THE RADIATION-INDUCED OXIDATION OF ORGANIC SUBSTRATES IN AQUEOUS SOLUTION

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by

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Abstract

The γ-radiation-induced oxidation of organic substrates in aqueous solution was studied in both the aerated and degassed states.

The oxidation of isopropylamine in the presence of hydrogen peroxide was found to be very unlike the isopropyl alcohol chain reaction. Unusual concentration effects were obtained.

Amines were found to inhibit the isopropyl alcohol chain reaction, but acid decreased the extent of inhibition, suggesting that the non-bonded electron pair of the nitrogen participated in the inhibition reaction. Mechanisms are discussed but found inadequate.

The radiation-induced autoxidation of isopropyl alcohol was investigated. The hydrogen peroxide concentration was found to increase and then decrease, an effect which could be repeated on reaeration. The presence of metal ions had little or no effect upon the reaction. Most other organic substrates displayed essentially the same hydrogen peroxide profile except the thiols which showed abnormal effects.

Cycles of irradiation and reaeration were found to reduce the Chemical Oxygen Demand of a glucose - glutamic acid solution. Possible applications of γ-irradiation to water treatment and purification are discussed.

Table of Contents

1. Introduction

Radiation chemistry deals with the chemical reactions which are initiated by the absorption of high energy radiation by a system. This radiation may be either electromagnetic, such as X-rays and γ-rays, or corpuscular, such as α- and β-particles and fast neutrons. Excellent discussions of the interaction of all types of radiation with solutions may be found in Allen (1), Swallow (2), and Vereshchinskii and Pikaev (3). The present work is limited solely to a consideration of reactions induced by γ-rays from a Co^{60} source.

1.1 Energy Transfer from Photons to Electrons

A photon may interact with the absorbing medium by three distinct processes. Photoelectric absorption is the most important process for photons of relatively low energy. It consists of the total absorption of the photon by the electron cloud of an atom, and the subsequent emission of a bound electron. The energy in excess of E_o, the energy required to ionise the electron, appears as the kinetic energy of the electron, given by

$$E_k = h\nu - E_o$$

where $h\nu$ is the energy of the photon. Compton scattering involves the elastic collision of the photon with a bound electron. A part, E, of the energy of the incident photon is given up to the electron, which is ejected from the molecule. The remaining energy appears as a scattered photon

of reduced energy $h\nu'$, according to the equation

$$E = h\nu - h\nu'$$

The scattered photon may then interact further either by Compton scattering or by the photoelectric effect, or it may escape from the system. Pair production occurs when the photon, passing very close to a heavy nucleus, is replaced by a positron-electron pair. Part of the photon energy is converted into the rest mass mc^2 of each particle, and the remainder into the kinetic energy of the two particles, according to the equation

$$E_p + E_e = h\nu - 2mc^2$$

Obviously, pair production cannot occur at photon energies less than $2mc^2 = 1.02$ MeV, and in practice, considerably higher energies are required in order that the two particles do not annihilate. Pair production is not an important process in the case of Co^{60} γ-radiation chemistry under consideration because the γ-rays are not of sufficiently high energy and because the nuclei present in aqueous systems are not heavy enough.

The photoelectric and Compton effects together result in the presence, within the system, of electrons with high and widely varying kinetic energies. It is these electrons which are responsible for the ionization and excitation of molecules and the induction of chemical reactions.

As the high energy electrons pass through the system, they slowly lose energy by means of interactions with the molecules of the medium. In these interactions, outer

electrons are either excited to higher energy levels, or ejected from the molecule leaving a positive ion. The ejected electrons, called secondary electrons, may produce further interactions with outer electrons, either along their own tracks if they are of high enough energy (in which case they are called δ-rays), or in small clusters near the original ion if they are of low energy. It is generally believed that about half of the electron energy is dissipated within the δ-rays, and the other half within the clusters or spurs.

The rate of energy loss from a charged particle is called the Linear Energy Transfer (LET). It is related to the velocity of the particle and increases as the particle slows down.

The ultimate effect of these energy transfer processes is the formation of many widely spaced spurs of small radius, containing several ion pairs and excited molecules, together with isolated near-thermal electrons, within about 10^{-16} seconds of the passing of the photon. It is the subsequent reactions of these species which form the foundation of radiation chemistry.

1.2 Primary Processes in Aqueous Systems

Primary products are those derived from interactions of the excited molecules (H_2O^*), the electrons (e^-) of greater than thermal energy, and the ionized molecules (H_2O^+) with the system. Since, in dilute aqueous systems, water molecules are by far the most predominant, the primary products are essentially those derived from water.

The ionized water molecules react rapidly with water, transferring a proton

$$H_2O^+ + H_2O \longrightarrow H_3O^+ + OH \qquad (1)$$

The excited water molecules may either dissociate

$$H_2O^* \longrightarrow H + OH \qquad (2)$$

or deactivate by means of quenching

$$H_2O^* \xrightarrow{M} H_2O \qquad (3)$$

The electrons become thermalized by repeated collision with water molecules, eventually orienting the surrounding molecules by means of polarization, and forming the stable solvated electron

$$e^-_{thermal} + nH_2O \longrightarrow e^-_{aq} \qquad (4)$$

Therefore, within approximately 10^{-11} seconds of the passing of the photon, there are present within the spurs the species e^-_{aq}, H, OH, and H_3O^+ in relatively high concentration. Before diffusion takes place, recombination of the radicals may occur

$$2OH \longrightarrow H_2O_2 \qquad (5)$$

$$2H \longrightarrow H_2 \qquad (6)$$

$$2e^-_{aq} \longrightarrow H_2 + 2OH^- \qquad (7)$$

$$OH + e^-_{aq} \longrightarrow OH^- \qquad (8)$$

$$OH + H \longrightarrow H_2O \qquad (9)$$

$$e^-_{aq} + H \longrightarrow H_2 + OH^- \qquad (10)$$

resulting in the formation of the identifiable molecular products H_2O_2 and H_2. These molecular products may be further attacked by the radicals

$$OH + H_2 \longrightarrow H_2O + H \qquad (11)$$

$$OH + H_2O_2 \longrightarrow HO_2 + H_2O \qquad (12)$$

$$H + H_2O_2 \longrightarrow OH + H_2O \qquad (13)$$

$$e^-_{aq} + H_2O_2 \longrightarrow OH^- + OH \qquad (14)$$

but such reactions are unlikely in the presence of other solutes. The radical HO_2 disproportionates to H_2O_2 and O_2

$$2HO_2 \longrightarrow H_2O_2 + O_2 \qquad (15)$$

These reactions, occurring after 10^{-8} seconds of the passing of the photon, and before diffusion causes expansion of the spur, are largely independent of the presence of the solute.

As the spur expands, the reactive species preferentially attack the solute molecules. From the identification of the products and the study of the rates of solute consumption and product formation, the number and nature of the reactive intermediates may be deduced.

The hydrogen atom may behave either as an oxidizing or as a reducing agent. In abstracting a hydrogen atom from an organic substrate, a common reaction, it behaves as an oxidizing agent

$$H + RH \longrightarrow H_2 + R^\bullet \qquad (16)$$

In donating an electron, or adding to an unsaturated substrate

$$H + M^{+3} \longrightarrow H^+ + M^{+2} \qquad (17)$$

$$H + R_2C{:}CR_2 \longrightarrow R_2CH\dot{C}R_2 \qquad (18)$$

it behaves as a reducing agent. A common instance of the last case occurs in aerated systems, where atomic hydrogen adds onto an oxygen molecule forming the hydroperoxyl radical

$$H + O_2 \longrightarrow HO_2 \qquad (19)$$

The hydroxyl radical behaves exclusively as an oxidizing agent, by electron removal

$$OH + M^{+2} \longrightarrow OH^- + M^{+3} \qquad (20)$$

or by hydrogen atom abstraction

$$OH + RH \longrightarrow H_2O + R^\cdot \qquad (21)$$

or by addition to an unsaturated substrate.

The solvated electron, in general, acts as a reducing agent. Electron attachment can occur only if the reactant has available orbitals of low energy, such as olefins and carbonyls. Saturated compounds including water react slowly if at all. Reduction of metal cations occurs the same way as with the hydrogen atom

$$e^-_{aq} + M^{+3} \longrightarrow M^{+2} \qquad (22)$$

The primary yields of the various radicals have been determined in a number of experiments (see (1) for example), and appear to be dependent upon the pH of the solution. This effect is due to the acid-base aquilibria of some of the radicals

$$e^-_{aq} + H_3O^+ \longrightarrow H + H_2O \qquad (23)$$

$$H + OH^- \longrightarrow e^-_{aq} + H_2O \qquad (24)$$

$$H + H^+ \rightleftharpoons H_2^+ \qquad (25)$$

$$OH \rightleftharpoons O^- + H^+ \qquad (26)$$

$$HO_2 \rightleftharpoons H^+ + O_2^- \qquad (27)$$

$$H_2O_2 \rightleftharpoons H^+ + HO_2^- \qquad (28)$$

since the conjugate radicals cannot be expected to react in the same way at the same rate.

Yields of radiation chemical reactions are normally

quoted as G-values, defined as the number of particles formed or removed per 100 eV. absorbed by the system. G_x denotes the primary yield of a reactive intermediate; G(x) denotes the measured yield of a permanent product.

Excellent descriptions of the means used to evaluate primary radical yields may be found in Allen (1), Vereshchinskii and Pikaev (3), and Balkas et al.(4). The results obtained are somewhat dependent upon the method used to obtain them. Balkas et al obtained the following values, for pH greater than 2.2

$$G_{H_2} = 0.48 \pm 0.05$$
$$G_{H_2O_2} = 0.74 \pm 0.09$$
$$G_{-H_2O} = 3.7 \pm 0.2$$
$$G_{OH} = 2.14 \pm 0.04$$
$$G_{H+e^-_{aq}} = 2.80 \pm 0.15$$

Hayon (5) obtained $G_H = 0.55 \pm 0.05$, so $G_{e^-_{aq}} = 2.25 \pm 0.20$. These values are all consistent with the equation of material balance

$$G_{-H_2O} = G_{OH} + 2G_{H_2O_2} = G_{e^-_{aq}} + G_H + 2G_{H_2}$$

1.3 Radiation-Induced Oxidation of Isopropyl Alcohol in Neutral Aqueous Solution

In this laboratory, the radiation-induced oxidation of isopropyl alcohol by hydrogen peroxide has been investigated (6) over a wide range of alcohol and peroxide concentrations. The concentration dependence of the acetone yield and the peroxide destruction yield, and the absence of a dose rate

effect were in contradiction to the previously accepted mechanism, and a new mechanism was proposed.

The hydrogen peroxide destruction yields, in the presence of constant isopropyl alcohol concentration, were found to be independent of initial peroxide concentration in the range 5×10^{-2} M. to 10^{-3} M. Values of $G(-H_2O_2)$ for different alcohol concentrations are shown in Table 1.1.

Table 1.1

Variation of $G(-H_2O_2)$ with isopropyl alcohol concentration

isopropyl alcohol	$G(-H_2O_2)$
0.13 M.	36.6
0.52 M.	49.8
1.05 M.	68.1

Extrapolating to zero alcohol concentration gave $G^o(-H_2O_2) = 32.0 \pm 1.0$.

The initial acetone formation yields, in the presence of constant hydrogen peroxide concentration (0.01 M.) was found to be strongly dependent on alcohol concentration. G(acetone) was found to increase to about 100 at 3.66 M. isopropyl alcohol and then decrease to a limiting value of 15.7 + 0.4 in pure alcohol. Values of G(acetone) for different alcohol concentrations are given in Table 1.2.

At concentrations less than 1.05 M. isopropyl alcohol, the curve was linear and stoichiometrically equivalent to the hydrogen peroxide curve. Extrapolating to zero alcohol concentration gave $G^o(\text{acetone}) = 29.8 \pm 0.9$. This large value indicated the presence of a large alcohol-independent term

Table 1.2

Variation of G(acetone) with isopropyl alcohol concentration

isopropyl alcohol	G(acetone)
0.13 M.	34.7
0.26 M.	38.4
0.52 M.	49.8
0.78 M.	55.9
1.05 M.	67.4
2.09 M.	74.4
3.66 M.	99.3
5.23 M.	92.0
9.15 M.	51.1
pure	15.7

to be accounted for by the kinetic expression.

Both the acetone formation yield and the peroxide decomposition yield were found to be independent of pH.

The following mechanism was proposed to describe the oxidation of isopropyl alcohol in concentrations less than 1.02 M. The specific interaction of the γ-radiation with the solvent produced the species e^-_{aq}, H, OH, H_3O^+, H_2O_2, and H_2 as described in section 1.2. This was followed by

$$e^-_{aq} + H_2O_2 \longrightarrow OH^- + OH \qquad (14)$$

$$H + (CH_3)_2CHOH \longrightarrow H_2 + (CH_3)_2\dot{C}OH \qquad (29)$$

$$H + (CH_3)_2CHOH \longrightarrow H_2 + CH_3(\dot{C}H_2)CHOH \qquad (30)$$

$$OH + (CH_3)_2CHOH \longrightarrow H_2O + (CH_3)_2\dot{C}OH \qquad (31)$$

$$OH + (CH_3)_2CHOH \longrightarrow H_2O + CH_3(\dot{C}H_2)CHOH \qquad (32)$$

$$(CH_3)_2\dot{C}OH + H_2O_2 \longrightarrow (CH_3)_2CO + OH + OH^- \qquad (33)$$

$$CH_3(\dot{C}H_2)CHOH + (CH_3)_2CHOH \longrightarrow (CH_3)_2CHOH + (CH_3)_2\dot{C}OH \quad (34)$$

$$2\ CH_3(\dot{C}H_2)CHOH \longrightarrow (CH_3)_2CHOH + (CH_3)_2CO$$

$$\text{or } CH_3CH(OH)CH_2CH_2CH(OH)CH_3 \quad (35)$$

where steps (31) and (33) constituted the chain propagation steps, step (34), the conversion reaction, was the rate-determining reaction, and step (35) was the terminating reaction.

Assuming steady state conditions, the acetone formation yield could be expressed as follows:

$$G(\text{acetone}) = \frac{k_{31}}{k_{32}}(G_{OH} + G_{e^-_{aq}}) + \frac{k_{29}(k_{31} + k_{32})}{k_{32}(k_{29} + k_{30})} G_H + \frac{k_{34}(k_{31} + k_{32})\,[\text{isopropyl alcohol}]\, G_R^{\frac{1}{2}}}{k_{32}\,(2k_{35}\,D)^{\frac{1}{2}}}$$

and the peroxide destruction yield as follows:

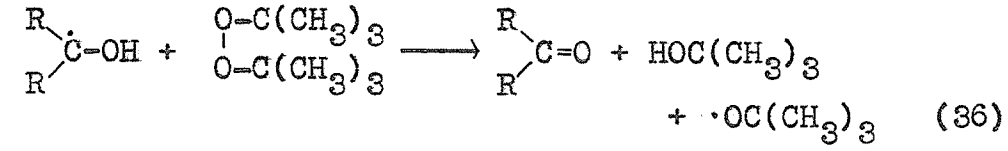
$$G(-H_2O_2) = G_{e^-_{aq}} - G_{H_2O_2} + G(\text{acetone})$$

where $G_R = G_{OH} + G_H + G_{e^-_{aq}}$ and D was the dose rate. The expressions predicted alcohol-independent chain yields, which agreed with the observed values of $G^o(-H_2O_2) = 32.0$ and $G^o(\text{acetone}) = 29.8$. The ratio k_{31}/k_{32} was calculated to be 5.9, indicating that the α-hydrogen in isopropyl alcohol was about 30 times more reactive to hydrogen abstraction by OH than β-hydrogen. The rate constant for the conversion reaction (34) was calculated to be $59 \pm 20\ M^{-1}\ sec^{-1}$. The observed independence of $G(-H_2O_2)$ on hydrogen peroxide concentration was also predicted.

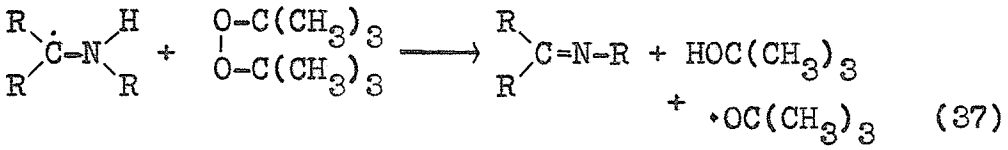
1.4 Radiation-Induced Oxidation of Amines in Aqueous Solution

The isopropyl alcohol - hydrogen peroxide chain reaction was based upon hydrogen atom abstraction from the alcohol molecule and subsequent attack of the ketyl radical on the hydrogen peroxide. This chain might be expected to occur as well with isopropylamine.

Huyser, Bredewig and Van Scoy (7) observed that primary and secondary amines caused induced decomposition of dialkyl peroxides in a manner similar to that of alcohols

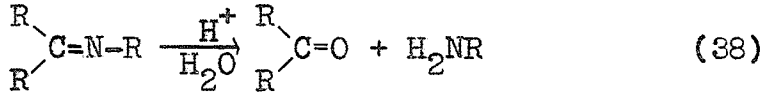


(36)



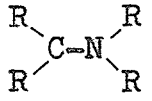
(37)

In the presence of acid, a ketone was formed from the imine



(38)

Radicals obtained from tertiary amines



with no amino hydrogen, did not participate in these reactions.

Lack of induced decomposition in the presence of the free radical scavenger α-methylstyrene supported the postulation of a free radical mechanism. They proposed the reaction sequence

$$(CH_3)_3COOC(CH_3)_3 \longrightarrow 2\ (CH_3)_3CO\cdot \qquad (39)$$

$$(CH_3)_3CO\cdot + R_2CHNHR \longrightarrow (CH_3)_3COH + R_2\dot{C}NHR \qquad (40)$$

$$R_2\dot{C}NHR + (CH_3)_3COOC(CH_3)_3 \longrightarrow R_2C{=}N{-}R + (CH_3)_3COH + (CH_3)_3CO\cdot \qquad (37)$$

$$R_2\dot{C}NHR + (CH_3)_3CO\cdot \longrightarrow R_2C{=}N{-}R + (CH_3)_3COH \qquad (41)$$

Such a mechanism suggests that primary and secondary amines should support a hydrogen peroxide chain reaction.

The nature of radical attack on amines is somewhat more complex than on alcohols. Garrison (8), in work on the derivatives of ammonia, observed that the radiation chemistry of such species could be determined by the reactivity both of the alkyl substituents and of the nitrogen atom.

For primary amines, he proposed that all three of

$$(NH_3)^+CH_2R + OH \longrightarrow (NH_3)^+\dot{C}HR + H_2O \qquad (42)$$

$$NH_2CH_2R + OH \longrightarrow NH_2\dot{C}HR + H_2O \qquad (43)$$

$$NH\ CH\ R + OH \longrightarrow \cdot NHCH_2R + H_2O \qquad (44)$$

were probable. Attack on the neutral molecule by e^-_{aq} or by H he regarded as unlikely. Reaction (45)

$$(NH_3)^+CH_2R + e^-_{aq} \longrightarrow NH_3 + \cdot CH_2R \qquad (45)$$

he regarded as possible, with no experimental evidence either for or against it. Subsequent reactions of the various amine radicals formed in (42), (43), and (44) have not been examined closely in deaerated solution.

For secondary amines, he predicted similar reactions, chiefly abstraction by OH of the α-hydrogen (either one, in the case of unsymmetrical amines) and of the amino hydrogen,

to form ultimately a primary amine and an aldehyde. In no case, however, did he elaborate on the nature or reactivity of the intermediates.

Studying the vapour phase reactions of methyl radicals with tri- and di-ethylamine, Kozak and Gesser (9) concluded that only alkyl hydrogen atoms were abstracted. This conclusion was based upon the activation energies E_{46} = 8.0 kcal mole^{-1}, E_{47} = 5.3 kcal mole^{-1}, and E_{48} = 5.7 kcal mole^{-1} which were measured in the reactions

$$\cdot CH_3 + (CH_3)_3N \longrightarrow CH_4 + \cdot CH_2N(CH_3)_2 \qquad (46)$$

$$\cdot CH_3 + (CH_3CH_2)_3N \longrightarrow CH_4 + \cdot(C_2H_4)N(CH_2CH_3)_2 \qquad (47)$$

$$\cdot CH_3 + (CH_3CH_2)_2NH \longrightarrow CH_4 + \cdot(C_2H_4)NHCH_2CH_3 \qquad (48)$$

They did not, however, specify whether the alkyl hydrogens were α- or β- to the amino group.

