$ (3-143)

$HCHO + CH_3\bullet CHCOCH_3 \rightarrow H\bullet CO + CH_3CH_2COCH_3$

$k = 1.00 \times 10^3\ dm^3\ mol^{-1}\ s^{-1}$ (3-144)

3.4.6 CO_2 and CO Reactions

The influence of the chemistry of carbon dioxide on the overall system was found to be very important, because of the buffering ability of bicarbonate. Carbon dioxide reacts thermally with the hydroxide ion to produce bicarbonate, (HCO_3^-), which may further react with another hydroxide to give carbonate (CO_3^{2-}) or with protons to form carbonic acid (H_2CO_3). All of these species react with the primary water radiolysis species to give radicals.

Carbon dioxide was present in the air used to purge the solution, and thus also has to be considered as an initial reactant. The total concentration of bicarbonate obtained after a 30-minute air purge at pH 10.0 was measured by titration to be ~ 1.4 x

10^{-4} M. Considering the errors involved in this measurement, an initial value of 1.0 x 10^{-4} M was assumed. From the well established pK_a values for bicarbonate of 6.37 and 10.25 [45], initial concentrations of bicarbonate and carbonate of 6.4 x 10^{-5} and 3.6 x 10^{-5} M respectively were used as initial values in our modeling. The initial concentration of gas-phase carbon dioxide was taken as 1.34 x 10^{-5} M.

The reactions of carbon dioxide that were incorporated into this model were [16,45,56,58,59].

$CO_2 + OH^- \rightleftharpoons HCO_3^-$ $k_f = 8500\ dm^3\ mol^{-1}\ s^{-1},\ k_b = 2.0 \times 10^{-4}\ s^{-1}$ (3-145)

$CO_2 + H_2O \rightleftharpoons H_2CO_3$ $k_f = 0.03\ dm^3\ mol^{-1}\ s^{-1},\ k_b = 20\ s^{-1}$ (3-146)

$H_2CO_3 \rightleftharpoons HCO_3^- + H^+$ $k_f = 4.3 \times 10^4\ s^{-1},\ k_b = 1.0 \times 10^{10}\ dm^3\ mol^{-1}\ s^{-1}$ (3-147)

$HCO_3^- \rightleftharpoons CO_3^{2-} + H^+$ $k_f = 0.484\ s^{-1},\ k_b = 1.0 \times 10^{10}\ dm^3\ mol^{-1}\ s^{-1}$ (3-148)

$HCO_3^- + \bullet OH \rightarrow \bullet CO_3^- + H_2O$ $k = 8.50 \times 10^6\ dm^3\ mol^{-1}\ s^{-1}$ (3-149)

$CO_3^{2-} + \bullet OH \rightarrow OH^- + \bullet CO_3^- + H_2O$ $k = 3.90 \times 10^8\ dm^3\ mol^{-1}\ s^{-1}$ (3-150)

$CO_3^- + e_{aq}^- \rightarrow CO_3^{2-}$ $k = 3.90 \times 10^5\ dm^3\ mol^{-1}\ s^{-1}$ (3-151)

$CO_2 + e_{aq}^- \rightarrow \bullet CO_2^-$ $k = 7.70 \times 10^9\ dm^3\ mol^{-1}\ s^{-1}$ (3-152)

$CO_2^- + O_2 \rightarrow CO_2 + O_2\bullet^-$ $k = 2.40 \times 10^9\ dm^3\ mol^{-1}\ s^{-1}$ (3-153)

$CO_2 + \bullet H + H_2O \rightarrow \bullet CO_2H + H_2$ $k = 1.00 \times 10^6\ dm^3\ mol^{-1}\ s^{-1}$ (3-154)

$CO_2 + \bullet OH \rightarrow \bullet CO_3^-$ $k = 1.00 \times 10^6\ dm^3\ mol^{-1}\ s^{-1}$ (3-155)

$CO_2^- + \bullet H \rightarrow \bullet CO + OH^-$ $k = 1.00 \times 10^6\ dm^3\ mol^{-1}\ s^{-1}$ (3-156)

$\bullet CO_3^- + H_2O_2 \rightarrow HCO_3^- + \bullet HO_2$ $k = 5.00 \times 10^5\ dm^3\ mol^{-1}\ s^{-1}$ (3-157)

The radiolysis reactions of carbon monoxide, have also been added to this general model, because it is the product of some previous reactions [16,60-62].

$CO + e_{aq}^- + H_2O \rightarrow H{\bullet}CO + OH^-$ $k = 1.60 \times 10^9\ dm^3\ mol^{-1}\ s^{-1}$ (3-158)

$CO + {\bullet}OH \rightarrow {\bullet}CO_2H$ $k = 2.00 \times 10^9\ dm^3\ mol^{-1}\ s^{-1}$ (3-159)

${\bullet}CH_3 + CO \rightarrow CH_3{\bullet}CO$ $k = 2.00 \times 10^6\ dm^3\ mol^{-1}\ s^{-1}$ (3-160)

3.4.7 Methyl Radical Reactions

Methyl radicals will react with dissolved oxygen to form methyl peroxy radicals that will decay by self-termination reactions via the tetroxide intermediate. The products are formaldehyde and hydrogen peroxide. The reactions incorporated into the model were [16,63,64].

${\bullet}CH_3 + {\bullet}OH \rightarrow CH_3OH$ $k = 1.00 \times 10^{10}\ dm^3\ mol^{-1}\ s^{-1}$ (3-161)

${\bullet}CH_3 + O_2 \rightarrow CH_3O_2{\bullet}$ $k = 3.70 \times 10^9\ dm^3\ mol^{-1}\ s^{-1}$ (3-162)

$CH_3O_2{\bullet} + CH_3O_2{\bullet} \rightarrow HCHO + CH_3OH + O_2$

$k = 4.00 \times 10^8\ dm^3\ mol^{-1}\ s^{-1}$ (3-163)

$CH_3O_2{\bullet} + CH_3O_2{\bullet} \rightarrow HCHO + HCHO + H_2O_2$

$k = 3.00 \times 10^8\ dm^3\ mol^{-1}\ s^{-1}$ (3-164)

3.4.8 2-Butanol Reactions

Lastly, the reactions of the 2-butanol radical, formed from electron capture of MEK, have also been included in this model. It is expected that the major pathway for the loss of this radical would occur by reaction with oxygen. The specific reactions included are [47,50,59,65,66].

$CH_3CH_2CH(OH)CH_3 + {\bullet}OH \rightarrow CH_3CH_2{\bullet}C(OH)CH_3 + H_2O$

$k = 3.10 \times 10^9\ dm^3\ mol^{-1}\ s^{-1}$ (3-165)

$CH_3CH_2CH(OH)CH_3 + {\bullet}H \rightarrow CH_3CH_2{\bullet}C(OH)CH_3 + H_2$

$k = 1.20 \times 10^6\ dm^3\ mol^{-1}\ s^{-1}$ (3-166)

$2\ CH_3CH_2{\bullet}C(OH)CH_3 \rightarrow CH_3CH_2COCH_3 + CH_3CH_2CH(OH)CH_3$

$k = 2.40 \times 10^9\ dm^3\ mol^{-1}\ s^{-1}$ (3-167)

$CH_3CH_2{\bullet}C(OH)CH_3 + O_2 \rightarrow CH_3CH_2C(O_2{\bullet})(OH)CH_3$

$k = 4.20 \times 10^9\ dm^3\ mol^{-1}\ s^{-1}$ (3-168)

$CH_3CH_2C(O_2{\bullet})(OH)CH_3 \rightarrow CH_3CH_2COCH_3 + HO_2{\bullet}$

$k = 1.00 \times 10^2\ s^{-1}$ (3-169)

$2\ CH_3CH_2C(O_2{\bullet})(OH)CH_3 \rightarrow 2\ CH_3CH_2COCH_3 + H_2O_2 + O_2$

$k = 1.10 \times 10^7\ dm^3\ mol^{-1}\ s^{-1}$ (3-170)

$CH_3CH_2{\bullet}C(OH)CH_3 + H_2O_2 \rightarrow CH_3CH_2COCH_3 + {\bullet}OH + H_2O$

$k = 2.30 \times 10^5\ dm^3\ mol^{-1}\ s^{-1}$ (3-171)

3.5 Model Performance

The predictions of the model were compared with the measured experimental data, as shown in Figures 3-5a, 3-5b and 3-5c. The calculated dose dependence for the radiation-induced degradation of MEK is shown as the solid line in Figure 3-5a. Although a little lower than the measured data at longer times, there is very good agreement between theory and experiment. The predicted temporal behavior of the intermediate products acetaldehyde, formaldehyde, 3-hydroxy-2-butanone and acetic acid (or acetate) are given in Figure 3-5b. Quantitative agreement for these compounds is seen to be within 20 - 30%, and there is very good agreement to the experimental data for the formation and decay profiles of these species. The model predicts the rapid formation of 3-hydroxy-2-butanone, arising from the termination reaction of the MEK peroxy radicals, as well as its subsequent quick decrease resulting from the loss of MEK in the irradiated solution. The predicted formation of acetaldehyde is somewhat faster than observed experimentally, its concentration peaks at a lower dose but shows a slower decay then for observed data. The calculated concentration profile for formaldehyde is predicted to have a slower initial growth, it peaks at a higher dose, and then decays even more slowly than acetaldehyde.

The formation of acetic acid/acetate is of particular importance, as it is one of the major products in the radiation-induced degradation of MEK, and because of its large influence on the solution pH. The experimentally determined profile of acetic

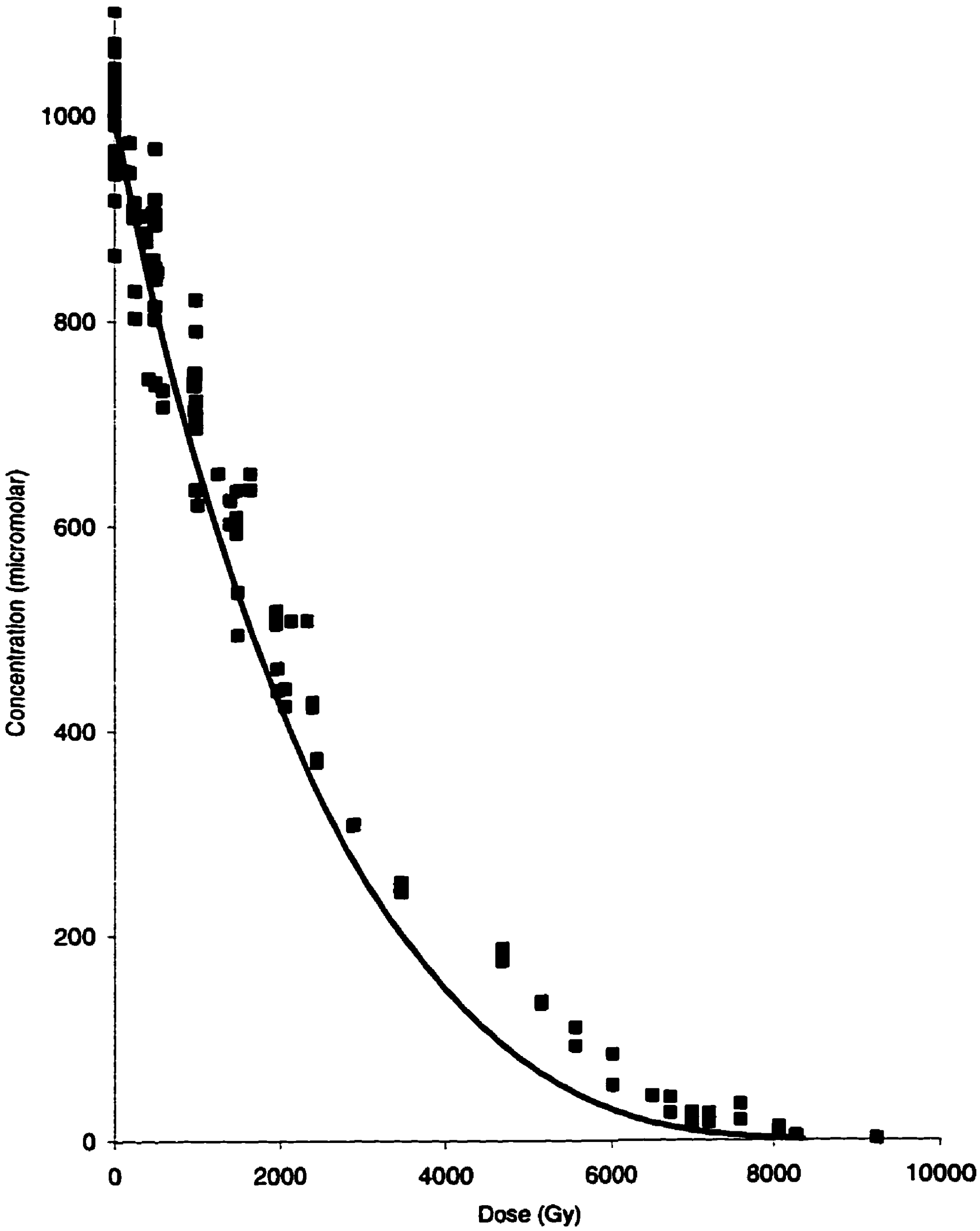
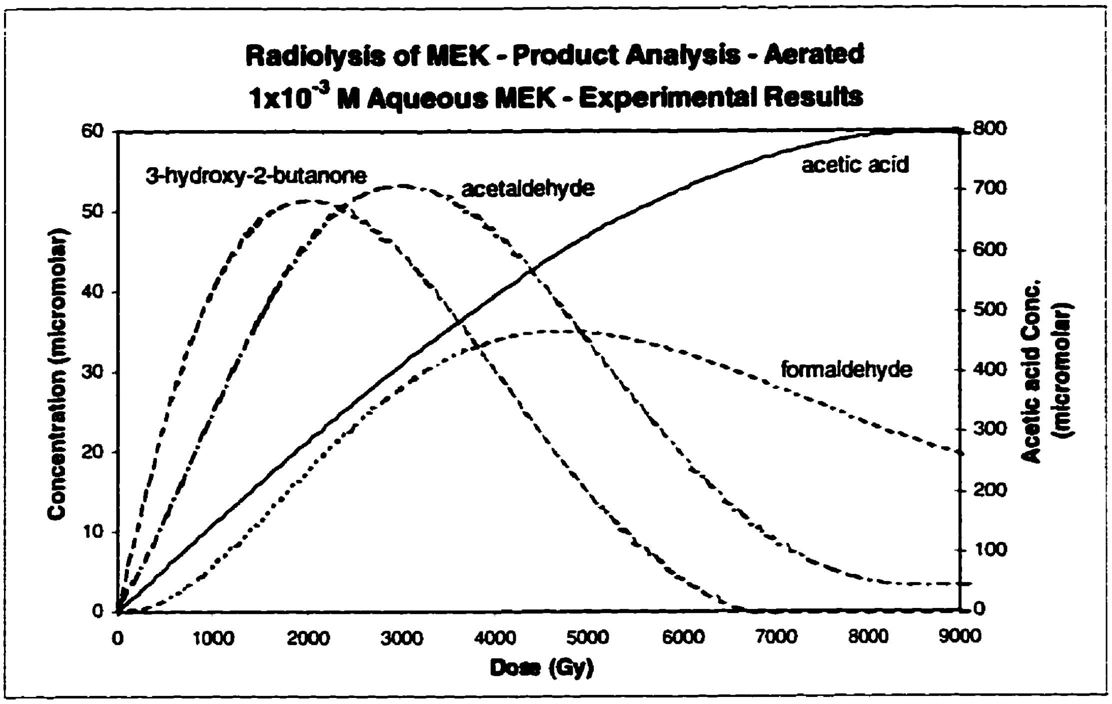


Figure 3-5a - Comparison of MEK decay observed experimentally (■) and predicted (solid line) by the computer model.