Brinton (10), on the other hand, noted that the Arrhenius parameters for hydrogen atom abstraction from various primary and secondary amines by methyl radicals in the gas phase were very nearly constant, suggesting that abstraction was from the amino group rather than from the alkyl gruops.

Gray and Thynne (11) studied the vapour phase reaction of methyl radicals with methylamine and the deuterated methylamines. They obtained the following Arrhenius parameters for amino hydrogen abstraction

$$A = 10^{9.66} = 4.56 \times 10^9 \text{ mole}^{-1} \text{ cm}^3 \text{ sec}^{-1}$$

$$E = 5.86 \text{ kcal mole}^{-1}$$

and for methyl hydrogen abstraction

$$A = 10^{11.1} = 1.26 \times 10^{11} \text{ mole}^{-1} \text{ cm}^3 \text{ sec}^{-1}$$

$E = 8.85$ kcal mole^{-1}

from methylamine. Thus, at a temperature of about 150° C. approximately three-fifths of the hydrogen atoms abstracted came from the amino group and two-fifths from the methyl group. The amino hydrogen atoms were therefore about twice as reactive as the methyl hydrogen atoms.

Similar work by Gray, Jones, and Thynne (12) on dimethylamine and deuterated dimethylamines showed that, at about 150° C., approximately seven-ninths of the hydrogen atoms abstracted came from the amino group and two-ninths from the methyl groups. Thus, the amino hydrogen atoms were about twenty times as reactive as the methyl hydrogen atoms. They concluded that the rate of hydrogen abstraction from the amine group increased as methyl groups were introduced into ammonia as follows:

NH_2-H	NH_2-CH_3	$NH(CH_3)_2$
1	11	168

Extrapolation of these data to the condensed phase is questionable at best but it can be seen, at least, that hydrogen abstraction is possible from both the amino and the alkyl groups of a primary or secondary amine.

1.5 Radiation-Induced Oxidation of Organic Solutes in Aerated Aqueous Solution

Jayson, Scholes, and Weiss (13) exposed dilute aqueous ethanol solutions which had been air-saturated to the action of 200 kv. X-rays, and followed the rate of formation of both acetaldehyde and hydrogen peroxide with dose. They

determined that hydrogen peroxide was formed at a rate linear with dose up to a total dose of about 8×10^{-6} eV /N per ml. followed by a rapid decrease in yield. The maximum peroxide concentration was about 2.7×10^{-4} M. They explained these results on the basis of the two competing reactions

$$H + O_2 \longrightarrow HO_2 \qquad (19)$$

$$H + H_2O_2 \longrightarrow H_2O + OH \qquad (13)$$

Before the break point, when there was a large quantity of dissolved molecular oxygen present, reaction (19) predominated. The HO_2 radicals disproportionated by reaction (15) to H_2O_2 and O_2, giving an overall reaction (19 + 15) of

$$2\ H + O_2 \longrightarrow H_2O_2 \qquad (49)$$

As the concentration of hydrogen peroxide built up, reaction (13) became important, and led to a decrease in peroxide concentration. As long as the hydrogen atoms reacted solely by reaction (19), or (49), oxidation of ethanol to acetaldehyde could proceed only by means of the primary hydroxyl radicals. Reaction (13), however, resulted in the formation of additional OH radicals which would increase the rate of acetaldehyde formation. The observation of just this effect supported this type of mechanism.

The oxidation of ethanol by means of hydroxyl radicals was thought to proceed by the following sequence:

$$CH_3CH_2OH + OH \longrightarrow CH_3\dot{C}HOH + H_2O \qquad (50)$$

(product analysis revealed that only the α-radical was formed)

$$CH_3\dot{C}HOH + O_2 \longrightarrow CH_3\underset{\dot{O}_2}{C}HOH \qquad (51)$$

$$CH_3\overset{\dot{O}_2}{\underset{|}{C}}HOH + HO_2 \longrightarrow CH_3CHO + H_2O_2 + O_2 \qquad (52)$$

$$CH_3\overset{\dot{O}_2}{\underset{|}{C}}HOH + O_2^- \longrightarrow CH_3\overset{O_2H}{\underset{|}{C}}HOH + O_2 \qquad (53)$$

$$HO_2 \rightleftharpoons H^+ + O_2^- \qquad (27)$$

$$2\ CH_3\overset{\dot{O}_2}{\underset{|}{C}}HOH \longrightarrow CH_3\overset{O_2H}{\underset{|}{C}}HOH + CH_3CHO + O_2 \qquad (54)$$

$$2\ CH_3\overset{\dot{O}_2}{\underset{|}{C}}HOH \longrightarrow CH_3\overset{OH}{\underset{|}{C}}HOO\overset{OH}{\underset{|}{C}}HCH_3 + O_2 \qquad (55)$$

$$2\ HO_2 \longrightarrow H_2O_2 + O_2 \qquad (15)$$

After the oxygen was totally consumed, the α-radical reacted according to the following reactions:

$$2\ CH_3\dot{C}HOH \longrightarrow CH_3CH(OH)CH(OH)CH_3 \qquad (56)$$

$$CH_3\dot{C}HOH + OH \longrightarrow CH_3CHO + H_2O \qquad (57)$$

$$CH_3\dot{C}HOH + H \longrightarrow CH_3CH_2OH \qquad (58)$$

$$2\ H \longrightarrow H_2 \qquad (6)$$

It is of note that neither of these reaction sequences constitutes a chain reaction.

They further established that, although the rate of acetaldehyde formation was strongly dependent on ethanol concentration, the rate of hydrogen peroxide formation was essentially independent of alcohol concentration and had a G-value of 3.5 in neutral solution.

Garrison (14) proposed a simpler, more general mechanism for the oxidation of organic compounds in aerated solution

$$RH + OH \longrightarrow R\cdot + H_2O \qquad (21)$$

$$R\cdot + O_2 \longrightarrow R'H + HO_2 \qquad (59)$$

$$e^-_{aq} + O_2 \longrightarrow O_2^- \quad (60)$$

$$e^-_{aq} + H_3O^+ \longrightarrow H + H_2O \quad (23)$$

$$H + O_2 \longrightarrow HO_2 \quad (19)$$

$$HO_2 \rightleftharpoons H^+ + O_2^- \quad (27)$$

$$2\ HO_2 \longrightarrow H_2O_2 + O_2 \quad (15)$$

differing from the previous mechanism in the reaction of molecular oxygen with the organic radical. He did not, however, consider reactions past the break point. For oxygenated ethylamine, he quoted a value for the initial $G(H_2O_2)$ of 3.3.

Purdie (15) studied the γ-radiolysis of cystine in aqueous solution, and proposed a mechanism, whose initial step was

$$CySSCy + OH \longrightarrow CySOH + CyS\cdot \quad (61)$$

Both CySOH and CyS· were ultimately oxidized, but no H_2O_2 was formed.

Packer and Winchester (16) proposed a mechanism for the γ-radiolysis of aqueous cysteine:

$$CySH + OH \longrightarrow CyS\cdot + H_2O \quad (62)$$

$$CySH + e^-_{aq} \longrightarrow Cy\cdot + HS^- \quad (63)$$

$$CySH + H \longrightarrow CyS\cdot + H_2 \quad (64a)$$

$$CySH + H \longrightarrow Cy\cdot + H_2S \quad (64b)$$

$$e^-_{aq} + O_2 \longrightarrow O_2^- \quad (60)$$

$$H + O_2 \longrightarrow HO_2 \quad (19)$$

$$CySH + O_2^- \longrightarrow CyS\cdot + HO_2^- \quad (65)$$

$$CySH + HO_2 \longrightarrow CyS\cdot + H_2O_2 \quad (66)$$

$$CyS\cdot + O_2 \longrightarrow CySO_2\cdot \quad (67)$$

$$CySO_2\cdot + CySH \longrightarrow CySO_2H + CyS\cdot \quad (68)$$

$$2\ CyS\cdot \longrightarrow CySSCy \qquad (69)$$

$$CySO_2H + 3\ CySH \longrightarrow 2\ CySSCy + H_2O \qquad (70)$$

Here, steps (67) and (68) constitute a chain reaction, and $G(H_2O_2)$ and G(-RSH) were both found to depend upon the cysteine concentration. The values of $G(H_2O_2)$ of 6.4 and 9.4 for cysteine concentrations of 10^{-3}M. and 3×10^{-3} M. in oxygen-saturated solutions were both greater than values obtained for other solutes. Why cysteine should sustain a chain reaction when other solutes did not was not explained.

Many other organic solutes have been irradiated in air-saturated aqueous solution, and mechanisms have been postulated for many (see, for example, (1) pp. 142,157, (2) p.142, (3) p. 162). But in all cases save the work by Jayson, Scholes, and Weiss (13), research has stopped short of total oxygen consumption. Since almost all organic solutes are reactive to hydrogen abstraction by the hydroxyl radical, it would appear reasonable to predict a similar hydrogen peroxide profile to that obtained in (13), accompanied by oxidation of the substrate.

2. Experimental

2.1 Radiation Source

The radiation source used throughout this work was a Gammacell 220 unit installed by the Atomic Energy of Canada Limited, which supplied γ-rays of an average energy of 1.25 MeV. The active Co^{60} was contained in rods arranged vertically about the sample chamber, a cylinder six inches in diameter and eight inches high. Hence, the dose provided to a sample was dependent upon its position within the chamber, and reproducible positioning was essential.

For dose rate effect studies, a lead attenuator was used which reduced the dose rate to approximately 30%. This attenuator was a hollow lead cylinder of outer diameter 5 5/16 inches, inner diameter 4 3/8 inches, and height 7 7/8 inches.

2.2 Dosimetry

The dose delivered to the irradiated samples was estimated by means of the ferrous ammonium sulfate dosimeter. The solution used was 1×10^{-3} M in $Fe(NH_4)_2(SO_4)_2$ and 0.4 M in H_2SO_4. When such an air-saturated solution absorbs ionising radiation, the ferrous ion is oxidised to ferric and can be estimated spectrophotometrically.

Because the dose delivered to samples in the irradiation chamber was such a sensitive function of position, the dose rate had to be estimated for both types of sample holders used. For the studies on air-saturated solutions, test tubes were filled to a prescribed level; for studies of degassed solutions, glass bulbs were filled with 10 ml of solution. In both cases, samples were irradiated for var-

ious lengths of time, and the concentration of ferric ion was estimated by comparing each sample to an unirradiated reference at 304 nm. using a Carl Zeiss PMQ II spectrophotometer.

The dose rate was computed by means of the following equation:

$$D = \frac{dA}{dt} \times \frac{6.02 \times 10^{23}}{\epsilon_{Fe^{+3}}} \times \frac{100}{G(Fe^{+3})}$$

where dA/dt is the slope of the absorbance-time graph; $\epsilon_{Fe^{+3}}$, the extinction coefficient of the ferric ion, is 2200 M^{-1} cm^{-1}; and $G(Fe^{+3})$ is 15.6 ions /100 eV.

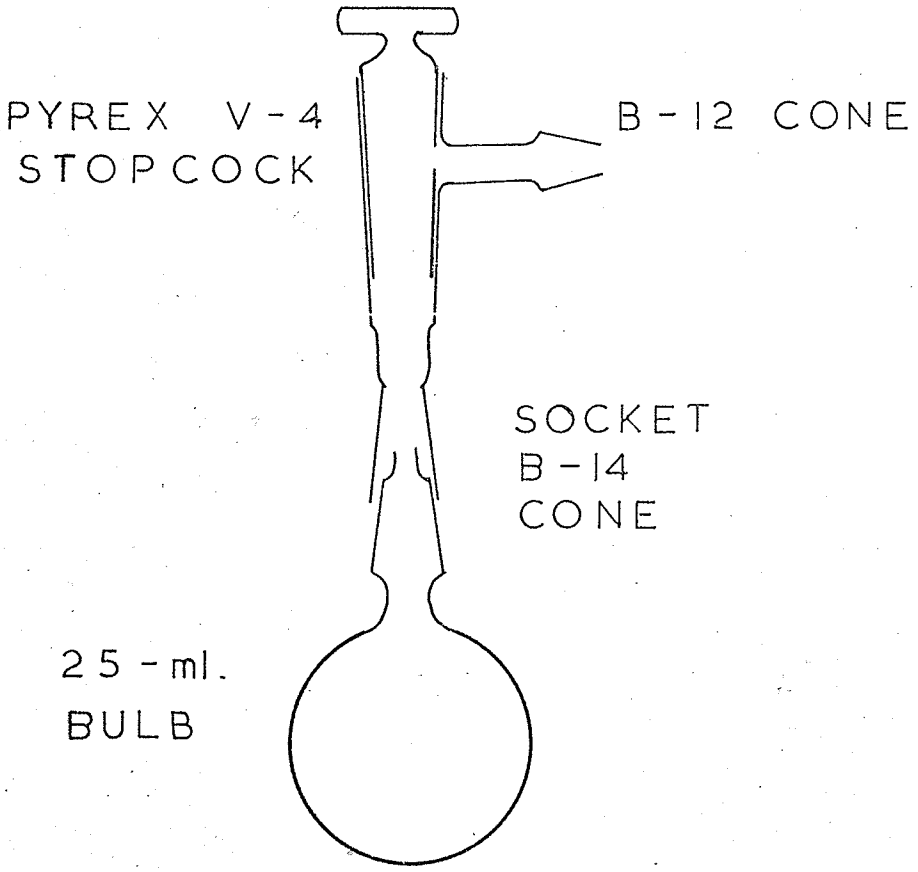
Since radiation is absorbed primarily by means of energy transfer to electrons, the dose absorbed by a solution is proportional to the electron density of the solution. A sample calculation of actual absorbed dose is shown in the Appendix I. In practice, the correction was found to be too small to be necessary within the limits of experimental accuracy.

2.3 Irradiation Cells

Irradiation cells used were of two types. For air-saturated samples, ground glass-stoppered test tubes, 150 mm. long and 16 mm. in diameter, were used. These were generally filled to a mark on the label, except for a few runs using oxygen-saturated solutions, when they were filled to the top. For degassed samples, 25 ml. Pyrex bulbs with ground joints, shown in Figure 2.1, were used. These were always filled with 10 ml. of solution.

Figure 2.1

Irradiation bulb for degassed solutions.



In order to place the cells reproducibly within the irradiation chamber, aluminum cell holders were used. These are illustrated in Figure 2.2. For use with the lead attenuator, a holder similar to the bulb holder shown, but 4 5/16 inches in diameter and 4 inches high, to contain only two bulbs, was also used.

2.4 Materials

Water used for irradiation and for washing glassware was triply distilled, obtained by distilling laboratory distilled water once from alkaline permanganate and once from acid dichromate. The still arrangement was the same as that shown in Figure 1 of reference (26).

H_2O_2 (Fisher Reagent 30%) was used without further purification as the oxidising agent.

$HClO_4$ (Baker and Adamson ACS 70%) was used in acidifying the solutions.

$Fe(NH_4)_2(SO_4)_2 \cdot 6H_2O$, $FeSO_4 \cdot 7H_2O$, $FeNH_4(SO_4)_2 \cdot 12H_2O$, $CoCl_2 \cdot 6H_2O$, and $Ni(NO_3)_2 \cdot 6H_2O$ (Baker and Adamson or equivalent) were used as sources of Fe^{+2}, Fe^{+2}, Fe^{+3}, Co^{+2}, and Ni^{+2} ions respectively.

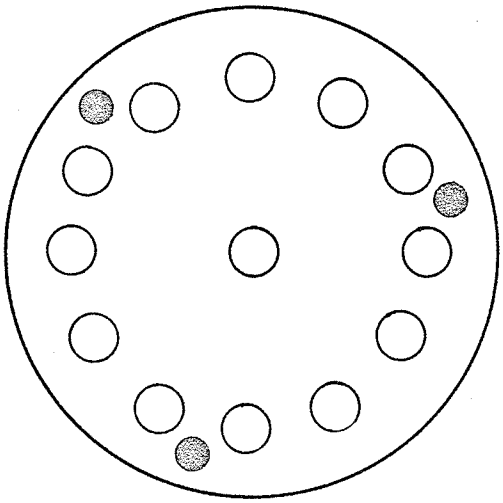
All the amines except n-butylamine (Fisher certified) were from Eastman Organic Chemicals. Glutamic acid (L-(+)-) was from Matheson, Coleman and Bell. All other organic solutes were Fisher certified or equivalent.

Figure 2.2

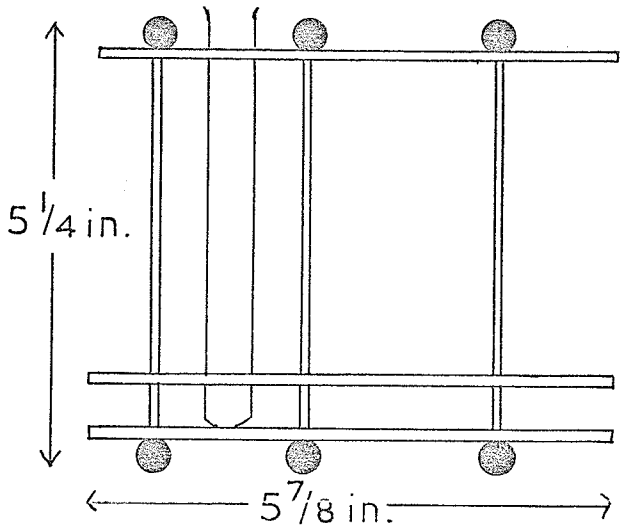
Aluminum cell holders for use with irradiation cells.

Test tube holder

Top view

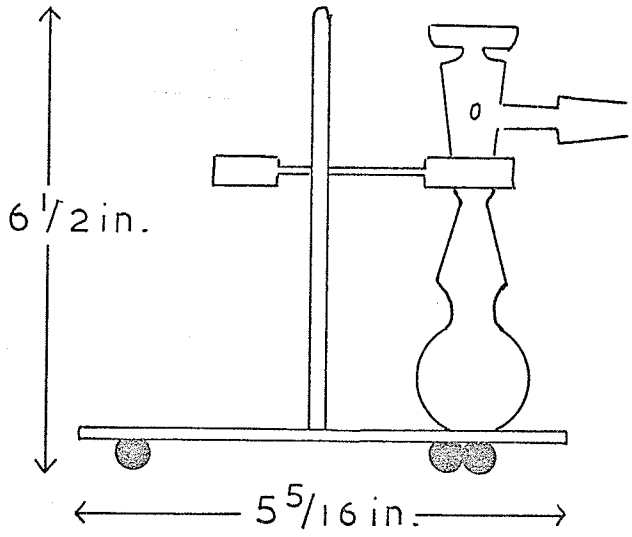


Side view

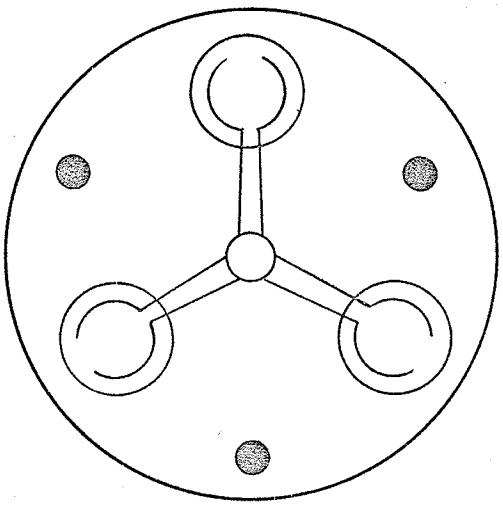


Bulb holder

Side view



Top view



2.5 Sample Preparation

All glassware used in preparing and irradiating samples was washed carefully in the sequence: water, permanganic acid (or chromic acid for pipettes), water, and nitric acid to which had been added a few drops of H_2O_2; and then rinsed several times each with distilled and triply distilled water. Irradiation vessels were always drain-dried before the addition of the sample. Test tubes were filled to the mark; bulbs were filled with 10 ml. of sample.