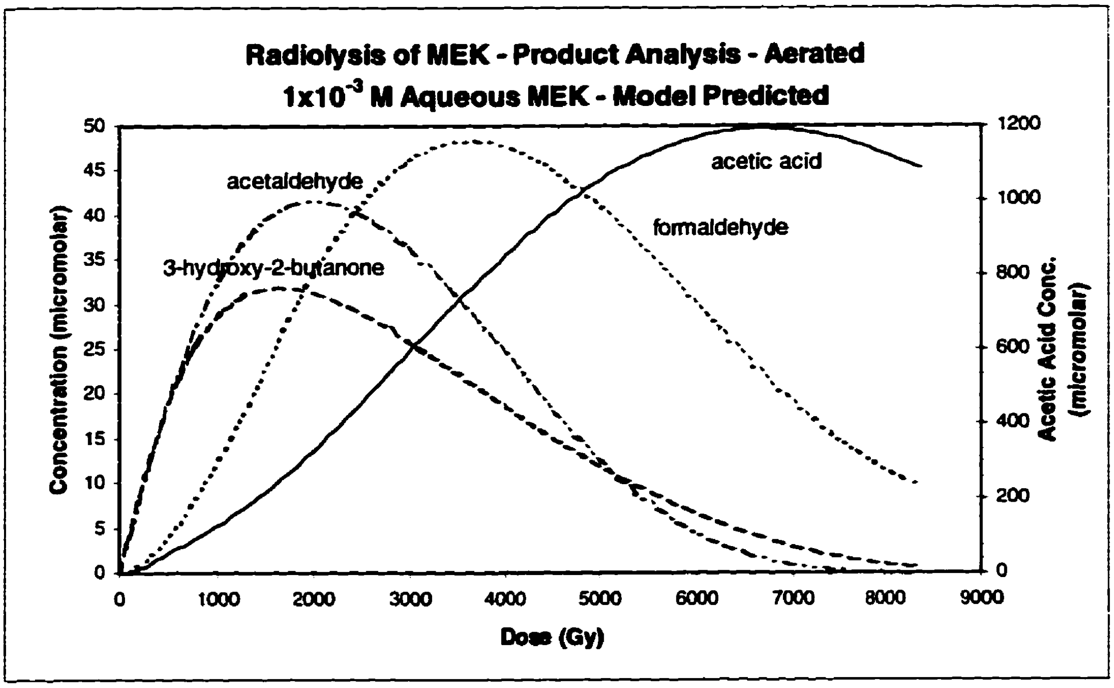


Figure 3-5b - Comparison of experimental and model predicted temporal profiles for intermediate products, 3-hydroxy-2-butanone, acetaldehyde, formaldehyde, and acetic acid formed in the radiolysis of aqueous MEK solutions. Experimental data has been fitted using a 5th order polynomial function.

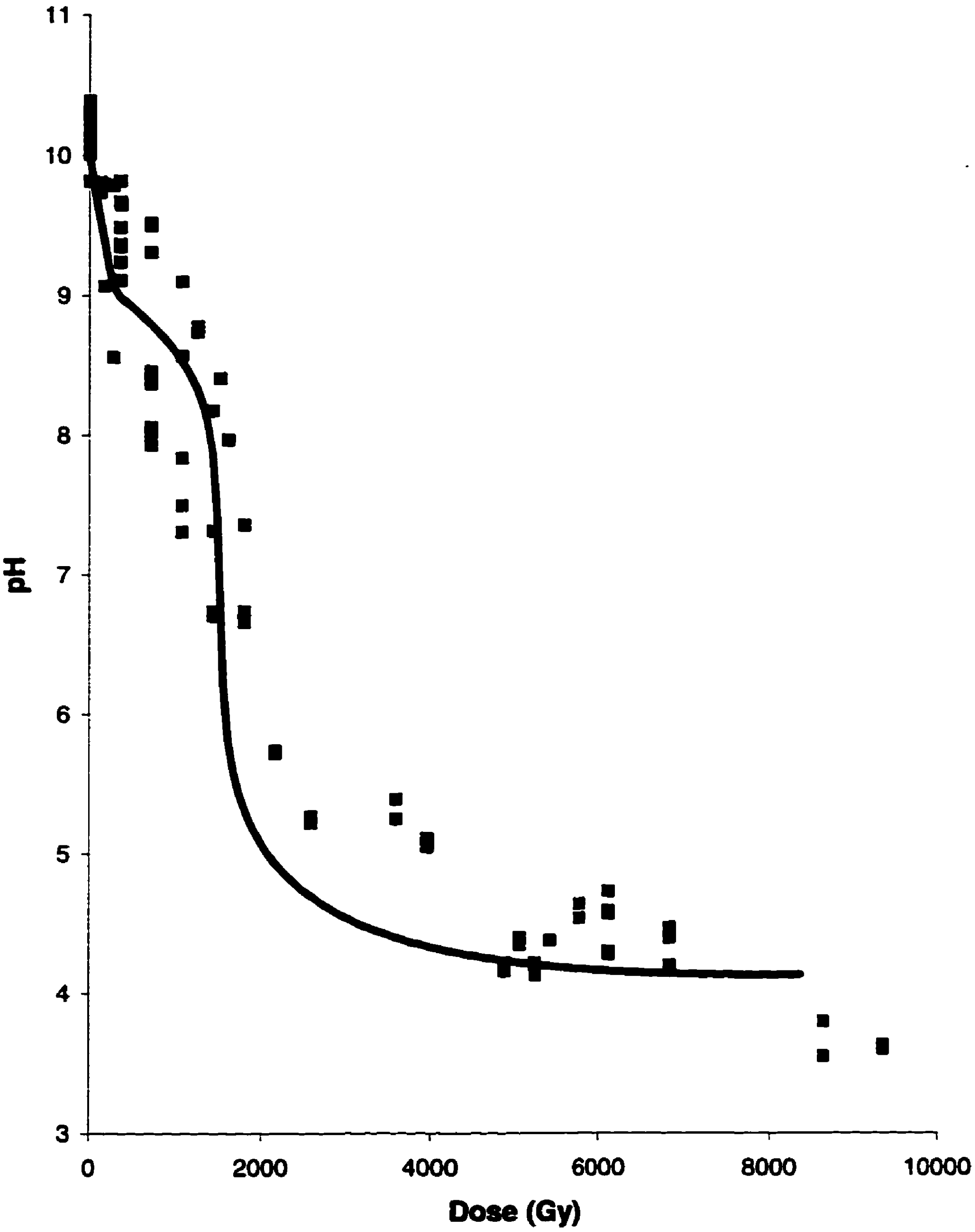


Figure 3-5c - Comparison of pH changes observed experimentally (■) and predicted (solid line) by computer model.

acid concentration is approximately linear to a dose of about 8000 Gy, whereupon a plateau is observed. The calculated values given by the model are shown in Figure 3-5b, which show a sigmoidal approach to a maximum value, followed by a slight decrease over the dose range of this study. Although the peak concentration for acetic acid formation is about 25% too high, this error is acceptable since the calculated dose dependent profile is in good agreement with the experimental data.

The calculated pH dependence is given as the solid line in Figure 3-5c, and is seen to be in very good agreement with the measured values. The predicted values follow the behavior expected for a system showing two buffered regions, as expected from the $CO_2/HCO_3^-/CO_3^{2-}$ equilibria. These calculated values include the initial bicarbonate/carbonate concentration of 1.0×10^{-4} M, obtained from the air purge of the MEK solutions, as described previously.

The product analyses that was performed in this study showed many minor products that were not identified nor quantified, and might may need to be incorporated into more refined versions of the model. For this study however, only the most important system parameters have been considered. These criteria were taken as the overall loss of MEK, the production of acetic acid and the total change in the solution pH. The concentration of dissolved oxygen was calculated to remain constant 2.5×10^{-4} M under these experimental conditions. Also, since the rate of addition of oxygen to organic radicals is near diffusion controlled even at relatively low concentrations, this reaction will predominate over second-order radical-radical and electron reactions in containment at even very low concentrations.

The absolute agreement to the experimental data could be further modified for any one of the MEK concentration, intermediate concentration or pH time profiles by changing the rate constants used in certain reactions. Of greatest sensitivity was the branching ratios used to determine the rate constants for the decay of the intermediate tetroxide formed by the self-termination reactions of the α-peroxy ketones. As stated previously, these values have not been determined for MEK, but were assumed to be the same as those measured for acetone. It should also be noted that in the solution pH dependence shown in Figure 3-5c, the width of the first plateau (300-1300 Gy) was quite sensitive to the initial values chosen for the concentration of bicarbonate before irradiation. The modeled values given here represent the best calculated fit to all the experimental data obtained in this study.

4.0 Solutions Containing Iodide

In the previous chapter an understanding of the decay pathways of aerated aqueous MEK in the presence of γ-radiolysis was elucidated under LOCA conditions. This work demonstrated that the presence of organic compounds under these conditions lowered the solution pH, due to the formation of low molecular weight organic acids, which would result in an increase in iodine volatility within containment [11]. In addition, the presence of organic compounds allows volatile iodoalkanes such as methyl iodide to be formed. Though the concentration of iodine (I_2) is expected to be higher than methyl iodide in containment under LOCA conditions, these small organic iodides are of importance since they have a lower liquid/gas phase partition coefficient than iodine (80 for iodine and 3.4 for methyl iodide) [11],, making them more difficult to contain in solution. As even small amounts of low molecular weight organic iodides in solution may significantly increase the levels of gaseous radioactive iodine in containment, an additional study on the effect of dissolved iodide on the radiolysis of aqueous MEK solutions was therefore undertaken.

For the γ-radiolysis of $1x10^{-3}$ M MEK solutions with $1x10^{-4}$ M added iodide, a variety of breakdown products were detected and analyzed, especially carbonyl compounds and methyl iodide. At this concentration of added iodide a competitive reaction of hydroxyl radicals (reaction 4-1) [16] depletes the amount of hydroxyl radicals available for reaction with MEK (reaction 3-2). Methyl iodide has been shown to be formed by the reaction of methyl radical with iodine (reaction 4-2) while no reaction with iodide was observed [67].

$$\bullet OH + I^- \rightarrow I\bullet + OH^- \qquad (4\text{-}1)$$

$$\bullet CH_3 + I_2 \rightarrow CH_3I + I\bullet \qquad (4\text{-}2)$$

The radical scavengers t-butanol and nitrous oxide were again used to remove hydroxyl radicals and hydrated electrons, respectively, so that decay pathways could be studied in isolation. To study non-aerated conditions dissolved oxygen was removed by purging with argon. By varying these conditions a qualitative description of the chemistry involved in this system was obtained. A summary of all the experiments involving added iodide is given in Table 2-1.

4.1 Aerated Solutions

The breakdown of 1×10^{-3} M MEK in the air-saturated aqueous solutions containing 5×10^{-4} M I^- was the slowest of all the experiments performed in this series (see Figure 4-1a). The initial pseudo first-order degradation rate constant was approximately an order of magnitude slower than that determined for only MEK radiolysis (see Figure 3-4a). This can mostly be attributed to the competitive reactions of the hydroxyl radicals listed above, where from the ratio of the rate constants the breakdown of MEK would be expected to be slower by a factor of about 7.

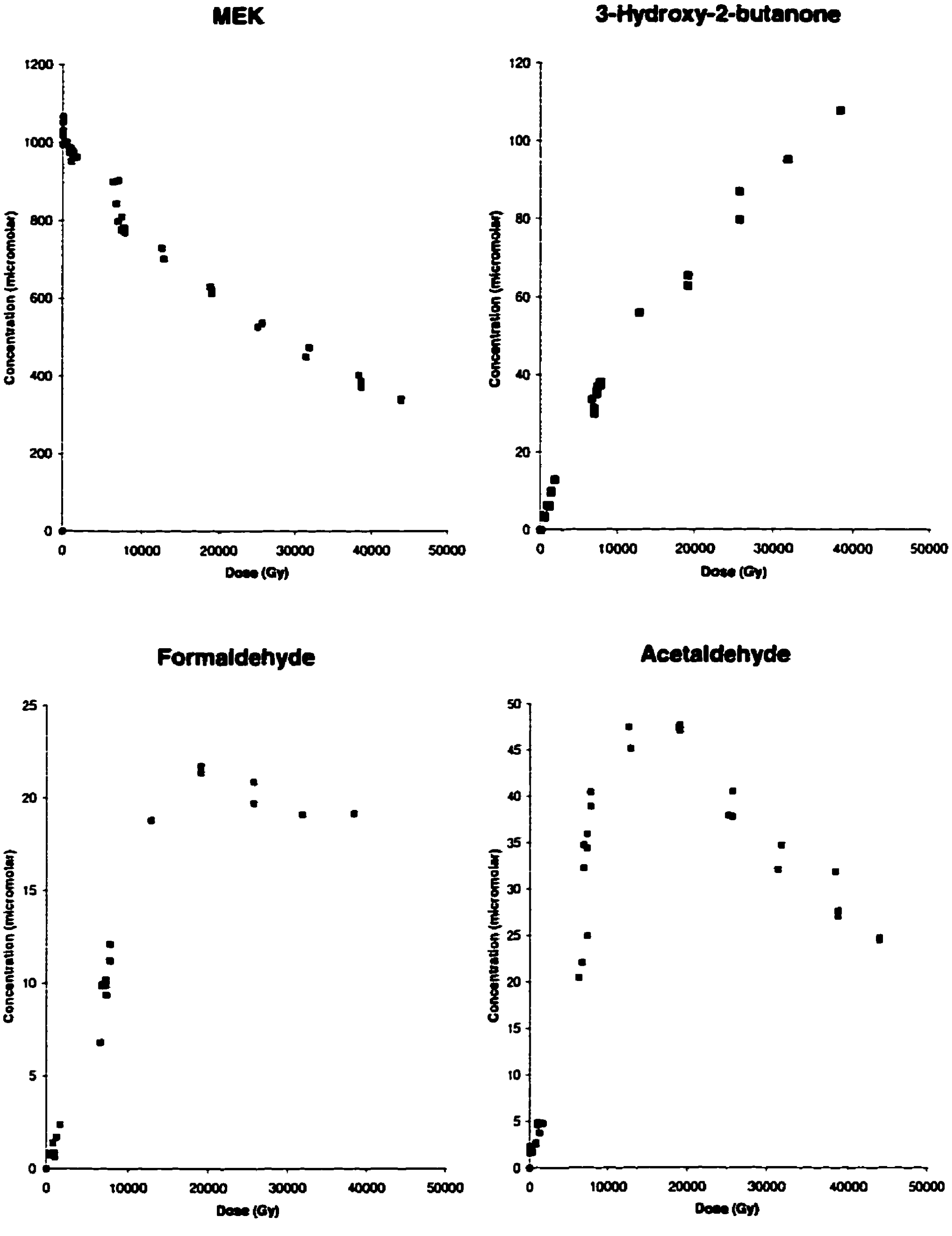


Figure 4-1a - Product analysis for the radiolysis of air-purged 1×10^{-3} M MEK solutions with 5×10^{-4} M iodide. The pseudo first order decay rate for MEK under these conditions is much slower then for the same solution without iodide (Figure 3-4a).