If degassing was necessary, the sample bulb and stopcock assembly was attached to a vacuum line. All stopcocks were sealed with "Apiezon N" vacuum grease. The samples were degassed by four cycles of freezing, pumping, and thawing. A mixture of solid CO_2 and acetone, or sometimes a mixture of liquid N_2 and ethanol, was used for freezing the samples.

2.6 Analytical Techniques

All of the analyses were performed spectrophotometrically using a Carl Zeiss PMQ II spectrophotometer.

Peroxides were generally determined by the iodide method (18). Solution A, containing 1.25 g. NaOH, 41.5 g. KI, and 0.125 g. $(NH_4)_6Mo_7O_{25}\cdot 4H_2O$ in 500 ml. triply distilled water, and Solution B, containing 12.5 g. KH phthalate in 500 ml. triply distilled water were mixed in equal quantities (usually 5 ml. of each) with an aliquot of sample and diluted to 25 ml. with water. The colour reaction which occurred was

$$H_2O_2 + 3\ I^- + 2\ H_3O^+ \longrightarrow 4\ H_2O + I_3^- \qquad (71)$$

The product I_3^- absorbed at 350 nm. with an extinction coefficient of 2.385×10^4 M^{-1} cm^{-1} (see Figure 2.3)

The titanium method was sometimes used, to distinguish organic peroxides from hydrogen peroxide, since it was sensitive only to hydrogen peroxide. The difference between the two peroxide analyses gave the total organic peroxide present. The method was essentially that of Snell and Snell (19) but the quantities were modified for convenience. Thus, 20.8 g. $Ti(SO_4)_2$, 21 ml. concentrated H_2SO_4, and 100 ml. water were left standing for 24 hours. Suspended solids were then filtered out, the solution was diluted to 250 ml. and then was left standing for two hours. Two ml. of this reagent and an aliquot (usually 10 ml.) of sample, diluted to 25 ml., developed a colour immediately according to the equation

$$Ti^{+4} + H_2O_2 + 2\ H_2O \longrightarrow H_2TiO_4 + 4\ H^+ \qquad (72)$$

The product H_2TiO_4 absorbed at 420 nm. with an extinction coefficient of 731.9 (see Figure 2.4).

Acetone was determined by the salicylaldehyde method of Berntsson (20), with the quantities changed somewhat for convenience. One ml. concentrated NaOH (425 g. per l.) and an aliquot of sample were diluted to about 10 ml. Then 250 μl. salicylaldehyde was added from a micropipette, and the solution was well shaken. Finally, 10 ml. concentrated NaOH was added, and the whole diluted to 25 ml. An acetone-salicylaldehyde complex developed slowly, with an extinction coefficient of 1.80×10^4 M^{-1} cm^{-1} at 474 nm. (see

Figure 2.3

Calibration curve used to measure the extinction coefficient of I_3^- at 350 nm.

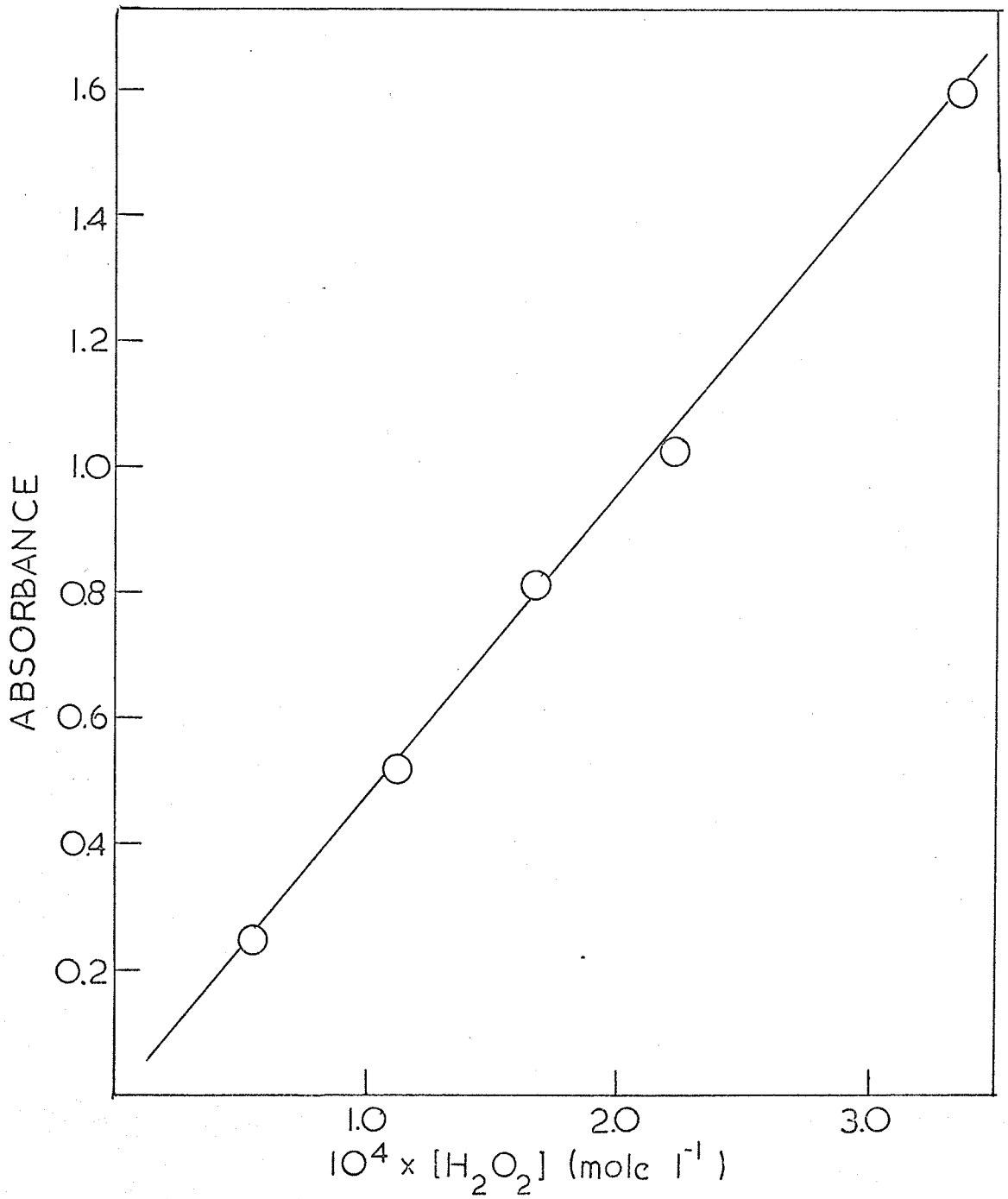


Figure 2.4

Calibration curve used to measure the extinction coefficient of H_2TiO_4 at 420 nm.

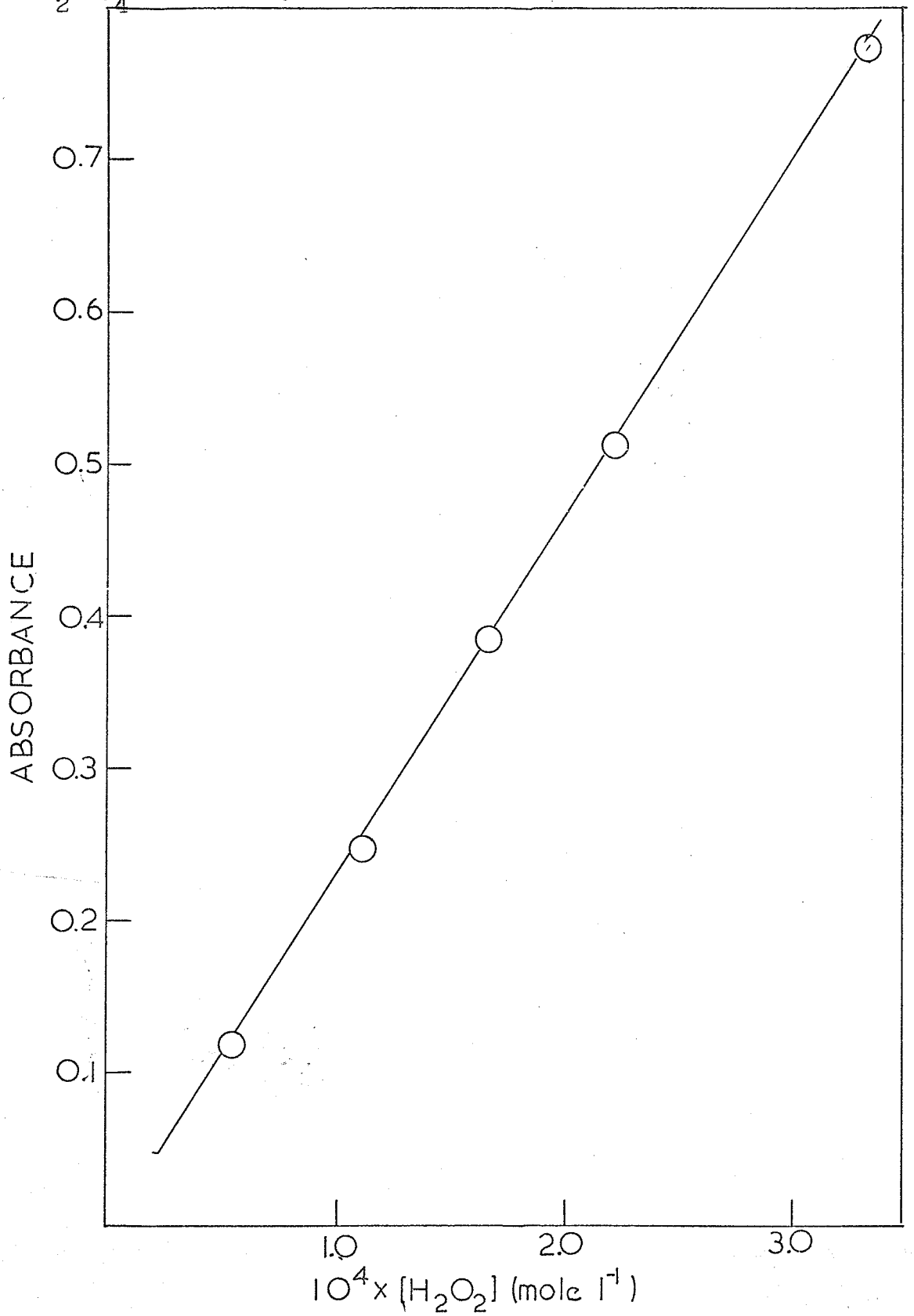
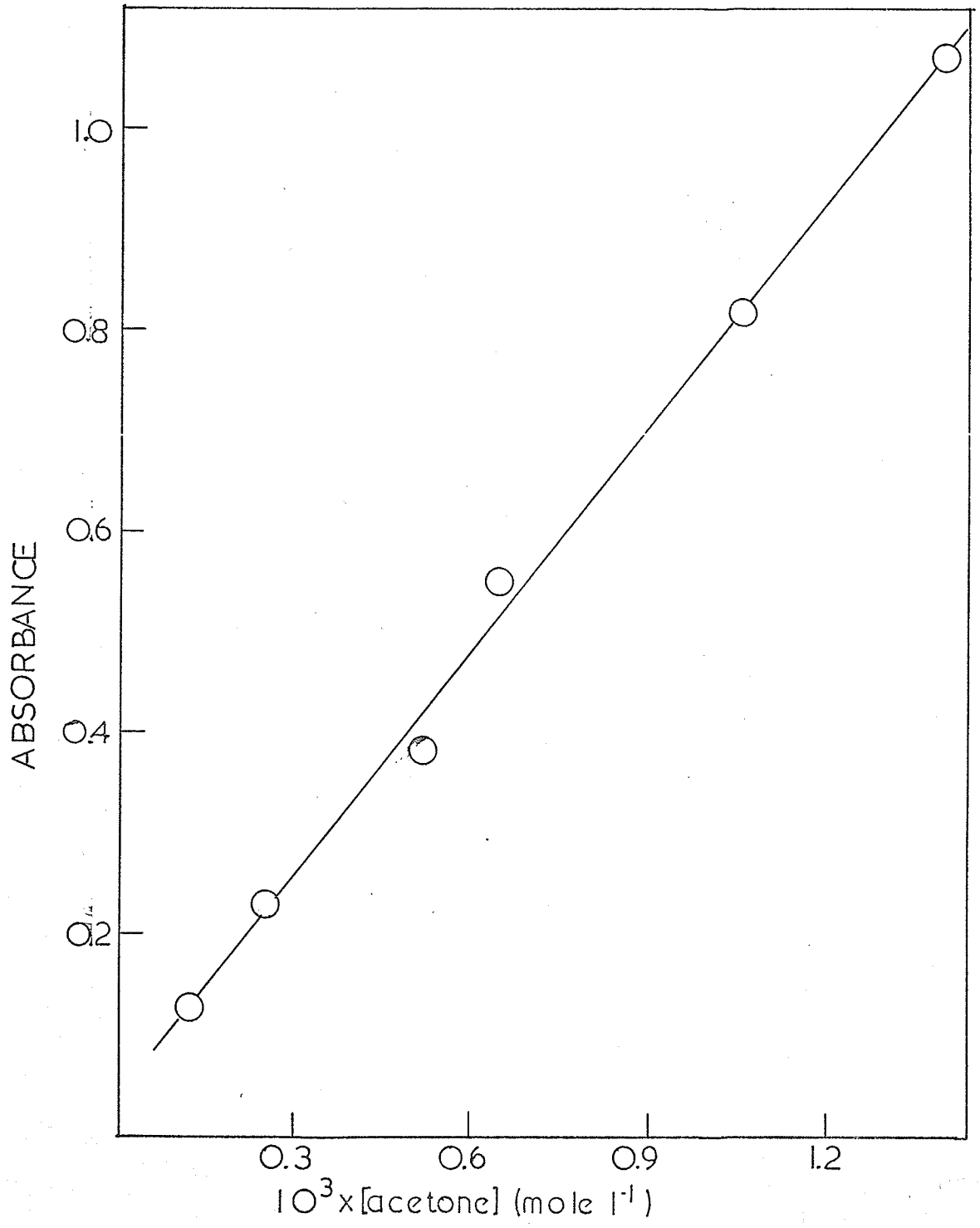


Figure 2.5) Colour development was a function of time and NaOH concentration, and where possible, readings were always made two hours after the solutions were made up.

An attempt was made to analyse for ammonia by means of the Nessler method (21). It was found, however, that acetone interfered strongly with this determination and the relatively high acetone concentration in all samples for which the ammonia concentration was desired rendered the analysis impractical.

Figure 2.5

Calibration curve used to measure the extinction coefficient of the acetone - salicylaldehyde complex at 474 nm.



3. Results

A. Radiation-Induced Peroxide Oxidation

3.1 Oxidation of Isopropylamine

A typical system used to study the chain oxidation of isopropyl alcohol was 0.52 M. in alcohol and 0.01 M. in hydrogen peroxide. This solution was vacuum degassed and irradiated up to a dose of 6×10^{22} eV. l^{-1}. (6). In a similar system of roughly 0.5 M. isopropylamine and 0.01 M. hydrogen peroxide, negligible peroxide was lost and negligible acetone was formed.

Since it was possible that at such a high pH (pH of a solution 0.5 M. in isopropylamine is about 12.2) the hydrogen peroxide was unstable, the procedure was repeated using $HClO_4$ to neutralise the amine before the addition of the peroxide. Similar results were obtained.

It appeared as though excess amine in some way inhibited the chain reaction. A much more dilute solution 5.85×10^{-3} M. in isopropylamine and 0.8×10^{-3} M. in hydrogen peroxide, irradiated to a total dose of 9.6×10^{21} eV. l^{-1}, was found to exhibit linear peroxide decomposition and acetone formation. The chain length, however, was considerably shorter than for the isopropyl alcohol oxidation. $G(-H_2O_2)$ and G(acetone) were 4.50 and 3.81 respectively, compared to minimum values of 32.0 and 29.8 (the intercept values) for the alcohol.

At this low amine concentration, the basicity of the solution would not be expected to decompose the peroxide.

However, since a study of the effect of amine concentration on $G(-H_2O_2)$ and G(acetone) was anticipated, it seemed reasonable to perform this study on the protonated amine throughout, to preclude any possible effect at higher concentration.

The G-values for peroxide destruction and acetone formation obtained with degassed solutions ranging in isopropylamine concentration from 5.85×10^{-3} M. to 0.351 M., with a constant hydrogen peroxide concentration of 0.8×10^{-3} M. are given in Table 3.1 and illustrated in Figure 3.1.

Table 3.1

Variation of $G(-H_2O_2)$ and G(acetone) with isopropylamine concentration with 0.8×10^{-3} M. H_2O_2 present.

[isopropylamine]	$G(-H_2O_2)$	G(acetone)
0.00585 M.	5.68	3.22
0.0117 M.	4.89	3.82
0.0293 M.	6.12	4.52
0.0585 M.	5.76	4.81
0.117 M.	1.28	2.06
0.351 M.	0.585	1.49

This anomalous effect was also obtained with di-isopropylamine, n-propylamine, and t-butylamine, as shown in Figure 3.2.

To determine the effect of aeration on the reaction, a solution 5.85×10^{-3} M. in isopropylamine (acidified with $HClO_4$) and 0.8×10^{-3} M. in hydrogen peroxide, and not degassed, was irradiated up to a total dose of 9.6×10^{21} eV. l^{-1}. The peroxide decomposition and acetone formation yields

Figure 3.1

Variation of $G(-H_2O_2)$ and of G(acetone) with concentration of isopropylamine in acid solution containing 0.8×10^{-3} M. H_2O_2.