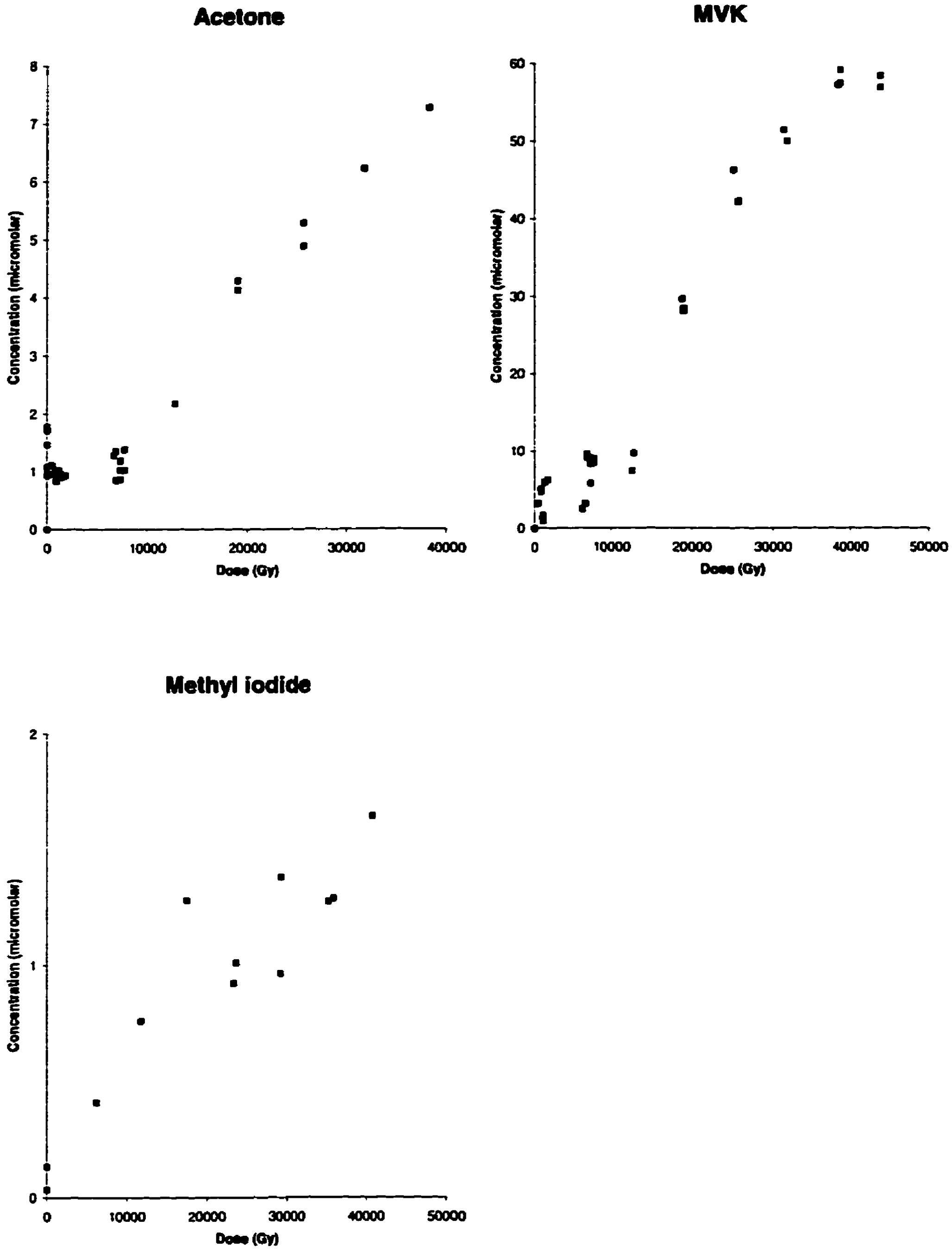


Figure 4-1b - Product analysis for the radiolysis of air-purged 1x10^{-3} M MEK solutions with 5x10^{-4} M iodide. A linear formation is observed for methyl iodide.

The formation of methyl iodide under these conditions was shown to be linear for the entire run, reaching a concentration greater than 1 µM after a dose of 4000 Gy dose (Figure 4-1b).

Standard carbonyl analysis showed the concentrations of 3-hydroxy-2-butanone, formaldehyde, acetaldehyde, and methyl vinyl ketone to be higher when iodide was present. The maximum concentration of MVK formed with added iodide was about 6 times higher than without iodide, while the increase for 2-hydroxy-2-butanone was about double. There was minimal acetone formed under these conditions, in agreement with the results obtained for non-iodide solutions (Figure 4-1b and 3-4b).

4.2 Argon-Saturated Solutions

For argon-saturated MEK solutions containing iodide, the loss of MEK was about 8 times slower than for the corresponding system without iodide, again attributed to the competitive scavenging of hydroxyl radical and hydrogen atom by iodide. Since there was no dissolved oxygen in solution, hydrated electrons were free to react with MEK, which would be expected to increase the degradative MEK rate relative to aerated solutions (Figure 4-2a).

The formation of Methyl iodide was again observed to be linear for this entire run, with a production rate that is approximately equal to that observed in the aerated system (Figure 4-2b).

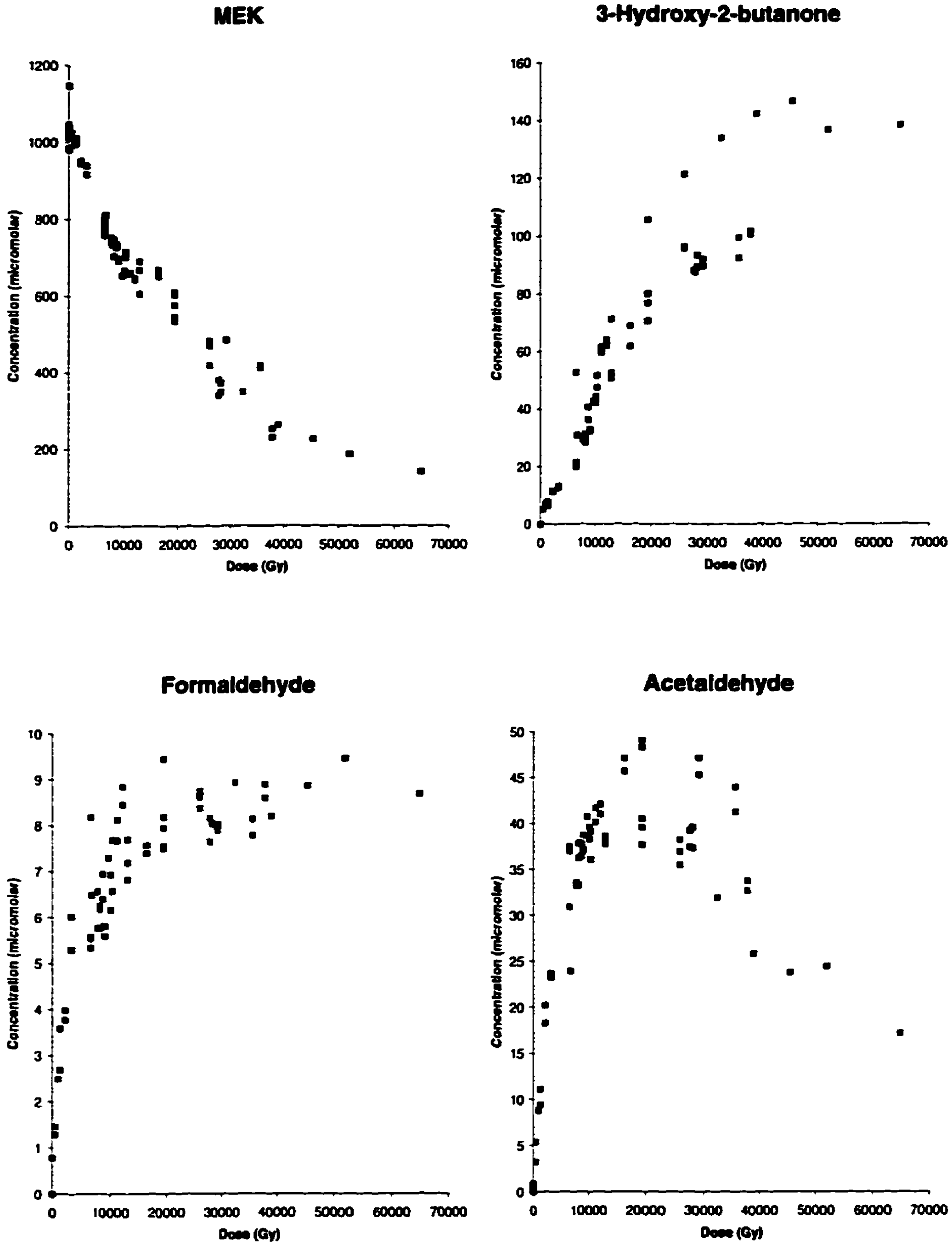


Figure 4-2a - Product analysis for the radiolysis of argon-purged 1×10^{-3} M MEK solutions with 5×10^{-4} M iodide. The pseudo first order decay rate for MEK under these conditions is again slower then for the same solution without added iodide.

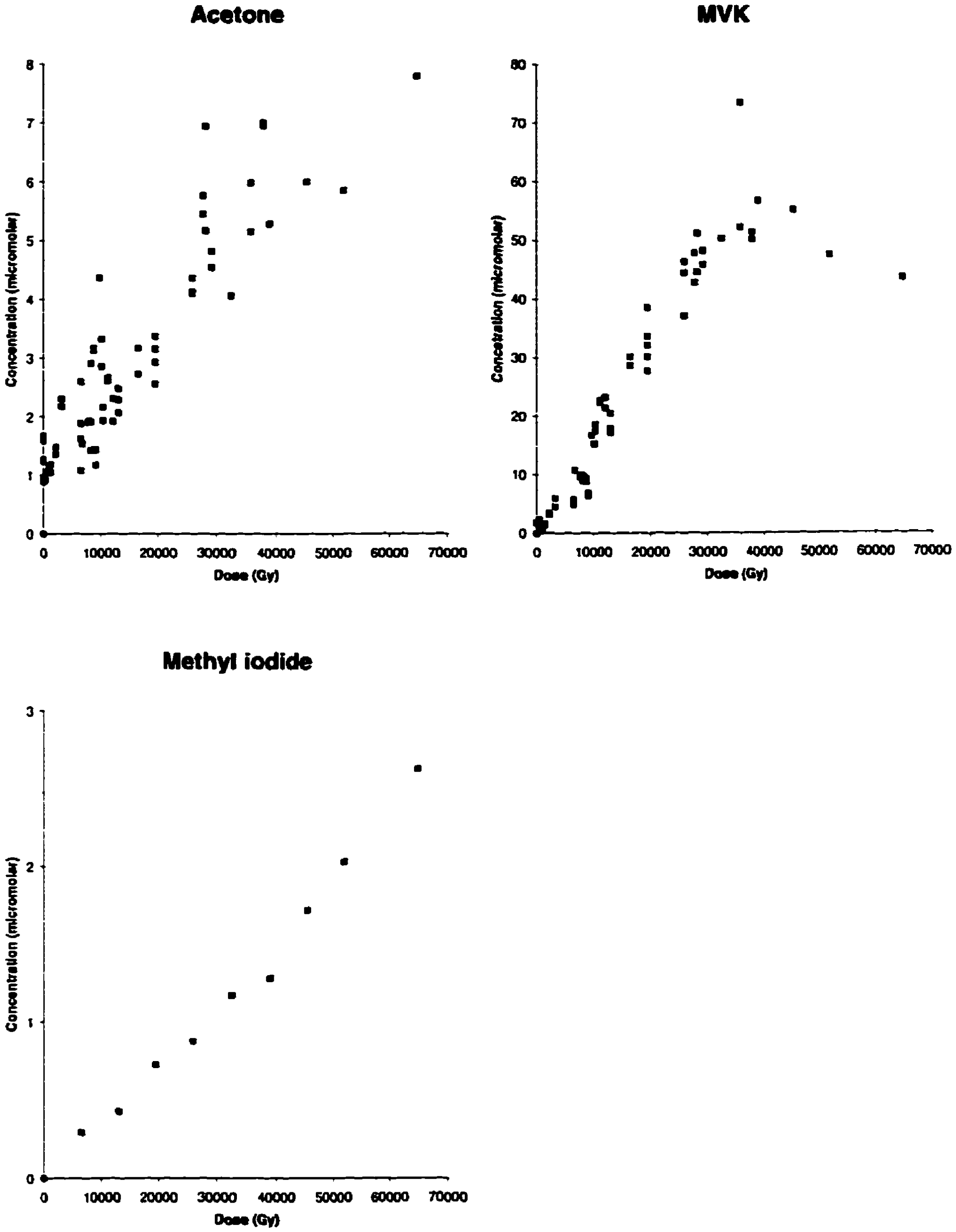


Figure 4-2b - Product analysis for the radiolysis of argon-purged $1x10^{-3}$ M MEK solutions with $5x10^{-4}$ M iodide.

This system again produced more carbonyl products than the corresponding system without iodide (Figures 4-2a and 4-2b). For example, 3-hydroxy-2-butanone was a major product with added iodide but only just above the detection limit in its absence. This may be due to additional reactions, involving the reaction of MEK radicals with I_2, to give an iodinated compound, which can subsequently be converted to 3-hydroxy-2-butanone by hydrolysis.

$$CH_3CO(\bullet CH)CH_3 + I_2 \rightarrow CH_3COCHICH_3 + I\bullet \tag{4-3}$$

$$CH_3COCHICH_3 + H_2O \rightarrow CH_3COCH(OH)CH_3 + I^- + H^+ \tag{4-4}$$

The maximum concentrations of acetaldehyde and MVK were more than an order of magnitude higher than observed in the system without iodide (see Figure 3-1b). The increased concentration of acetaldehyde is attributed to the radiolytic decay of the increased levels of 3-hydroxy-2-butanone, as discussed previously.

4.3 Nitrous Oxide-Saturated Solutions

Solution saturation by nitrous oxide increased the rate of MEK breakdown relative to the argon-purged system (Figure 4-3a). Nitrous oxide converts aqueous electrons to hydroxyl radicals to effectively double the concentration of hydroxyl radical in solution [16]. However, the addition of $5x10^{-4}$ M iodide

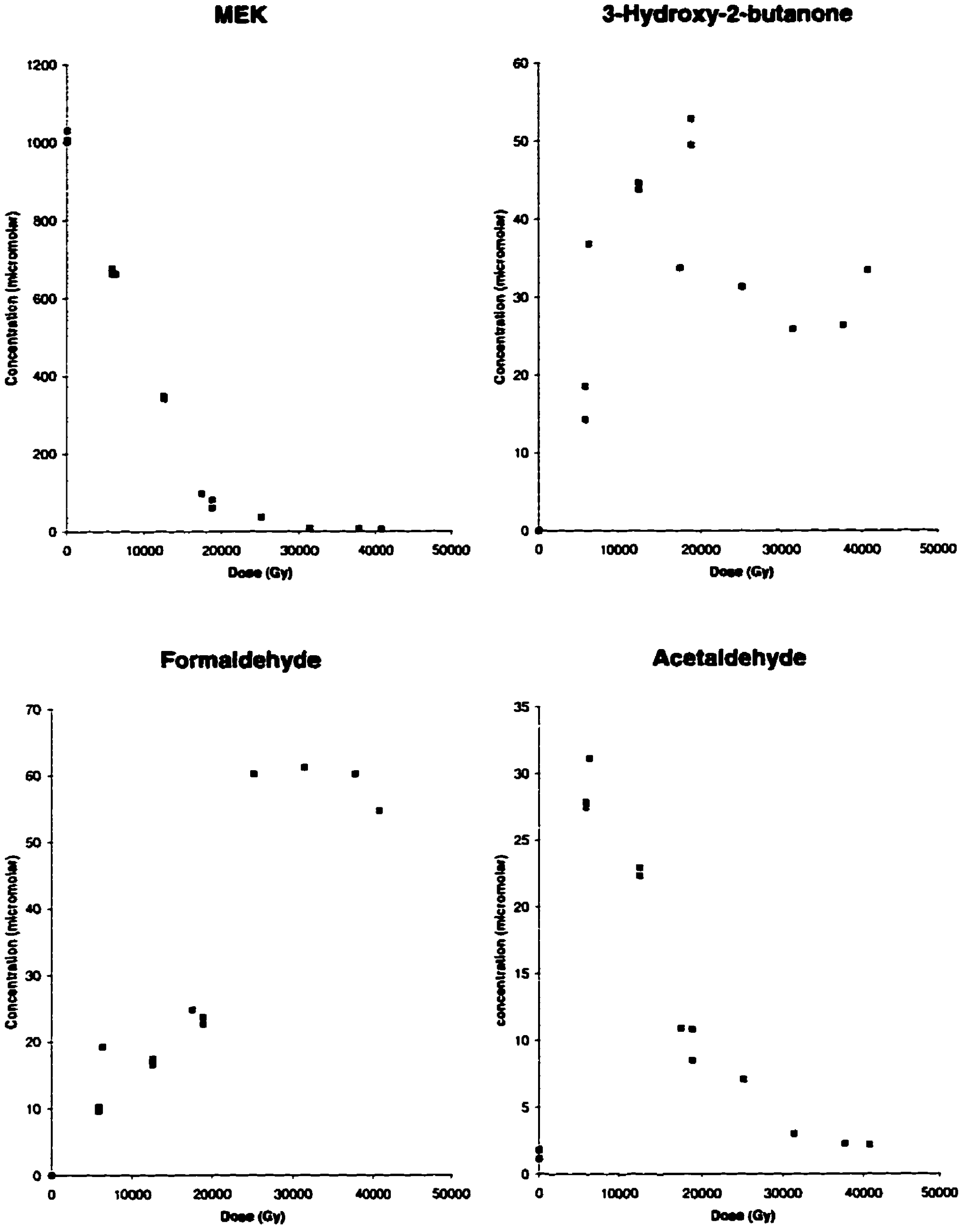


Figure 4-3a - Product analysis for the radiolysis of nitrous oxide-purged 1×10^{-3} M MEK solutions with 5×10^{-4} M iodide.