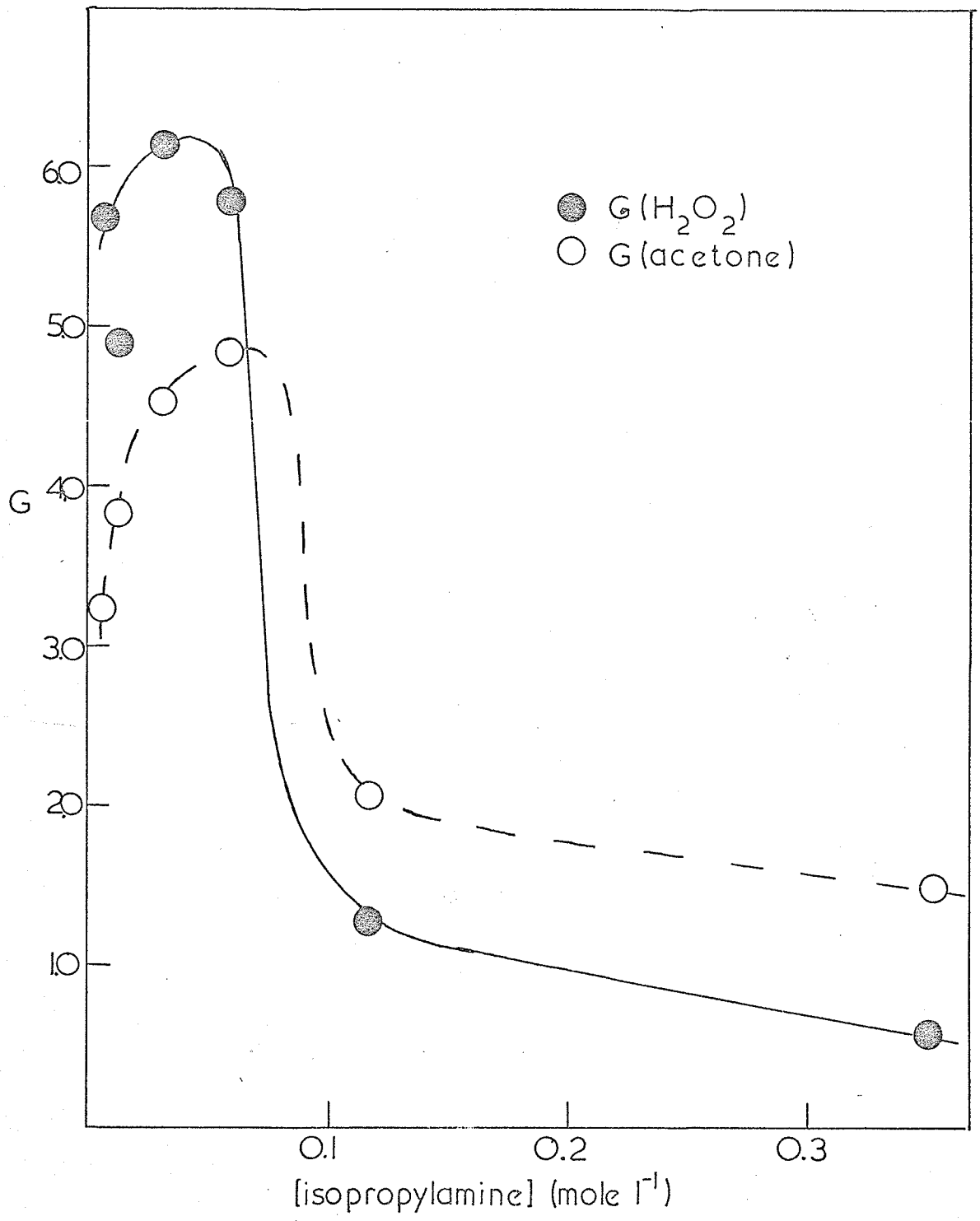
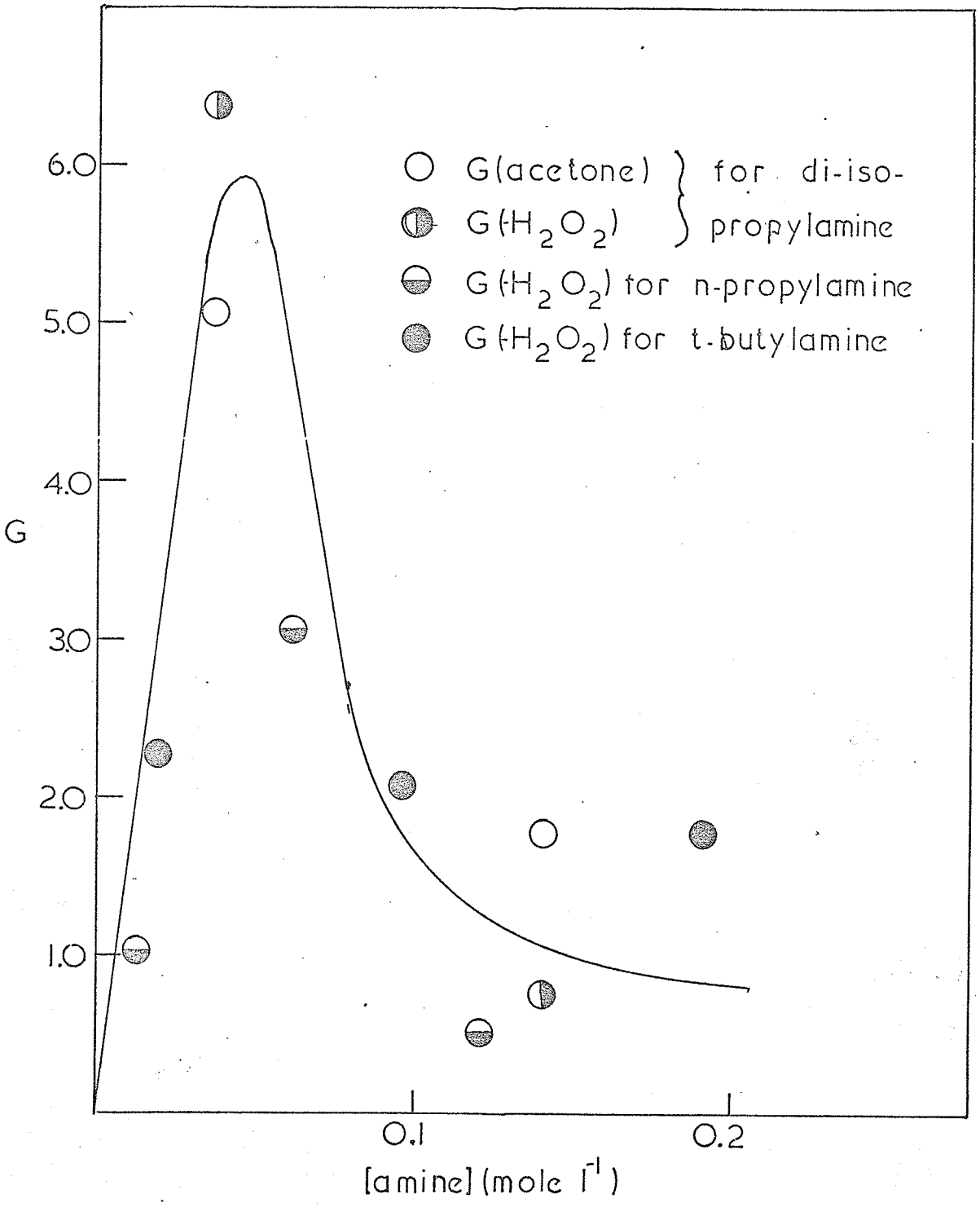


Figure 3.2

Variation of $G(-H_2O_2)$ and of G(acetone) with concentration of amine in acid solution containing 0.8×10^{-3} M H_2O_2 .



are compared with those for the degassed system in Table 3.2.

Table 3.2

Effect of aeration on G(acetone) and $G(-H_2O_2)$

	G(acetone)	$G(-H_2O_2)$
aerated	2.33	1.15
deaerated	3.81	4.50

Oxygen appears to have a small inhibiting effect upon the reactions, particularly upon H_2O_2 reduction.

Dose rate effects were studied using a 30% lead attenuator. A degassed solution 0.0293 M. in isopropylamine (acidified with $HClO_4$) and 0.8×10^{-3} M. in hydrogen peroxide was irradiated up to doses of 8.3×10^{21} eV. l^{-1} and 9.2×10^{21} eV. l^{-1} for the attenuated and unattenuated cases respectively. The peroxide decomposition and acetone formation yields for both cases are shown in Table 3.3, and demonstrate a negligible dose rate effect.

Table 3.3

Dose rate effects in isopropylamine-hydrogen peroxide solution

	G(acetone)	$G(-H_2O_2)$
attenuated	1.43	1.83
unattenuated	1.45	1.54

3.2 Inhibition of Isopropyl Alcohol Chain Reaction by Amines

Since the aliphatic amines appeared to be incapable of sustaining a chain reaction, and indeed seemed to have a self-inhibiting effect on whatever chain reaction did exist, it was thought that perhaps these amines might inhibit the known isopropyl alcohol chain (section 1.3).

A preliminary experiment was performed in an effort to duplicate the chain reaction. A solution 0.52 M. in isopropyl alcohol and 0.008 M. in H_2O_2 was irradiated to doses of 8.0×10^{20} eV. l^{-1}. The value obtained for G(acetone) of 58.8 was consistent with values obtained in (6).

The addition of small amounts of isopropylamine was found to inhibit the alcohol chain. For constant isopropyl alcohol and hydrogen peroxide concentrations of 0.52 M. and 0.008 M. respectively, the G(acetone) values obtained for various isopropylamine concentrations are given in Table 3.4.

Table 3.4

Variation of G(acetone) with concentration of isopropylamine

[isopropylamine]	G(acetone)
0.0 M.	58.8
0.00587 M.	30.3
0.0117 M.	24.4
0.0235 M.	21.4
0.0352 M.	18.3
0.0587 M.	16.7
0.117 M.	9.9

An identical inhibition effect was obtained using other amines. G(acetone) was found to be 19.9 for 0.0288 M. diisopropylamine and 18.8 for 0.0288 M. triethylamine.

To help determine the nature of the inhibition mechanism, the inhibiting effect of acidified amines was studied. Acid was previously shown (6) to have no effect upon the alcohol chain alone, but was found to have an irregular but

pronounced tendency to reduce the extent of the inhibition. The results are tabulated in Table 3.5. All the chain inhibition data are better illustrated in Figure 3.3.

Table 3.5

Variation of G(acetone) with concentration of acidified amine.

amine	concentration	G(acetone)
isopropyl	0.0587 M.	51.7
	0.0352 M.	52.3
di-isopropyl	0.0288 M.	52.8
triethyl	0.0288 M.	27.2

The dependence of G(acetone) of the inhibited chain on the isopropyl alcohol concentration was studied to compare it to that of the uninhibited chain. At constant isopropylamine and hydrogen peroxide concentrations of 0.0352 M. and 0.008 M. respectively, and with doses up to 2.4 x 10^{21} eV. l^{-1}, G(acetone) was determined for a range of isopropyl alcohol concentrations from 0.131 M. to 1.05 M. The results are given in Table 3.6 and illustrated in Figure 3.4.

Table 3.6

Variation of G(acetone) with concentration of isopropyl alcohol for the inhibited chain.

[isopropyl alcohol]	G(acetone)
0.131 M.	8.36
0.262 M.	11.50
0.392 M.	13.59
0.523 M.	15.15
0.785 M.	16.72
1.05 M.	20.38

Figure 3.3

Variation of G(acetone) with amine concentration in amine-inhibited chain reaction. [isopropyl alcohol] = 0.523 M. $[H_2O_2]$ = 0.008 M.

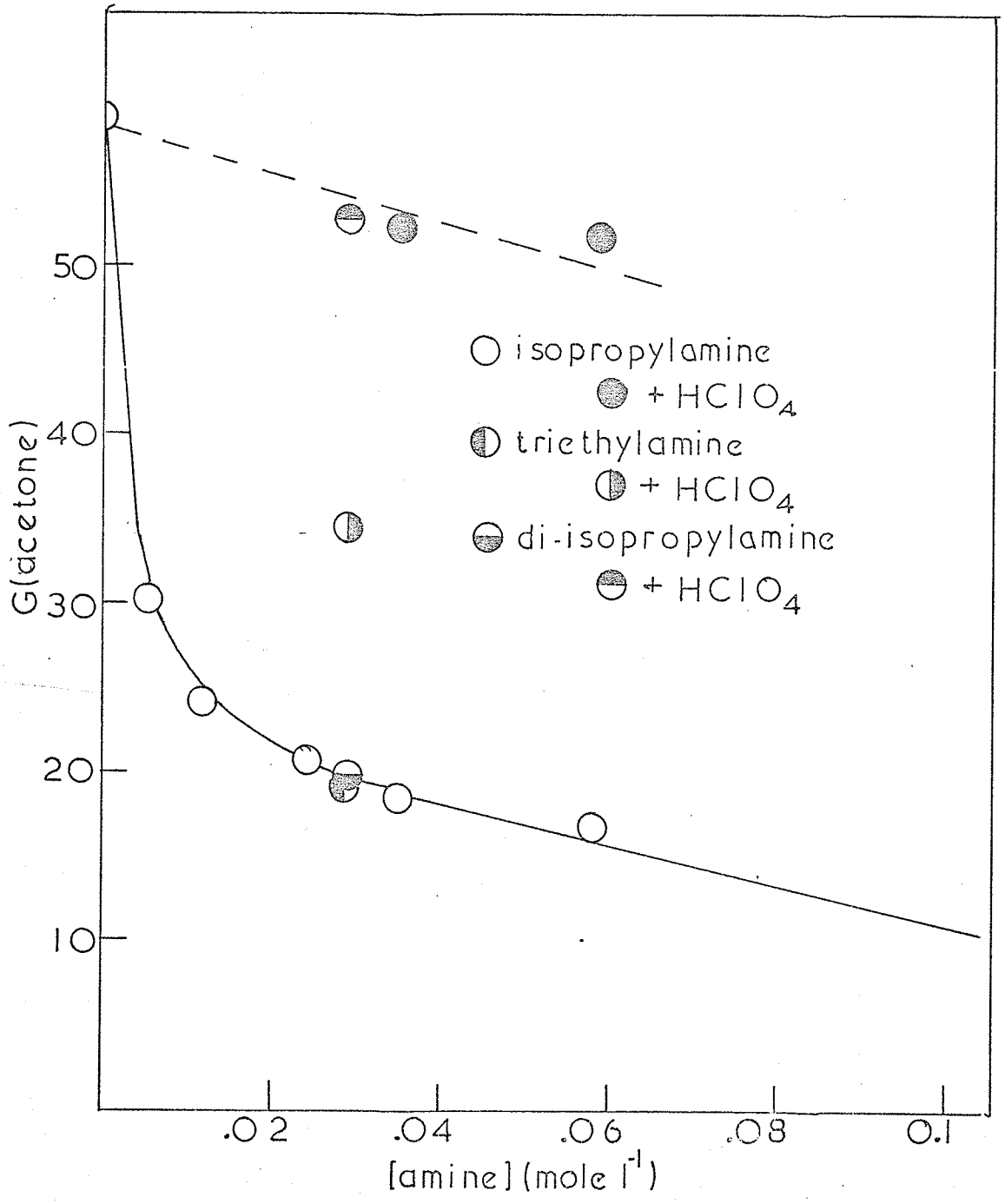
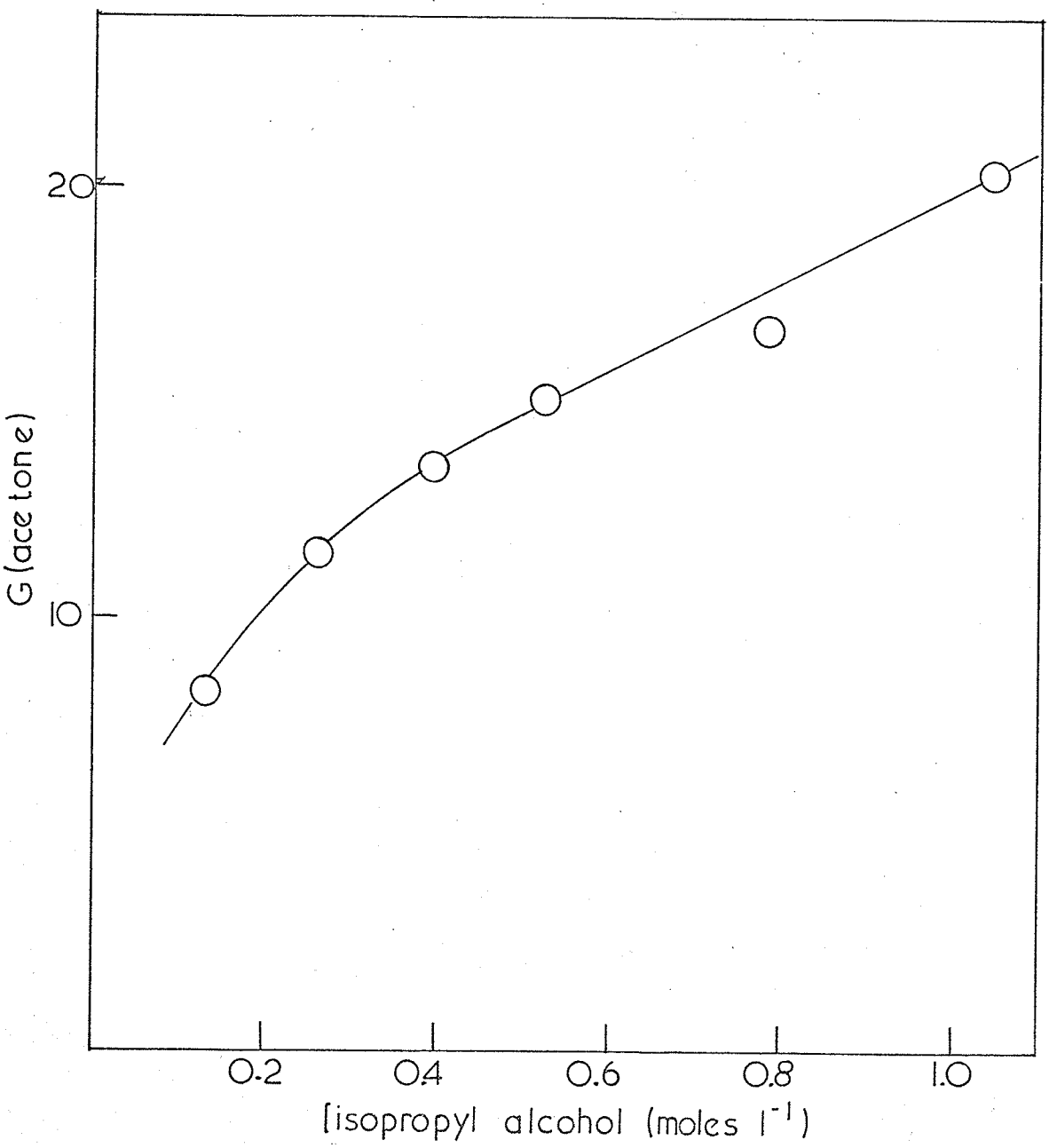


Figure 3.4

Variation of G(acetone) with isopropyl alcohol concentration in isopropylamine-inhibited chain reaction.

$[H_2O_2]$ = 0.008 M.

[isopropylamine] = 0.0352 M.



For the inhibited chain, G(acetone) curved down to a negligible intercept at zero alcohol concentration, contrasting with the linear dependence of G(acetone) on alcohol concentration and the considerable intercept value of 29.8 shown by the uninhibited chain.

The effect of changes in the hydrogen peroxide concentration was studied over the range 0.004 M. to 0.04 M. H_2O_2, in solutions 0.52 M. in isopropyl alcohol and 0.0352 M. in isopropylamine. The values of G(acetone) are shown in Table 3.7 for various peroxide concentrations and illustrated in Figure 3.5.

Table 3.7

Variation of G(acetone) with concentration of hydrogen peroxide for the inhibited chain.

$[H_2O_2]$	G(acetone)
0.004 M.	17.24
0.008 M.	15.67
0.016 M.	15.15
0.040 M.	8.36

The marked decrease in G(acetone) with increasing peroxide concentration was an unexpected result and contrasted with the independence of rate on peroxide concentration shown by the uninhibited chain.

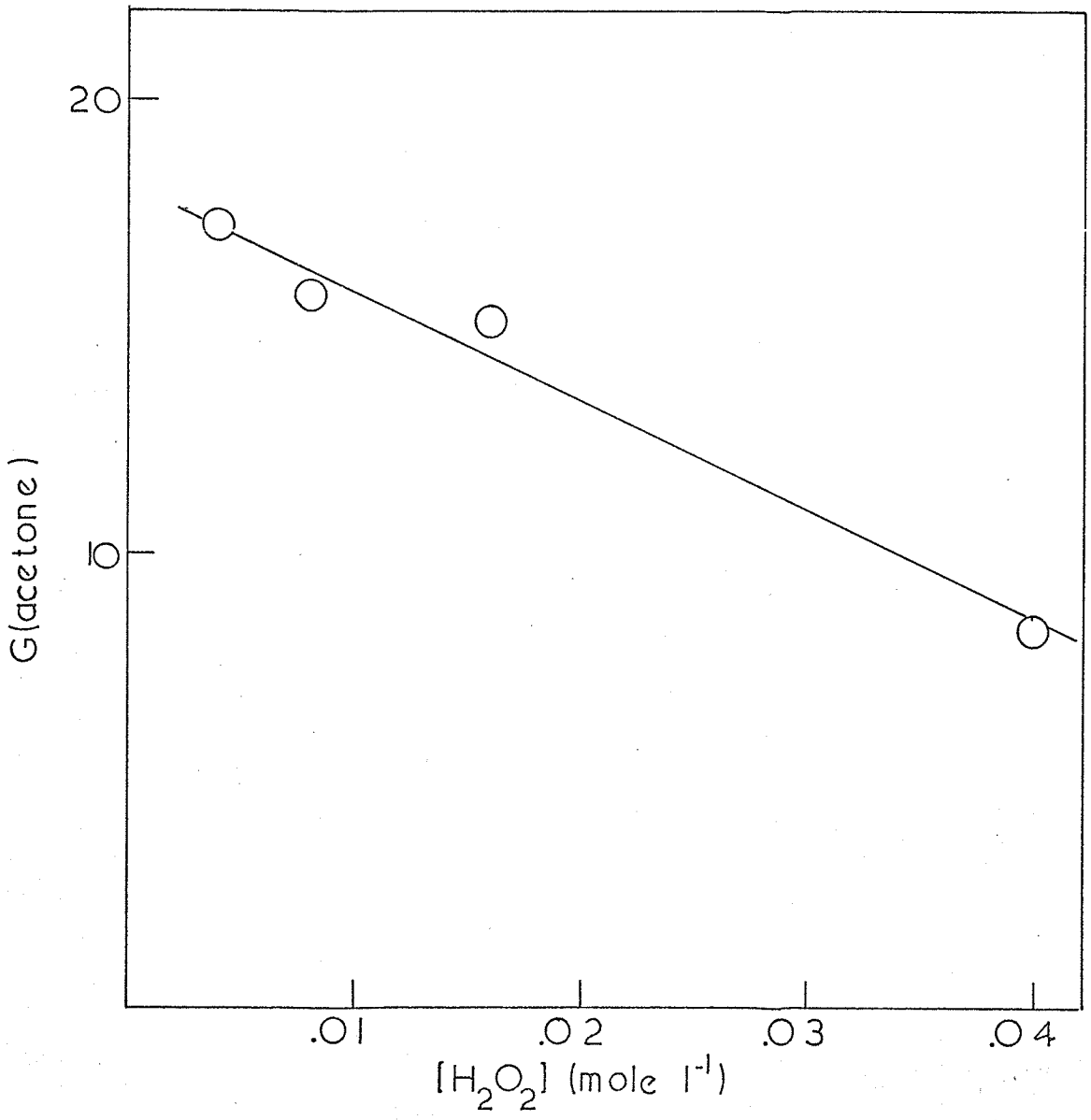
To ensure that acetone formation was accompanied by hydrogen peroxide removal, $G(-H_2O_2)$ was determined for one run. A solution 0.52 M. in isopropyl alcohol, 0.008 M. in hydrogen peroxide, and 0.117 M. in isopropylamine gave a

Figure 3.5

Variation of G(acetone) with hydrogen peroxide concentration in isopropylamine-inhibited chain reaction.