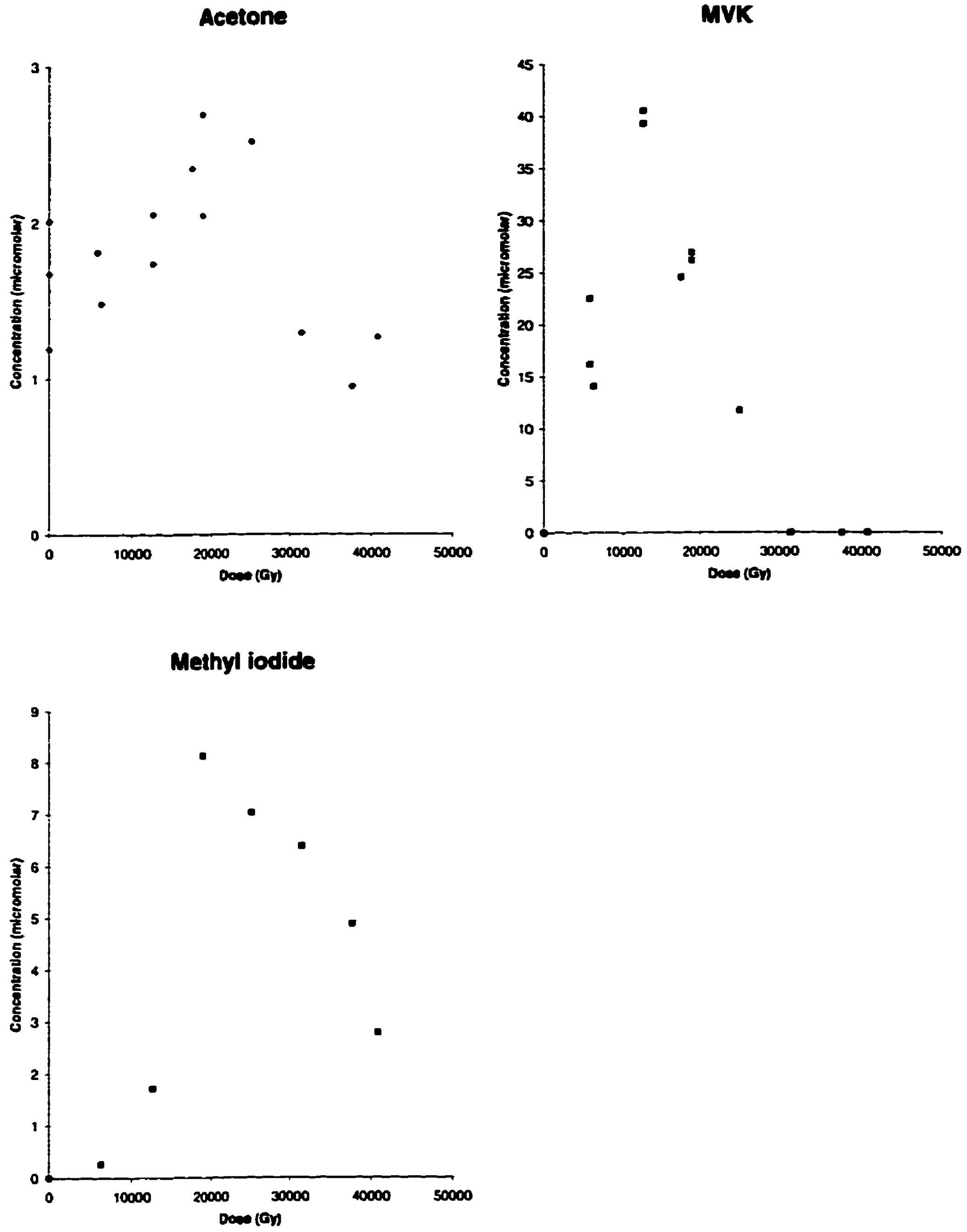


Figure 4-3b - Product analysis for the radiolysis of nitrous oxide-purged 1x10^{-3} M MEK solutions with 5x10^{-4} M iodide.

to the solution slowed the pseudo first-order decay of MEK by a factor of about 5 over the non-iodide solution. A factor of about 7 decrease in rate was expected by the scavenging effect of iodide at this concentration. At this point it is not clear why this decrease is less than anticipated. This solution condition produced more methyl iodide than all other conditions investigated in this study, reaching a maximum of more than 8 μM (Figure 4-3b). This is attributed to the increase in hydroxyl radical concentration, causing an increase in I_2 (reaction 3-144) and removal of hydrated electrons, which eliminates the reduction of I_2 to I^-.

Results of the analysis of carbonyl product for this run are given in Figures 4-3a and 4-3b. They also show much higher concentrations of carbonyl compounds than for the solutions without iodide. This again may be explained by the radiolytically-induced degradation of 3-hydroxy-2-butanone, via reactions 4-3 and 4-4.

4.4 0.5 M t-Butanol Solutions

The addition of 0.5 M t-butanol greatly increased the rate of breakdown for MEK (Figure 4-4). This result is puzzling since t-butanol should quantitatively scavenge hydroxyl leaving only hydrated electrons to breakdown MEK, thus slowing the overall breakdown [16].

Methyl iodide was not detected under these conditions. This is expected, since hydroxyl radicals have been removed and only hydrated electrons are present, so that any formed I_2 would be quickly reduced to I^-. This result also

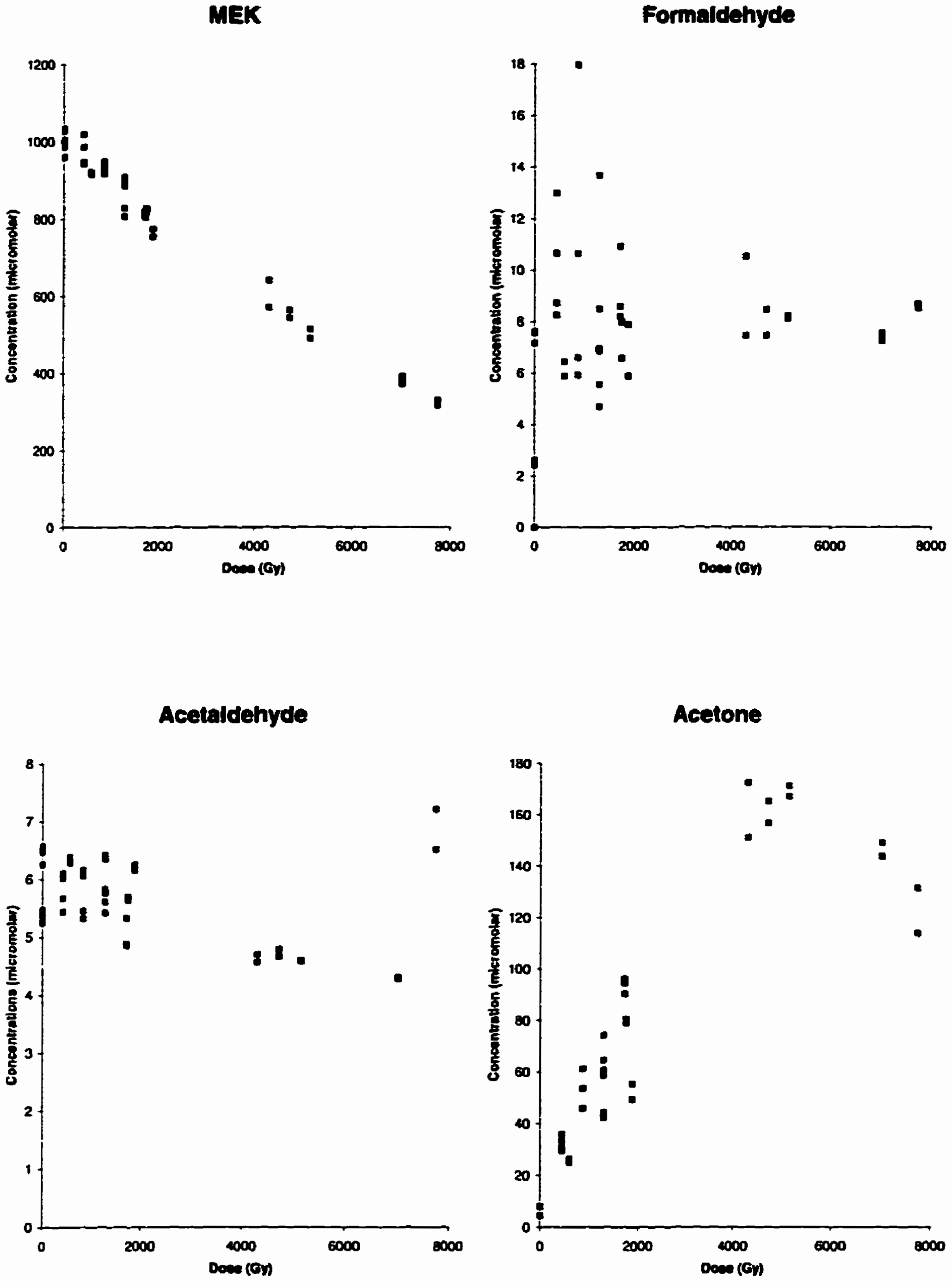


Figure 4-4 - Product analysis for the radiolysis of 0.5 M t-butanol, argon-purged $1x10^{-3}$ M MEK solutions with $5x10^{-4}$ M iodide.

corroborates the previous assumption that methyl iodide production is dependent on I_2 concentration.

As for the solution without iodide, carbonyl analysis revealed acetone to be the major product for this system formed by breakdown of t-butanol. Only small amounts of formaldehyde and acetaldehyde were detected (Figure 4-4).

Conclusions

This study of the radiolysis of the prototypical containment organic impurity MEK in aerated and non-aerated, aqueous solutions, initially at pH 10.0, was carried out. For aerated solutions, the MEK degradation produced a variety of products, of continually decreasing size. In contrast, in non-aerated solutions where hydroxyl radical was not scavenged (i.e. argon and nitrous oxide-saturated), evidence of dimerization was observed.

Under aerated conditions the main pathway for radiolysis is the abstraction of a hydrogen atom by hydroxyl radical attack to give MEK radicals that undergo reaction with dissolved oxygen, to give organic peroxides that recombination to form intermediate tetroxide intermediates that subsequently dissociate to mainly form 2,3-butanedione and 3-hydroxy-2-butanone. These species then undergo analogous reactions to continue producing intermediate tetroxides and continuously smaller products until eventually, carbon dioxide is formed, to give a final pH of approximately 4.

Analytical methods were developed to quantitatively follow the radiolysis of MEK and many of its radiolysis products. From this work, 2,3-butanedione and acetic acid were found to be major radiolytic products of the decay of aqueous aerated MEK. Studies of non-aerated solutions confirmed the role played by dissolved oxygen in aerated solutions by showing a ten-fold decrease in the formation of oxidation products such as acetic acid and 3-hydroxy-2-butanone during radiolysis, and the formation of dimers.

These experimental findings were used together with available literature data to construct a quantitative computer model. The predictions of this model are in very good agreement with the experimental data for pH evolution, MEK degradation and product carbonyl compounds and organic acid temporal dependence, indicating that a full understanding of the radiolytically induced degradation of MEK under LOCA conditions is being achieved.

The preliminary study of the effects of iodide on the decay of aqueous MEK under LOCA conditions supported the following conclusions.

Methyl iodide was formed and quantified for all solution conditions except under reducing conditions, which is evidence that the methyl iodide is formed by a reaction with iodine (I_2).

As compared to solutions without iodide, the measured rate of MEK loss was slow. This effect can be mostly explained by the competitive scavenging effect of added iodide on the hydroxyl radical (reaction 4-1). However, for aerated solutions, the first-order rate of MEK decay was slower that predicted by this simple iodide scavenging. The reason for this is not known at this time.

For argon- and nitrous oxide-saturated solutions containing iodide the formation of greater amounts of 3-hydroxy-2-butanone was observed. This is attributed to the reaction of MEK radical with iodine (I_2) to form an iodinated MEK compound that then undergoes hydrolysis to give 3-hydroxy-2-butanone.

For the 0.5 M t-butanol solutions the rate of decay for MEK was fastest, inconsistent with the observations of 0.5 M t-butanol solutions without added iodide. No reason for this increased rate can be given at this time.

Recommendations

- Despite the success of the computer model developed in this project, it soluld be noted that some of the rate constants used have not been experimentally determined, and were assigned by analogy to similar reactions. One of the most important assumed values was the rate constants used for the different breakdown pathways of the MEK tetroxide intermediate formed by the reaction of two MEK peroxide radicals under aerated conditions. While these values have been taken as equivalent to the rate constants measured for acetone degradation, the experimental verification of this assumption is necessary, as these values are key to the predictions of the computer model.

- Further study of the MEK dimer under non-aerated conditions where the reaction of hydroxy radicals with MEK dominates is required. Identification and quantification of the suspected MEK dimer peaks observed in the DNPH-HPLC analysis could be facilitated by the obtaining a MEK dimer standard for comparison. Since, the most likely dimer is not available commercially it would have to be synthesized in the laboratory.

- For irradiation of aerated MEK solutions, the early production of 2,3-butanedione is an important step suggested in this study. Quantification of the production of this compound would be useful to provide support for the overall mechanism.

- From the mechanism devised in this study, the reaction of MEK radical with dissolved oxygen has been shown to be of key importance to the mechanism of decay. In this study it was shown that the oxygen in the gas space for a 10:1 gas to liquid volume ratio decreased only marginally during an irradiation (see Figure 3-4d). It was assumed that partitioning between that gas and liquid phases would be rapid enough to replenish solution oxygen consumed during the irradiation. However, it would be useful to confirm this assumption experimentally by measuring the dissolved oxygen concentration as a function of absorbed dose for aqueous organic solutions.

- To extend this study to in-containment LOCA conditions to properly assess radioactive iodine volatility requires a thorough understanding of the mechanisms of organic degradation in the presence of iodine species. As observed in these preliminary experiments, the chemistry of these dual systems is not simple. Therefore, a more detailed investigation into this system, following the procedures established in this study, is required.

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Appendix - Definitions of Terms

Absorbed dose - The quantity of energy absorbed per unit mass of irradiated material. The SI unit for absorbed dose is joules per kilogram ($J\ kg^{-1}$) or gray (Gy).

β-scission - A process in which ketones with three or more carbons on either side of the carbonyl group cleave between the carbons α- and β- to the carbonyl carbon.

Containment building - A concrete building that is constructed over a nuclear reactor to prevent the release of fission products in the event of an accident.

Diffusion-controlled rate constants - Are rate constants for chemical reactions where the rate of reaction is governed by the rate the reactants can diffuse together. In aqueous solution at room temperature this gives a reaction constant on the order of $10^{10}\ dm^3\ mol^{-1}\ s^{-1}$.

Fricke solution - Uses the radiation-induced oxidation of ferrous ion to ferric ion at low pH in aerated solution to determine the amount of energy absorbed from a radiation field by solution.

G-values - Represents the radiation-chemical yield or the number of molecules created or destroyed per 100 eV of absorbed energy. The SI unit for radiation-chemical yield is $mol\ J^{-1}$.

Hydrogen abstraction - The removal of a hydrogen atom from a saturated organic compound by hydroxyl radical (or hydrogen atom) to give an organic radical and water (or hydrogen).

Linear Energy Transfer (LET) - Describes the linear rate of energy deposition provided by an ionizing particle moving through a medium. A common unit for LET is keV-μm^{-1}.

LOCA - A Loss-of-Coolant-Accident in a water cooled nuclear reactor involves a break in the primary circuit followed by fuel failure which may release some fraction of the total core inventory of radioactive material into the containment building.