[isopropyl alcohol] = 0.523 M.

[isopropylamine] = 0.0352 M.



value for $G(-H_2O_2)$ of 2.76.

It was of interest to determine whether the system containing isopropyl alcohol, hydrogen peroxide, and acidified isopropylamine exhibited the same reaction characteristics as the uninhibited chain reaction. The alcohol concentration dependence of the acidified system (0.008 M. in hydrogen peroxide and 0.0352 M. in isopropylamine, acidified with $HClO_4$) was studied over the concentration range 0.131 M. to 1.05 M. alcohol. The values of G(acetone) are tabulated in Table 3.8 and illustrated in Figure 3.6.

Table 3.8

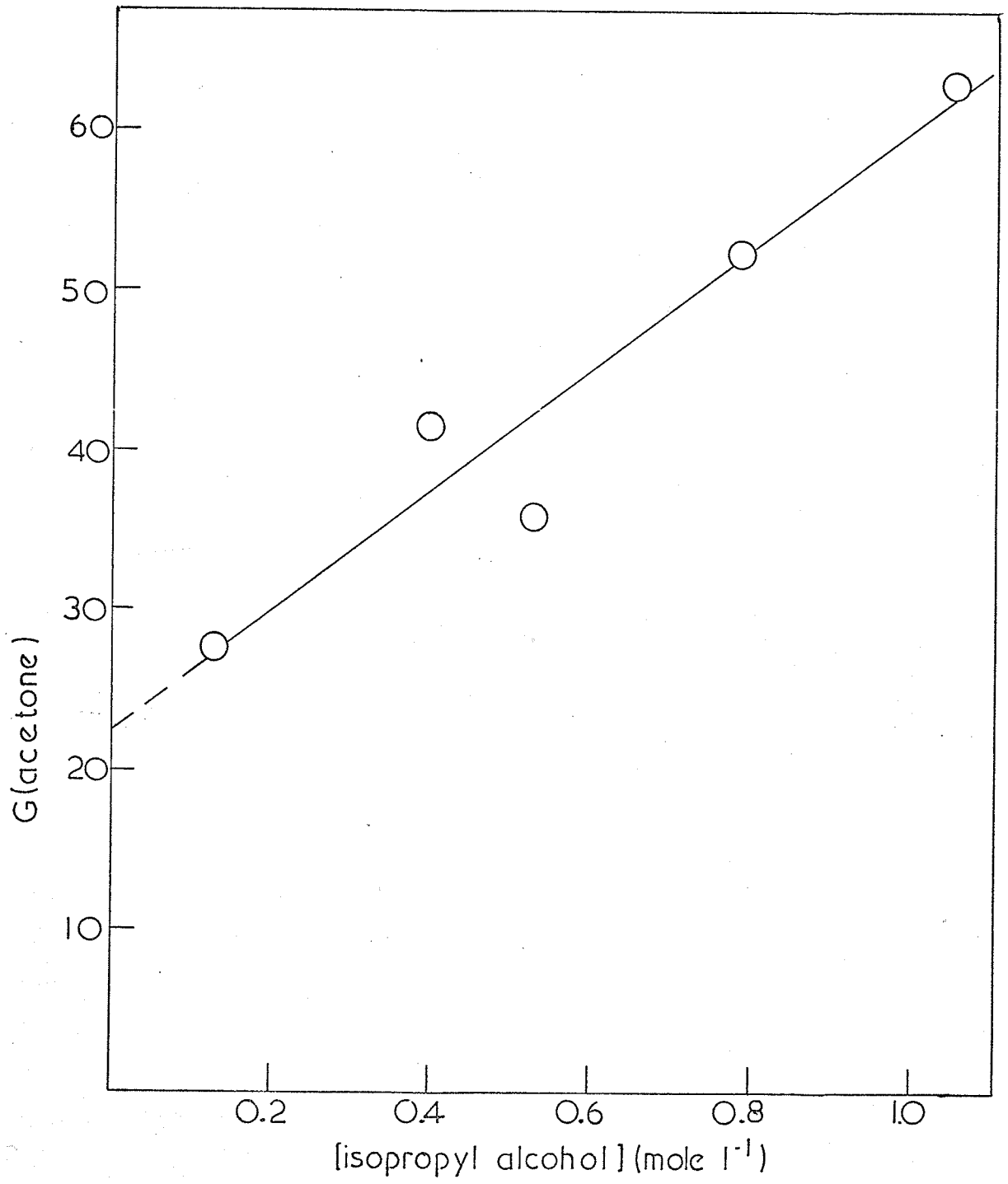
Variation of G(acetone) with concentration of isopropyl alcohol for the acidified system.

[isopropyl alcohol]	G(acetone)
0.131 M.	27.70
0.392 M.	41.28
0.523 M.	35.53
0.785 M.	52.26
1.05 M.	62.71

These results show a linear dependence of G(acetone) on isopropyl alcohol concentration and give a value for G(acetone) of 22.31 at zero alcohol concentration, quite comparable to the results of the uninhibited chain.

Figure 3.6

Variation of G(acetone) with isopropyl alcohol concentration in alcohol - hydrogen peroxide chain reaction containing acidified isopropylamine. $[H_2O_2]$ = 0.008 M.
[isopropylamine] = 0.0352 M.



B. Radiation-Induced Autoxidation

3.3 Oxidation of Isopropyl Alcohol

Following the work of Jayson, Scholes, and Weiss (13) with ethyl alcohol, an air-saturated solution 0.0105 M in isopropyl alcohol was irradiated up to a total dose of 7.5 x 10^{21} eV l^{-1}. The yield of hydrogen peroxide was found to increase to a value of 2.31 x 10^{-4} M at a dose of about 4.5 x 10^{21} eV l^{-1}, and then to decrease nearly to zero. The acetone concentration increased linearly, with a change of slope in the region where the peroxide curve peaked. The peroxide and acetone curves are shown in Figure 3.7. The initial product yields were $G(H_2O_2)$ = 3.65 and G(acetone) = 3.87. The value for $G(H_2O_2)$ was consistent with the value of 3.5 obtained by Jayson, Scholes, and Weiss (13) with ethanol and the value of 3.3 obtained by Garrison (8) with ethylamine.

If the system were reaerated after the completion of the above cycle and then further irradiated, it might be expected to exhibit a similar peroxide concentration profile, and a further increase in acetone formation. Thus, a solution irradiated to a dose of 7.5 x 10^{21} eV l^{-1} and then reaerated, gave the concentration-dose plot shown in Figure 3.8 upon irradiation to an additional 7.5 x 10^{21} eV l^{-1}. The initial product yields were $G(H_2O_2)$ = 3.85 and G(acetone) = 3.70.

By irradiating the same air-saturated alcohol solution to a dose of 3.75 x 10^{21} eV l^{-1} and reaerating, the second cycle was begun when the hydrogen peroxide concentration of the

Figure 3.7

Variation of acetone concentration and of hydrogen peroxide concentration with dose in 0.0105 M. isopropyl alcohol.

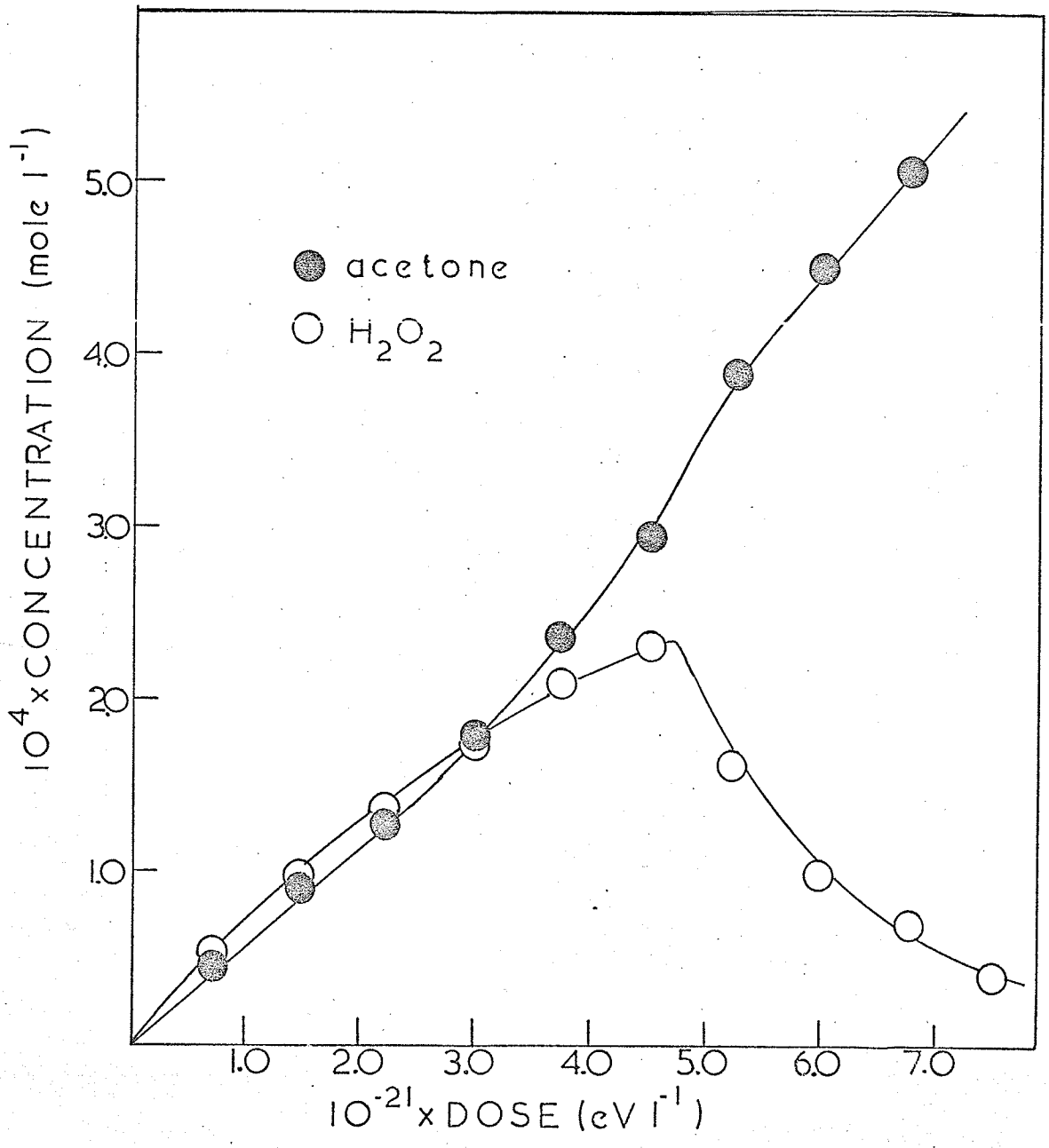
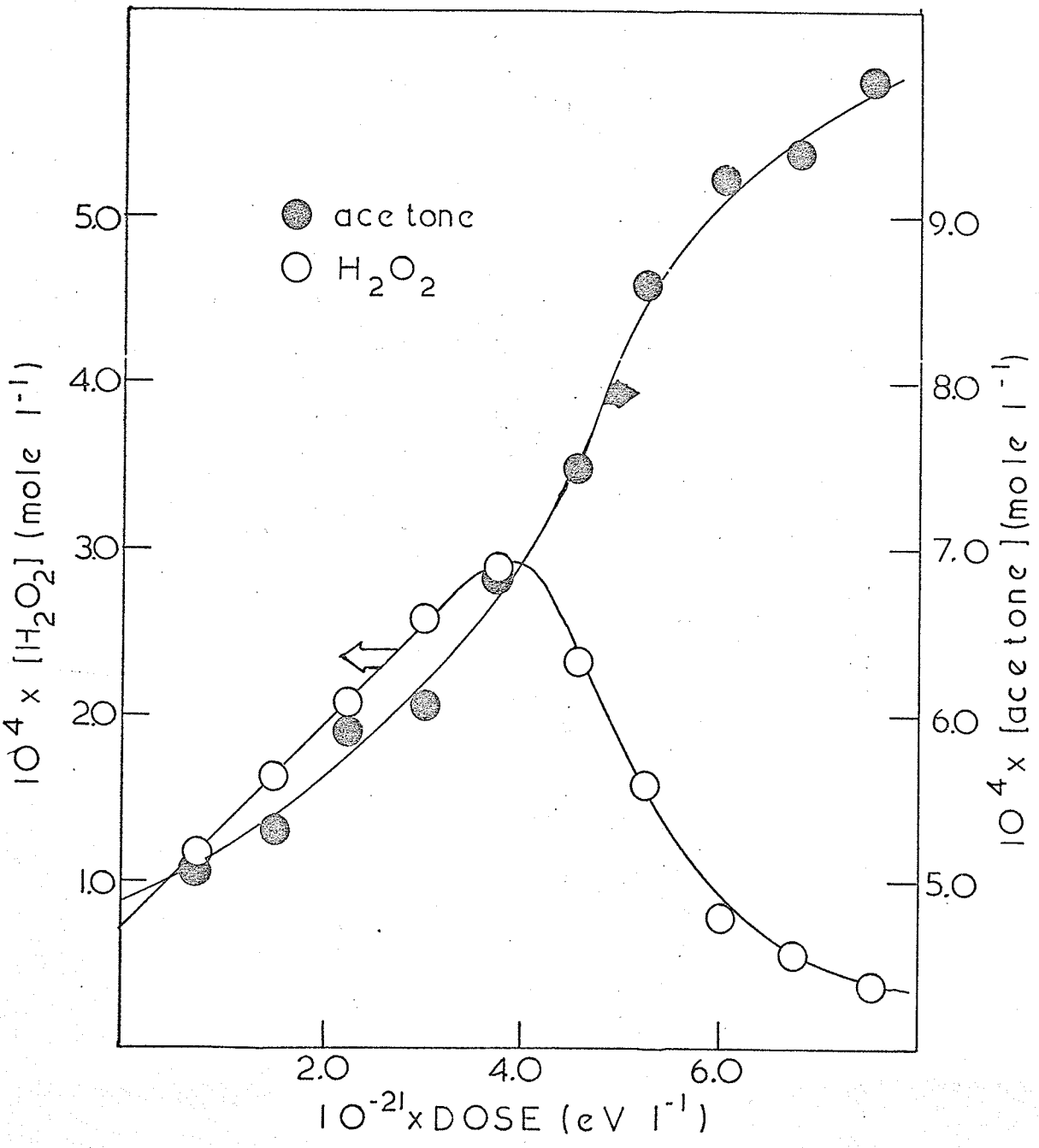


Figure 3.8

Variation of acetone concentration and of hydrogen peroxide concentration with dose in 0.0105 M. isopropyl alcohol after a dose of 7.5×10^{21} eV. l^{-1} and reaeration.



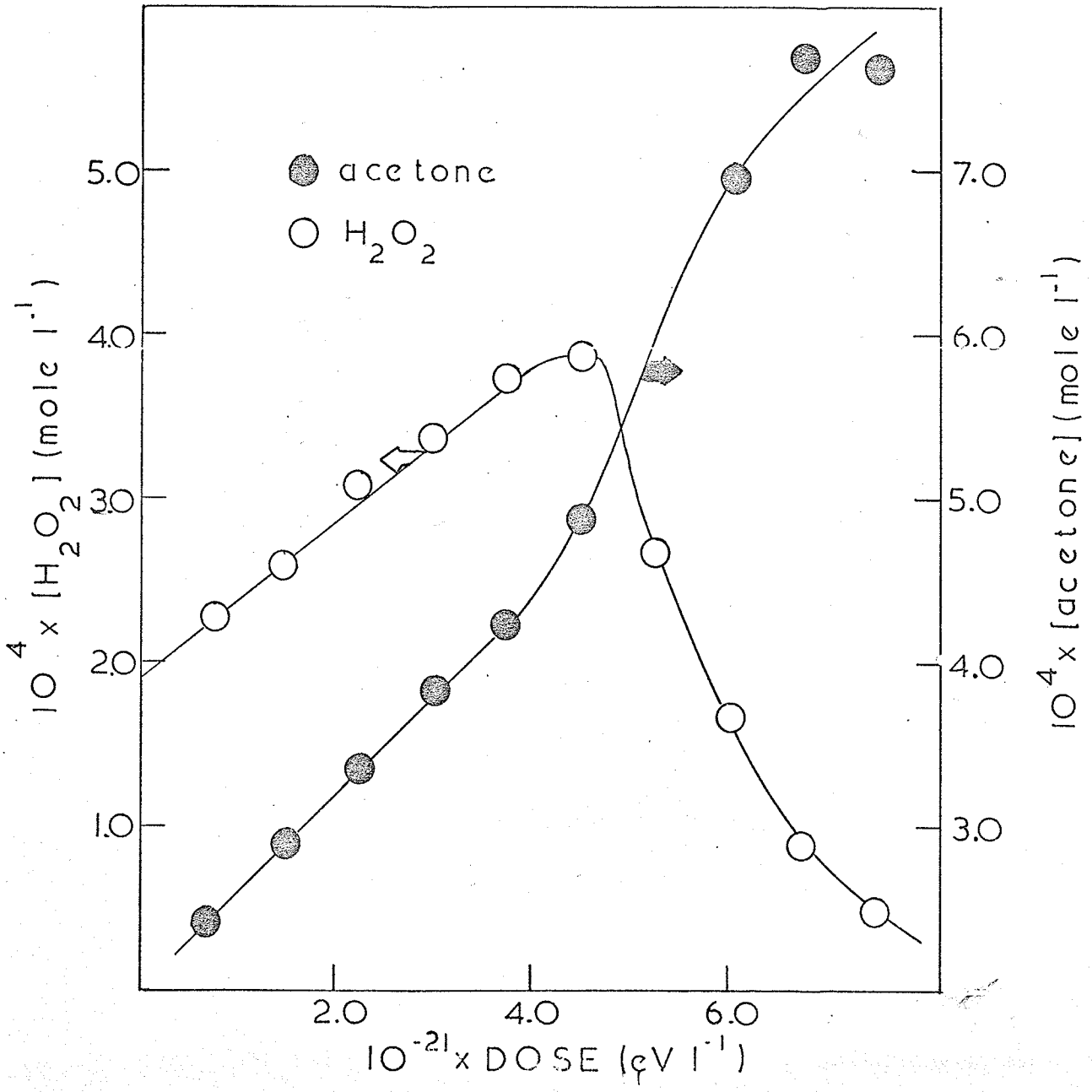
first cycle was at its maximum, giving the concentration-dose plot shown in Figure 3.9. The initial product yields were calculated to be $G(H_2O_2)$ = 3.04 and G(acetone) = 4.14.

Since reaeration after an irradiation cycle was sufficient to begin a second identical cycle, it appeared to be possible to consume all the organic substrate by repeated irradiation and reaeration. In Figure 3.8, two cycles were sufficient to form 9.8×10^{-4} M. acetone (and hence to consume 9.8×10^{-4} M. isopropyl alcohol). Therefore, a solution 10^{-3} M. in alcohol would be entirely consumed in three cycles. For this purpose, a solution 10^{-3} M. in isopropyl alcohol was exposed to three cycles of dose 7.76×10^{21} eV. l^{-1} each followed by reaeration. The maximum concentration of acetone formed was 6.96×10^{-4} M., corresponding to only 66% consumption of the alcohol. However, the decrease in acetone concentration during the third cycle suggested that, as the acetone concentration became comparable to the alcohol concentration, it was decomposed by the radiation as well. Therefore, the percentage consumption of the alcohol probably approached 100% by the end of the third cycle. (Figure 3.10)

It was of interest to determine whether the peroxide formed in the above experiments was entirely hydrogen peroxide, as predicted by Garrison (14), or whether organic peroxides formed as well, as predicted by Jayson, Scholes, and Weiss, (13). Consequently, a single sample 0.0105 M. in isopropyl alcohol was irradiated to a dose of 3.5×10^{21} eV. l^{-1}, and analysed for peroxide both by the iodide method (18),

Figure 3.9

Variation of acetone concentration and of hydrogen peroxide concentration with dose in 0.0105 M. isopropyl alcohol after a dose of 3.75×10^{21} eV. l^{-1} and reaeration.



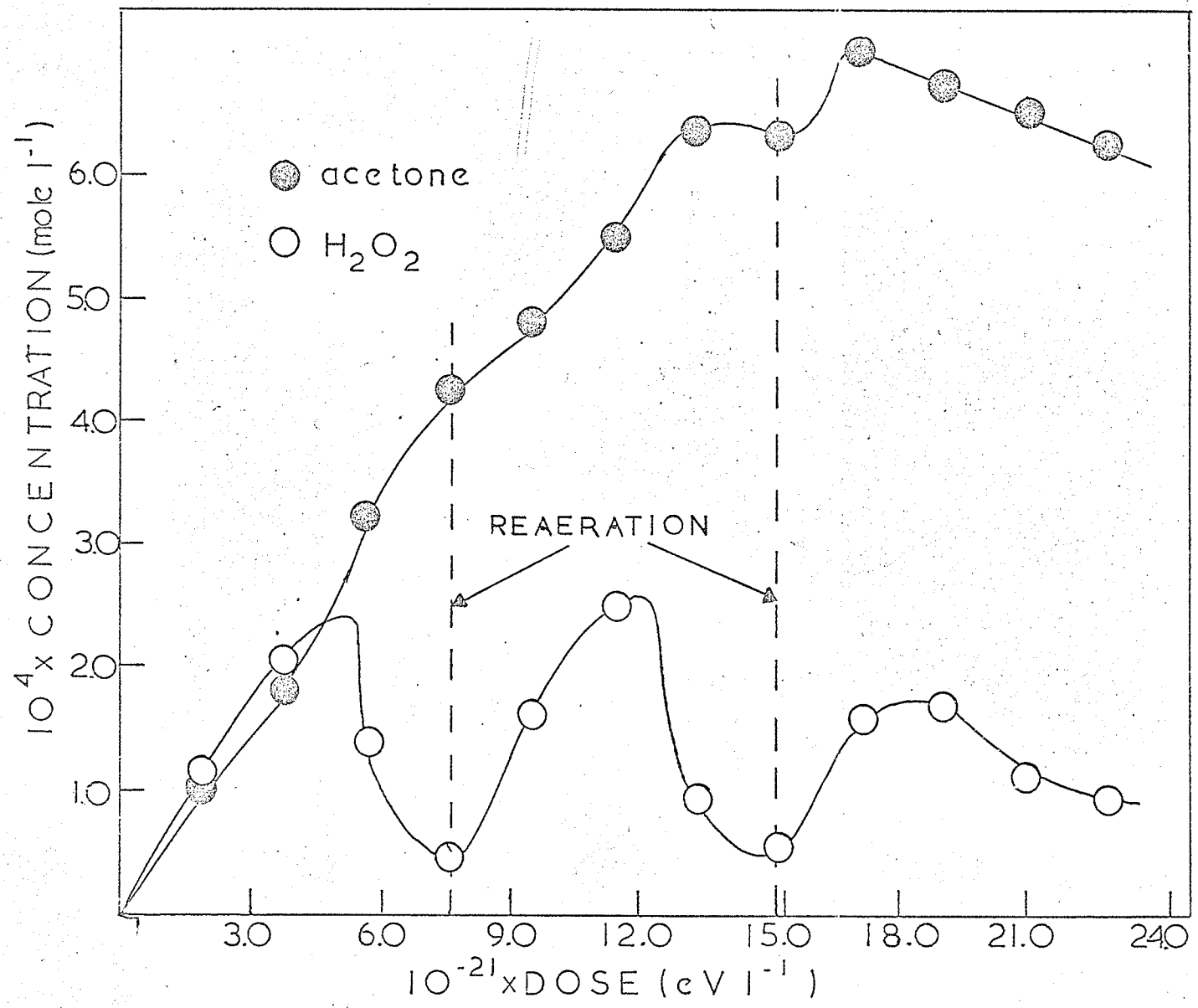


Figure 3.10

Variation of acetone concentration and of hydrogen peroxide concentration with dose in 0.00105 M. isopropyl alcohol.

which was sensitive to all peroxides, and by the titanium IV method (19), which was sensitive only to hydrogen peroxide. The peroxide concentrations obtained, 1.56 x 10^{-4} M. and 1.58 x 10^{-4} M. respectively, suggested that no organic peroxides were formed. Furthermore, it was useful to know that the two methods of analysis could be used interchangeably.

3.4 Effect of Metal Ions on the Oxidation of Isopropyl Alcohol

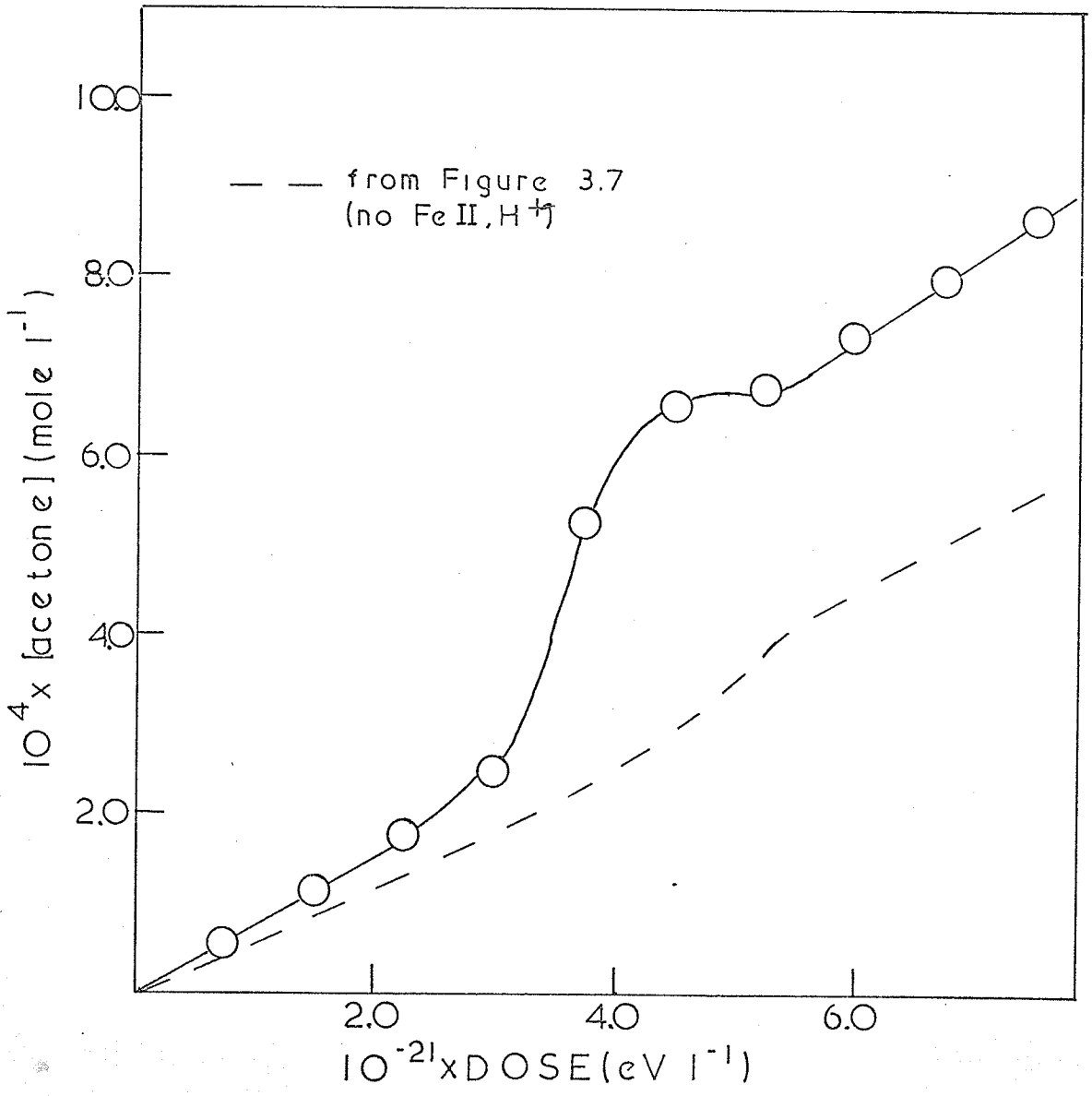
It was expected that because of the one-equivalent oxidation-reduction correspondence of such ion pairs as Fe (II)-Fe (III), Co (II)-Co (III), or Ni (II)-Ni(III), these might serve to catalyse the oxidation of isopropyl alcohol. To investigate this effect, solutions 0.0105 M. in isopropyl alcohol and 10^{-4} M. in metal ion were irradiated up to total doses of 7.5 x 10^{21} eV. l^{-1}. None of Fe (II), Fe (III), Co (II), or Ni (II) were found to affect the total acetone yield. When 2 ml. H_2SO_4 was added to the irradiating solution, Fe (II) gave a 50% increase in acetone yield, as shown in Figure 3.11.

3.5 Oxidation of Organic Substrates

Regardless of the reaction mechanism proposed, the oxidation of any organic substrate proceeds by the abstraction of hydrogen by OH. It was therefore predicted that most organic substrates would be oxidised in a manner similar to that of isopropyl alcohol, and would show the same hydrogen peroxide profile. Accordingly, the following solutions were irradiated through one cycle for a total dose of 7.5 x 10^{21} eV, l^{-1} : 10^{-2} M. solutions of t-butyl alcohol, D-mannitol,

Figure 3.11

Variation of acetone concentration with dose in 0.0105 M. isopropyl alcohol with 10^{-4} M. Fe (II) and 0.08 M. H_2SO_4.



D-glucose, allyl alcohol, ethylene glycol, n-butylamine, n-propylamine, isopropylamine, di-isopropylamine, phenol, and acetic acid; and a saturated solution of benzene. All of these systems showed the same increase in hydrogen peroxide concentration followed by a decrease (see Figures 3.12 to 3.15). That this was accompanied by oxidation of the substrate was shown by the formation of acetone from both isopropylamine and di-isopropylamine at rates nearly identical with the rate of formation of acetone from isopropyl alcohol.

An anomalous effect was observed when the same experiment was performed with 1-butanethiol. Packer and Winchester (16), in experiments with cysteine, found a dependence of $G(H_2O_2)$ and G(-cysteine) on cysteine concentration. A similar concentration dependence was obtained using 1-butanethiol. Peroxide curves for thiol concentrations of 1×10^{-3} M and 5×10^{-3} M are shown in Figure 3.16. A difficulty was encountered in performing the peroxide analyses. Thiols appeared to interfere with the stoichiometry of the iodide oxidation and therefore invalidated this method. Moreover, irradiation seemed to cloud the samples and it was necessary to correct for this turbidity by measuring the absorbance of the solutions with and without the Ti(IV) reagent. The resulting values, however, were strongly subject to error.

Figure 3.12

Variation of hydrogen peroxide concentration with dose in 0.01 M. solutions of isopropyl alcohol, t-butyl alcohol, D-mannitol, and D-glucose.

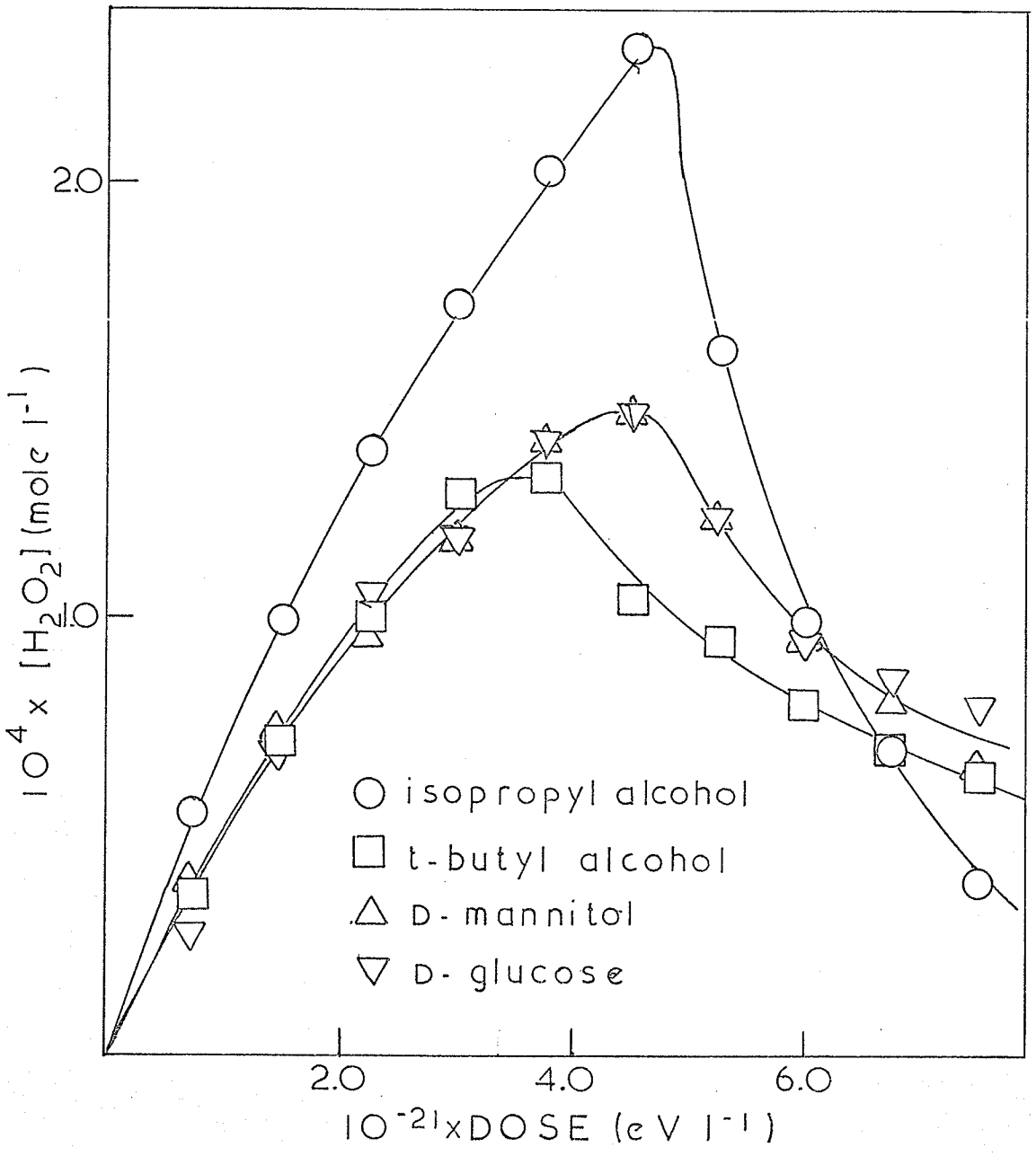


Figure 3.13

Variation of hydrogen peroxide concentration with dose in 0.01 M. solutions of allyl alcohol, ethylene glycol, and n-butyl amine.

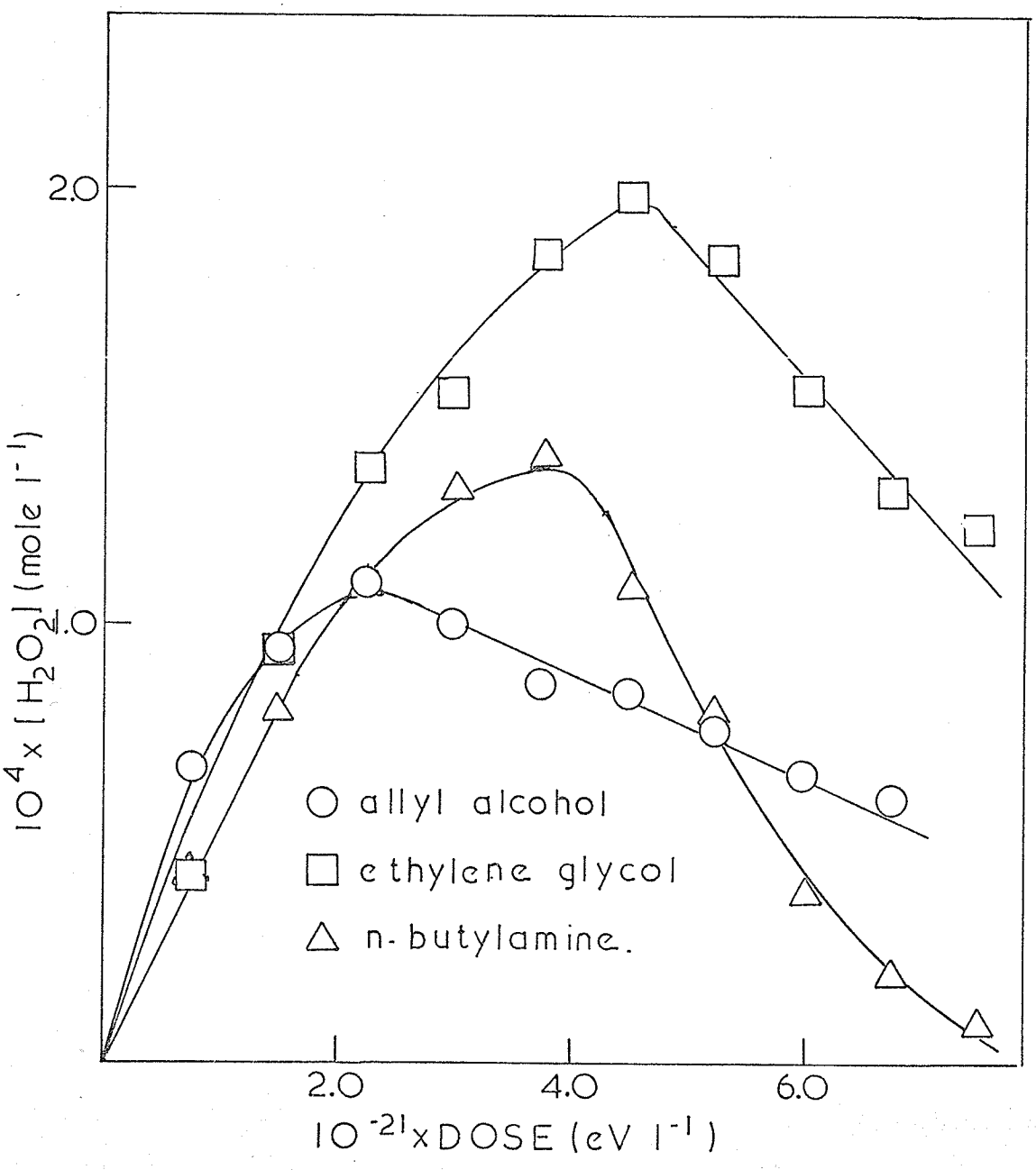


Figure 3.14

Variation of hydrogen peroxide concentration with dose in 0.01 M. solutions of n-propylamine, isopropylamine, and di-isopropylamine.

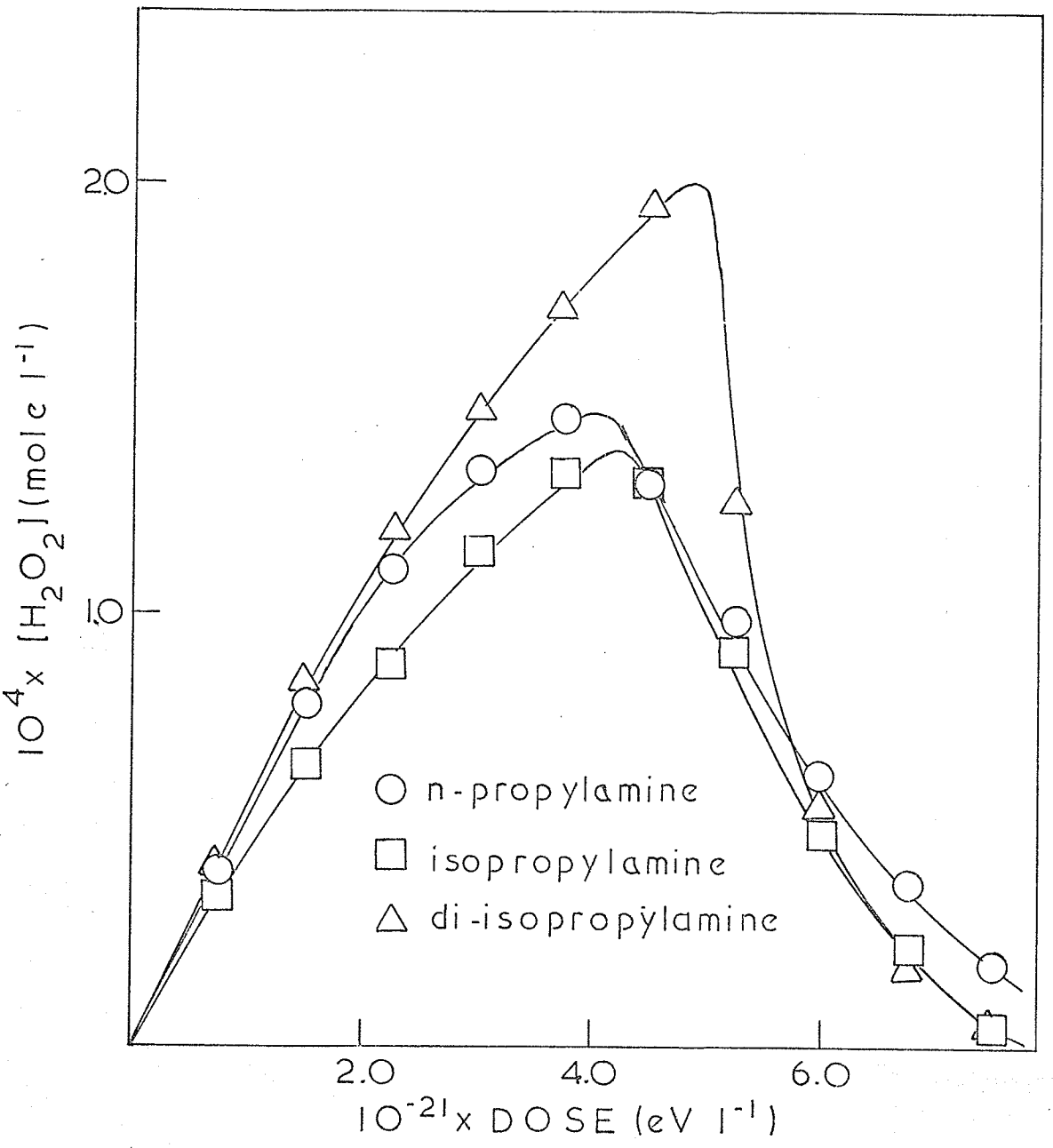


Figure 3.15

Variation of hydrogen peroxide concentration with dose in 0.01 M. solutions of phenol and acetic acid, and a saturated solution of benzene.

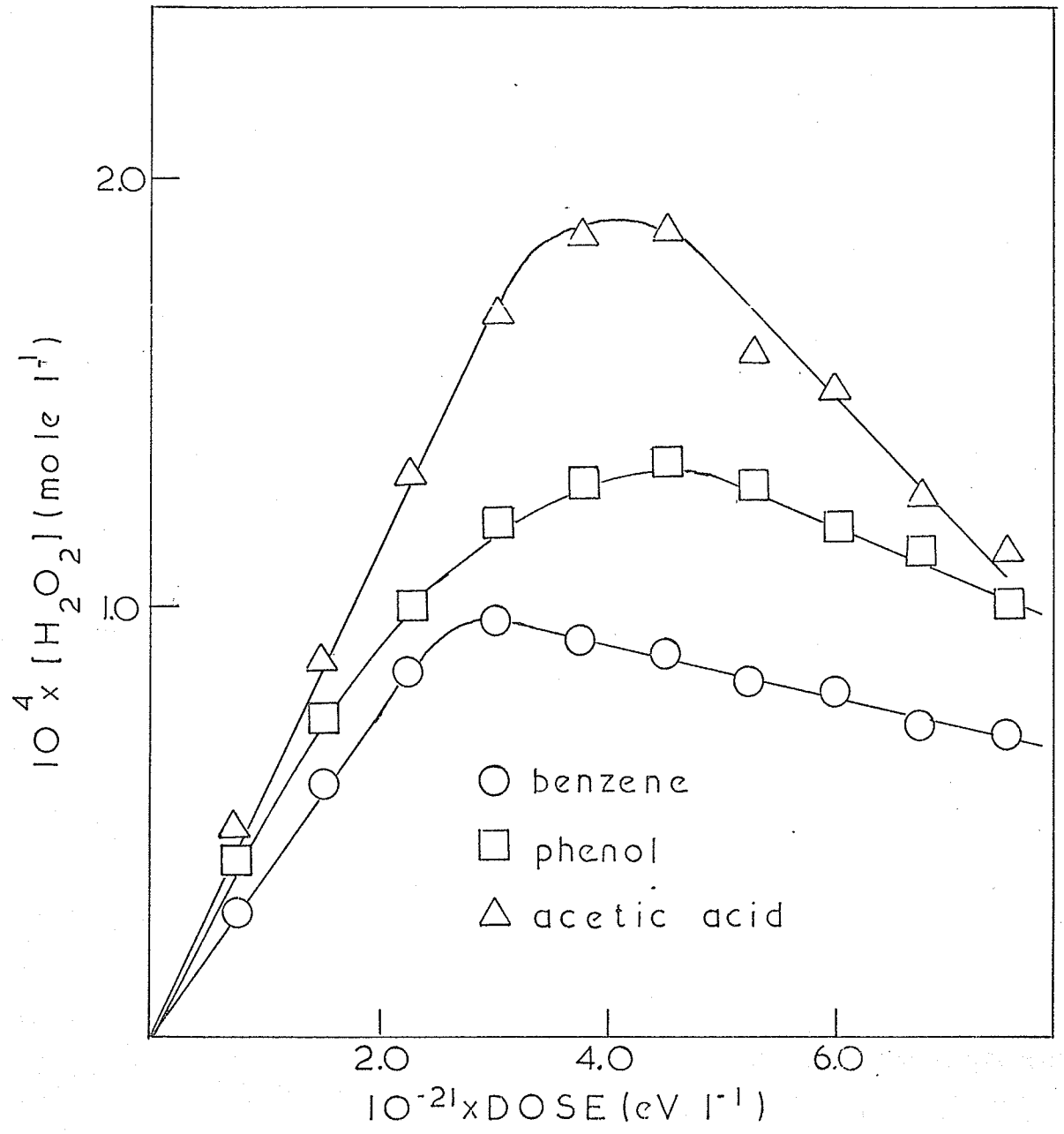
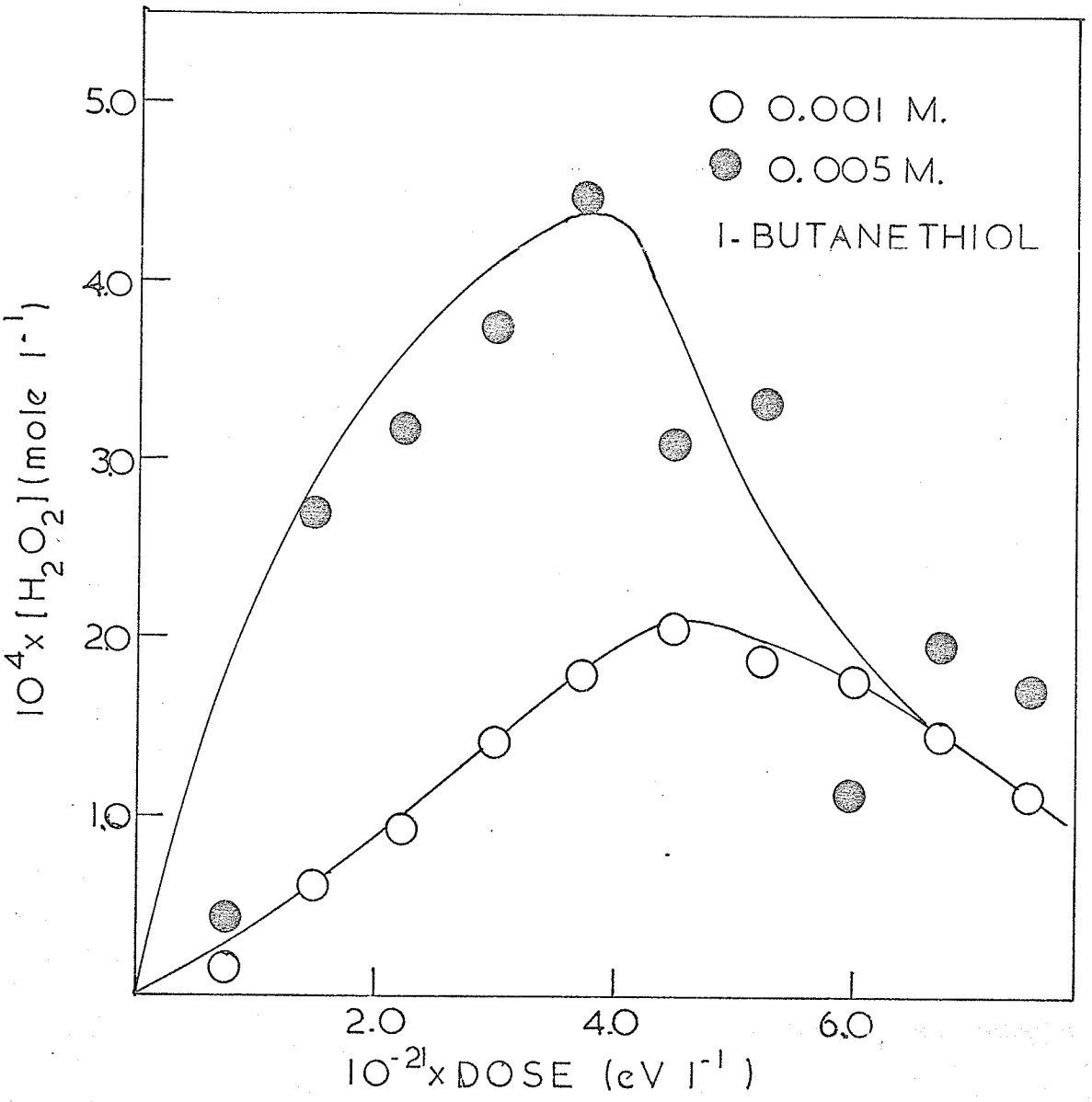


Figure 3.16

Variation of hydrogen peroxide concentration with dose in solutions of 1-butanethiol.



3.6 Chemical Oxygen Demand

Because most organic solutes appeared to react in the same manner on exposure to γ-rays in an air-saturated system, including aromatic species (benzene and phenol) and oxidised species (acetic acid), it was proposed that γ-irradiation might be of use in the purification of water, by oxidising the impurities to CO_2 and H_2O and some oxidised form of nitrogen. A process of γ-irradiation would have the advantage of killing and removing biological organisms as well as removing chemical impurities.

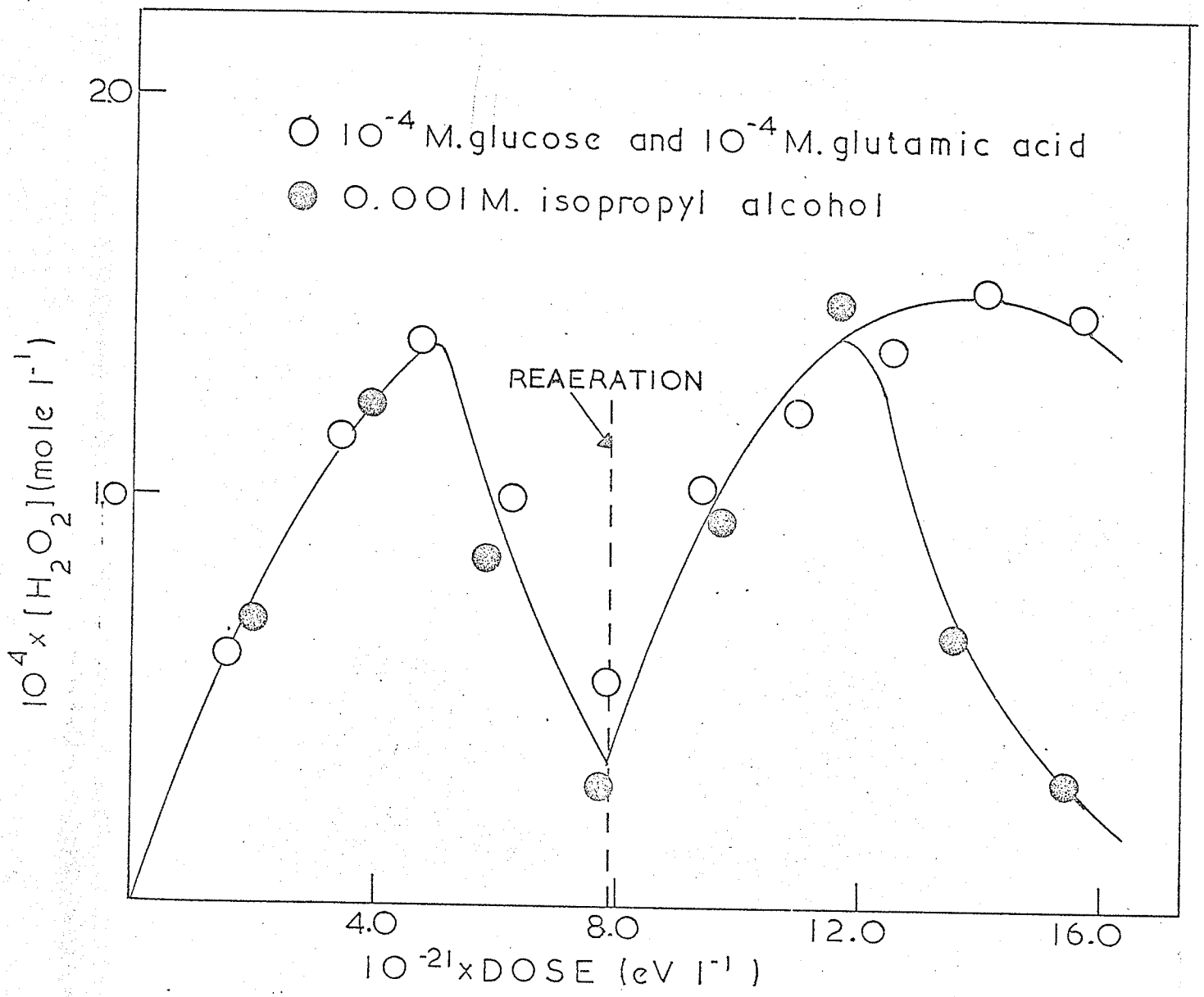
The total quantity of oxidisable material present in solution (oxidisable by dichromate in hot acid solution) is quoted in mg. O_2 per liter and is known as the Chemical Oxygen Demand or COD. A process of γ-irradiation would be impractical for wastes with a large COD. However, present waste treatment plants produce effluent with an oxygen demand of 30 mg. l^{-1}, a value of only borderline acceptability. This level corresponds to roughly 2×10^{-4} M. glucose and could perhaps be reduced by irradiation.

It was therefore important to determine whether the peroxide concentration-dose profile obtained at solute concentrations of 0.01 M. was preserved at lower concentrations. A solution 10^{-4} M. in each of glucose and glutamic acid, considered to be a typical waste, was irradiated to a total dose of 8.2×10^{21} eV. l^{-1} and was found to have a profile nearly identical to that of the more concentrated glucose solution, with a maximum hydrogen peroxide concentration of 1.37×10^{-4} M.

It was calculated that five cycles would be required to consume all of 2×10^{-4} M. glucose. To duplicate the last two of these cycles, a solution 0.4×10^{-4} M. in each of glucose and glutamic acid was irradiated to a dose of 8.2×10^{21} eV. l^{-1}, then reaerated and irradiated again for the same dose. The peroxide profile was essentially the same as that obtained for the first two cycles with 0.001 M. isopropyl alcohol, except that at the end of the second cycle, the concentration of hydrogen peroxide did not decrease (see Figure 3.17).

Since an oxygen-saturated system contains about five times as much oxygen as an air-saturated system, it should be theoretically possible to consume all of 2×10^{-4} M. glucose in one cycle instead of five, thus dispensing with the need for reaeration. A solution 10^{-4} M. in each of glucose and glutamic acid was accordingly oxygen-saturated by bubbling oxygen gas through the solution for fifteen minutes. The solutions were then exposed to irradiation for intervals of 250 seconds up to a total dose of 3.05×10^{22} eV. l^{-1}. The same peak profile was obtained, with a maximum peroxide concentration of 4.93×10^{-4} M. occurring at a dose of 1.75×10^{22} eV. l^{-1}. This actually corresponds to an increase of about 350% efficiency rather than the theoretical 500%, but the low value may be due to incomplete oxygen-saturation.

The Chemical Oxygen Demand of a solution 10^{-4} M. in each of glucose and glutamic acid was measured after each of five cycles, a cycle consisting of ten minutes irradiation



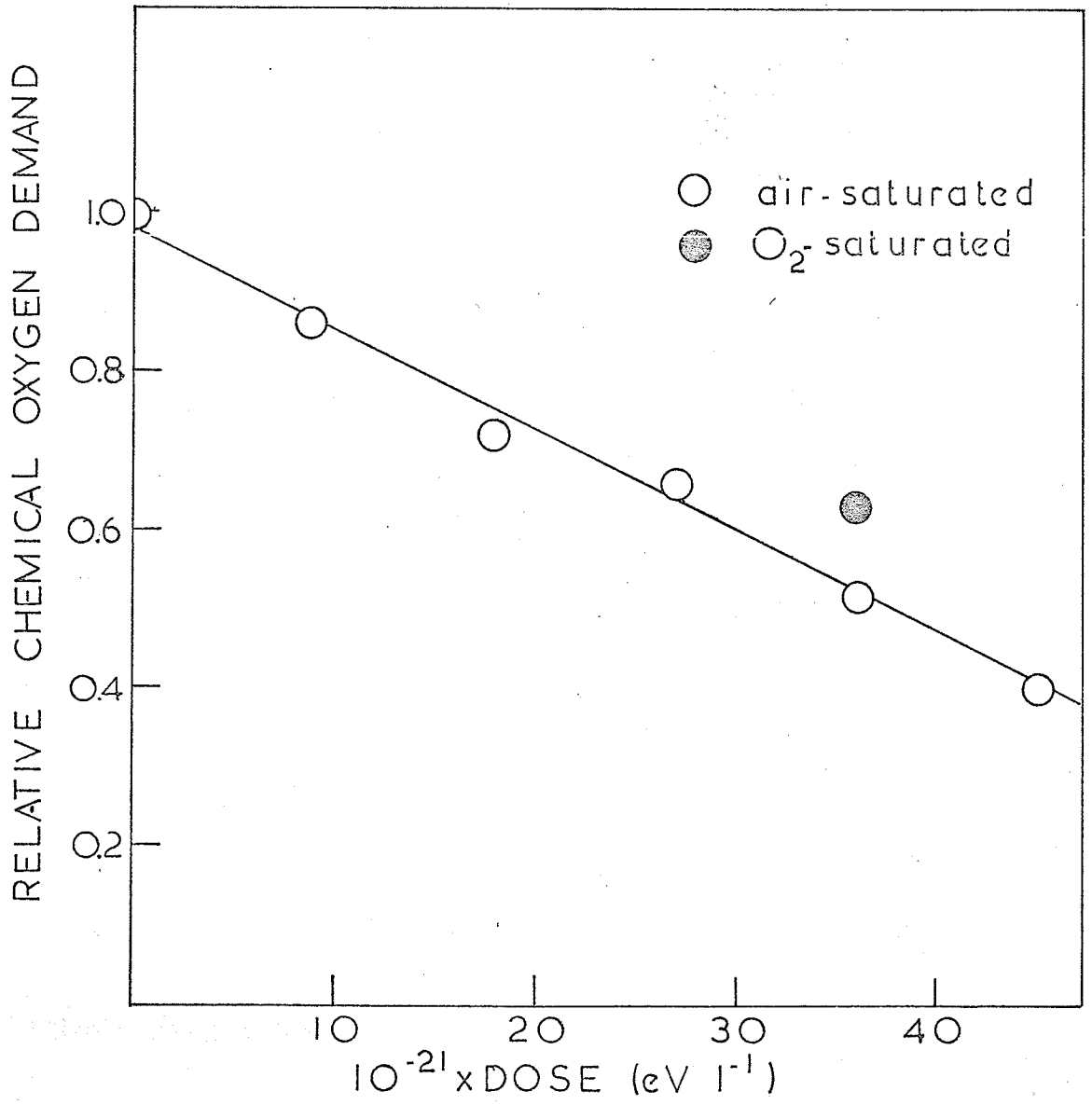
Variation of hydrogen peroxide concentration with dose in solutions 10^{-4} M. in glucose and glutamic acid and 10^{-3} M. in isopropyl alcohol.

Figure 3.17

(9.0×10^{21} eV. l^{-1}) and reaeration. The COD was found to decrease linearly to about one-third of its original value. A similar solution, oxygen-saturated, was irradiated for 40 minutes (3.6×10^{22} eV. l^{-1}) and had a COD of 0.63 relative to the initial value, corresponding, as predicted, to about 3.5 irradiation cycles. These values are shown in Figure 3.18. The theoretical COD for the original solution (sample calculation shown in Appendix II) was about 28.8, assuming that nitrogen forms NH_3.

Figure 3.18

Variation of Chemical Oxygen Demand with dose in a solution 10^{-4} M. in glucose and glutamic acid.



4. Discussion

4.1 Radiation-Induced Peroxide Oxidation

It was apparent that the oxidation of isopropylamine did not follow the same mechanism as the oxidation of isopropyl alcohol. The low values for G(acetone) and $G(-H_2O_2)$ (less than 5) were not consistent with a chain mechanism, although at their maxima they were slightly higher than would be expected for a completely non-chain process. The variation of G(acetone) and $G(-H_2O_2)$ with amine concentration was bewildering, especially when contrasted with the positive linear dependence on alcohol concentration shown by the isopropyl alcohol chain, and could not be explained. The very small effect of the presence of oxygen on the yields was also indicative of a non-chain process. The dose rate studies gave no information.

Amines were found, on the other hand, to be very effective at inhibiting the chain oxidation of isopropyl alcohol. The inhibited chain showed a negative linear dependence of G(acetone) on hydrogen peroxide concentration, compared with the independence shown by the uninhibited chain. Acidification of the amine removed the inhibition, suggesting that it was the amino group of the molecule that was responsible for the inhibiting effect. This was supported by the fact that all the amines tested had the same inhibiting properties. Moreover, the fact that triethylamine had the same inhibiting effect as the other amines showed that the electron pair on the nitrogen might be the inhibit-

ing agent, since triethylamine had no amino hydrogen atom. Reduction of inhibition on acidification would thus be due to the tying up of the electron pair by the proton. Once acidified, the amine apparently played no part whatever in the reaction, known to be independent of pH, since the slope of the G(acetone)-alcohol concentration curve was essentially the same as for the uninhibited chain, and the intercept only slightly lower.

The mechanism for the oxidation of isopropyl alcohol was (6)

$$e^-_{aq} + H_2O_2 \longrightarrow OH^- + OH \qquad (14)$$

$$H + (CH_3)_2CHOH \longrightarrow (CH_3)_2\dot{C}OH + H_2 \qquad (29)$$

$$H + (CH_3)_2CHOH \longrightarrow CH_3(\dot{C}H_2)CHOH + H_2 \qquad (30)$$

$$OH + (CH_3)_2CHOH \longrightarrow (CH_3)_2\dot{C}OH + H_2O \qquad (31)$$

$$OH + (CH_3)_2CHOH \longrightarrow CH_3(\dot{C}H_2)CHOH + H_2O \qquad (32)$$

$$(CH_3)_2\dot{C}OH + H_2O_2 \longrightarrow (CH_3)_2CO + OH + H_2O \qquad (33)$$

$$CH_3(\dot{C}H_2)CHOH + (CH_3)_2CHOH \longrightarrow (CH_3)_2CHOH + (CH_3)_2\dot{C}OH \qquad (34)$$

$$2\ CH_3(\dot{C}H_2)CHOH \longrightarrow \text{termination} \qquad (35)$$

Since amines did not sustain a chain reaction, it was unlikely that they would compete significantly with the alcohol molecules for either H or OH. Therefore, inhibition must arise through reaction of the amine with either or both of the two alcohol-derived radicals, that is, by the inclusion in the mechanism of either or both of

$$(CH_3)_2\dot{C}OH + (CH_3)_2CHNH_2 \longrightarrow \text{termination} \qquad (73)$$

$$CH_3(\dot{C}H_2)CHOH + (CH_3)_2CHNH_2 \longrightarrow \text{termination} \qquad (74)$$

The simplest kinetic expression was obtained from (74)

alone, because then termination occurred only by means of β-radicals. The expression for G(acetone) was given by

$$G(\text{acetone}) = \frac{k_{29}(k_{31} + k_{32})}{k_{32}(k_{29} + k_{30})} G_H + \frac{k_{31}}{k_{32}}(G_{OH} + G_{e^-_{aq}})$$

$$+ \frac{[(CH_3)_2CHOH]k_{34}(k_{31} + k_{32})}{k_{32}} \cdot$$

$$\frac{\sqrt{k_{74}^2[(CH_3)_2CHNH_2]^2 + 8k_{35}G_R D} - k_{74}[(CH_3)_2CHNH_2]}{4k_{35}D}$$

It predicted a linear alcohol concentration dependence with the same large intercept as for the uninhibited chain. The downward curve to a lower intercept shown by the actual results could be explained on the basis of primary inhibition at low alcohol concentration. By primary inhibition is meant the reaction of OH radicals (both the primary yield and those from (33)) with the amine, in competition with their reactions with the alcohol (31) and (32). At higher alcohol concentration primary inhibition would not be important and the predicted linear dependence was observed. At high amine concentration, G(acetone) would be predicted to approach the intercept value of 29.8 of the uninhibited chain. The lowering of this predicted value to the observed value of about 10 could also be due to such primary inhibition. The dependence of G(acetone) on hydrogen peroxide concentration could not be explained. It is concluded, however, that the inhibition reaction (74), coupled with primary inhibition when amine and alcohol concentrations are comparable, is consistent with the observed effects.

4.2 Radiation-Induced Autoxidation

The radiation-induced autoxidation of organic substrates in air-saturated solution appeared to occur, with the exception of thiols, by the same mechanism. The first step was almost certainly hydrogen abstraction from the molecule, by means of OH and probably H. Since no organic peroxides formed, the mechanism of Garrison appeared to be valid as long as oxygen remained in the system

$$RH + OH \longrightarrow R\cdot + H_2O \qquad (21)$$

$$RH + H \longrightarrow R\cdot + H_2 \qquad (16)$$

$$R\cdot + O_2 \longrightarrow R'H + HO_2 \qquad (59)$$

$$e^-_{aq} + O_2 \longrightarrow O_2^- \qquad (60)$$

$$H + O_2 \longrightarrow HO_2 \qquad (19)$$

$$H^+ + O_2^- \rightleftharpoons HO_2 \qquad (27)$$

$$2\ HO_2 \longrightarrow H_2O_2 + O_2 \qquad (15)$$

As the concentration of oxygen approached zero, and the concentration of hydrogen peroxide built up, the organic radicals would probably attack the peroxide in preference to the oxygen

$$R\cdot + H_2O_2 \longrightarrow R'H + H_2O + OH \qquad (75)$$

$$OH + RH \longrightarrow R\cdot + H_2O \qquad (16)$$

giving rise to a chain reaction. That this chain would have occurred at different rates and to different extents for different solutes would account for the differences in the decreasing part of the peroxide profiles of the different solutes. The anomalous results for 1-butanethiol were probably due to the addition of O_2 to the $CH_3CH_2CH_2CH_2S\cdot$ radical and the subsequent reactions proposed by Packer and Winchester (16).

4.3 Applications to Waste Disposal

The disposal of sewage and industrial waste is currently a problem of considerable magnitude. The discharge without treatment of such materials directly into natural watercourses may lead to pollution, and in particular, to conditions inhibitive to aquatic life and hazardous or at least objectionable to the community. The characteristics of waste which lead to these water conditions are usually restricted, to a greater or lesser extent, in waste effluent, necessitating some form of waste treatment. Such treatment, of course, varies with the nature of the wastes, and with the nature and use of the watercourse. Considerable detail on the various operations in sewage treatment may be found in many sources (22, 23, 24, 25, for example).

Division of the treatment steps into phases is somewhat arbitrary, but the pattern of Besselievre (22) tends to emerge. This pattern consists of the following five phases : interception of inert, extraneous objects; removal of solids by gravitation, with or without the aid of chemical additives; biological or chemical oxidation of polluting elements; polishing and refining; destruction of solids. In few cases are all five stages necessary or practised.

Aside from unsightly floating matter, which is objectionable but not harmful, and toxic materials, which are released relatively rarely, the most common cause of pollution is the high concentration of organic matter, which

decomposes with the evolution of foul gases and with the consumption of all the dissolved oxygen, rendering the water uninhabitable for aquatic life. The consumption of oxygen by either sewage or polluted water is called the Biological Oxygen Demand, which can be related to the Chemical Oxygen Demand for a waste of relatively constant composition. It is this quantity which must be regulated on sewage effluent and it is this quantity which is often the most difficult to reduce.

The natural decomposition of organic matter occurs in two steps, both of them by means of bacteria which break down the matter in order to feed on it. The first step, anaerobic biolysis, is the conversion of the complex organic compounds to simpler ones, in the absence of oxygen. In this stage, proteins are converted to urea, ammonia, mercaptans, hydrogen sulfide, and fatty and aromatic acids, carbohydrates to fatty acids, water, carbon dioxide, hydrogen, methane, and other gases, and fats and soaps to their original acids, carbon dioxide, hydrogen and methane. Cellulose decomposes very slowly. Dissolution of atmospheric oxygen occurs slowly, but in time, the second stage, aerobic biolysis, can occur, in which the products of the first stage are oxidised and nitrified to stable products. Carbon is in the form of carbon dioxide and some methane; nitrogen is converted to nitrates and nitrites which are useful as plant food. Both stages occur very slowly in nature; in treatment plants they can be speeded up and made to operate, to a certain extent,

concurrently by means of continual aeration.

Sewage is often classed as strong, medium, or weak, according to the following general composition:

component (mg/l)	strong	medium	weak
total solids	1000	500	200
BOD (at 20° C.)	300	200	100
total nitrogen	85	50	25
organic	35	20	10
free NH_3	50	30	15
fats	40	20	0

Primary treatment, or filtration, is the first step in most treatment procedures. It affords little or no reduction in the BOD, and up to 70% reduction in suspended solids.

Secondary treatment is usually either of a chemical or of a biological nature. Chemical precipitation, the addition of chemicals which produce a flocculent precipitate thus hastening sedimentation, will remove 50 to 75% of the BOD and 70 to 90% of the suspended solids (23). It is less effective than the biological methods but for medium or weak sewage, it provides adequate, inexpensive treatment. Biological oxidation is most generally carried out either on a trickling filter, or by use of activated sludge. A trickling filter consists of a bed of broken stone five to twelve feet deep onto which the waste water is sprayed. As the water filters through the medium, it becomes purified by the action of the bacterial slime on the rock. A trickling filter will

remove 80 to 95% of the BOD and 80 to 90% of the suspended solids (23). Activated sludge is sludge in which the biological activity has been maintained. When this is mixed with raw sewage and the whole aerated, it becomes a very efficient water purifier, removing 85 to 95% of the BOD and 85 to 95% of the suspended solids (23).

Another common method of treatment is the use of lagoons or ponds. A single lagoon, with or without artificial aeration, will give 39 to 45 % reduction of the BOD. A series of ponds will give 80 to 99% reduction (22). They rely on natural bacterial-algal decomposition and require far less maintenance or expense than the other methods.

The acceptable level of BOD and suspended solids of wastes discharged into natural watercourses must depend, in the final analysis, upon the nature of the watercourse itself. There are many important factors influencing the determination of acceptable levels : ratio between available and required oxygen; volume and velocity of the stream; presence of rapids, lake or ocean currents, tributary streams, and quiescent water; growth of green algae; other nearby waste disposal centres; nature of the outlet and distribution of sewage at the outlet; and proximity to communities or recreation areas. In general, the BOD level should be at most 30 mg. per litre and preferably considerably lower.

At present, sewage is discharged with a BOD somewhat in excess of this value, either because the raw sewage was so strong that even after biological treatment the BOD level

remained high, or because the sewage was so weak that no treatment at all was deemed necessary. For either case, a simple radiation system could possibly be used to reduce the BOD to an acceptable level.

The use of irradiation in water treatment could have many advantages. Some of these might be:

1. speed Assuming that a community with a population of 100,000 discharges 100 gallons of sewage per day per person, there are 10 million gallons of sewage per day to be treated. This is equivalent to about 1140 cubic feet per minute. Using a source capable of delivering 2×10^{20} eV l^{-1} sec^{-1} (10 times as high a dose rate as used in this work) to any volume, five minutes (1/10 as long as in this work) would suffice to reduce the BOD to about one-third of its original value. Therefore, oxygen-saturated sewage flowing at a rate of 1140 ft^3 min^{-1} through an irradiation facility of volume 1140 x 5 or 5700 ft^3 would be treated in five minutes. Microbial oxidation to a similar BOD level would require days.

2. volume Radiation treatment would be essentially an in-line process, requiring no storage. Biological oxidation, requiring five days, for example, would necessitate tanks with a capacity of at least 50 million gallons in the example cited above.

3. low temperature efficiency While microbial activity slows down at low temperature and essentially ceases below 0° C, the increased oxygen solubility at low temperature would actually increase the effectiveness of radiation treatment.

4. cost No attempt can be made to evaluate the relative costs of the various methods. All that would be required for radiation treatment would be a source (possibly used fuel rods from a nuclear reactor, which must be disposed of anyway), adequate protection from the radiation, provision for changing sources, a length of pipe, and a method for recycling oxygen. For wastes of widely varying flow rates, a pond for equalising the flow might also be necessary. This should not be prohibitive compared to the cost of storage lagoons, land, and cleaning facilities.

5. sterility A dose of 0.2 Mrad $min.^{-1}$ (equivalent to 2×10^{20} eV. l^{-1} sec^{-1}) x 5 min. or 1 Mrad is known to be sufficient to kill all microorganisms and disease bacteria in water. This would obviate the need for chlorination as a post-treatment requirement.

6. no slime buildup Where biological and chemical methods of treatment give rise to large quantities of slime and sludge settling out, radiation treatment, which converts dissolved organic impurities either to gases (CO_2, CH_4) or to volatile compounds, would be a relatively clean process.

It is, moreover, of increasing importance to develop means of reusing waste water, due to the increasing water shortage. For areas of limited water supply, wastes and sewage which have been given some form of tertiary treatment could probably be used for irrigation and industrial purposes if not for domestic consumption. Communities which must contemplate the spending of vast amounts of money

to build or increase their water supply systems could probably spend their money to better advantage if they gave thorough tertiary and polishing treatment to their wastes, and reused them.

It is not possible, of course, to evaluate here the practicality of such techniques. But, especially in areas of acute water shortage and with ready access to suitable radiation sources, water purification by means of irradiation might be worthy of consideration.

Appendix I

Sample Calculation of Actual Absorbed Dose for a Solution Irradiated for 10 Minutes

The electron density of a solution is calculated as follows:

$$D_M = \left(\frac{\rho_M \times 1000 - \sum_i c_i M_i}{18.02} \right) \times 10 + \sum_i c_i z_i$$

where D_M is the electron density of solution M

ρ_M is the bulk density of solution M

c_i is the molarity of solute i

M_i is the molecular weight of solute i

z_i is the number of electrons per formula weight of solute i

For the Fricke dosimeter solution, $\rho = 1.024$ g./ml. For the solutes

solute	c_i(M.)	M_i	z_i	$c_i M_i$	$c_i z_i$
$Fe(NH_4)_2(SO_4)_2$	10^{-3}	284	144	0.284	0.144
H_2SO_4	0.4	98	50	39.2	20.0
				39.5	20.1

Thus

$$D_M = \left(\frac{1024 - 39.5}{18.02} \right) \times 10 + 20.1$$

$$= 566.4 \text{ moles } l^{-1}.$$

A typical irradiation solution had a density of 0.9925 g./ml. and the solutes were

solute	c_i(M.)	M_i	z_i	c_iM_i	c_iz_i
$(CH_3)_2CHOH$	0.52	60	34	31.2	17.68
$(CH_3)_2CHNH_2$	0.03	59	34	1.77	1.02
H_2O_2	0.01	34	18	0.34	0.18
				33.3	18.9

Thus

$$D_M = \left(\frac{992.5 - 33.3}{18.02}\right) \times 10 + 18.9$$

$$= 551.2 \text{ moles } l^{-1}.$$

If the dose absorbed by the dosimeter solution was 1.6×10^{19} eV. l^{-1} sec^{-1} x 10 sec or 1.6×10^{20} eV. l^{-1}, then the dose absorbed by the sample was

$$1.6 \times 10^{20} \times \frac{551.2}{566.4} = 1.56 \times 10^{20} \text{ eV } l^{-1}.$$

The correction is negligible within the limits of experimental error of these experiments.

Appendix II

Sample Calculation Of Theoretical Chemical Oxygen Demand

Consider a solution 10^{-4} M. in each of glucose and glutamic acid.

$$C_6H_{12}O_6 + 6\ O_2 \longrightarrow 6\ CO_2 + 6\ H_2O$$

Thus 10^{-4} M. glucose requires 6×10^{-4} M. O_2.

$$C_4H_7NO_4 + 3\ O_2 \longrightarrow 4\ CO_2 + 2\ H_2O + NH_3$$

Thus 10^{-4} M. glutamic acid requires 3×10^{-4} M. O_2.

The solution thus has a combined requirement of 9×10^{-4} M. O_2 or $9 \times 10^{-4} \times 32 \times 1000 = 28.8$ mg./l. The theoretical COD is then 28.8.

References

1. A.O. Allen, "The Radiation Chemistry of Water and Aqueous Solutions", Van Nostrand, Princeton, New Jersey (1961)

2. A.J. Swallow, "Radiation Chemistry of Organic Compounds", Pergamon Press, Oxford (1960)

3. I.V. Vereshchinskii and A.K. Pikaev, "Introduction to Radiation Chemistry", Israel Program for Scientific Translations, Jerusalem (1964)

4. T. Balkas, F.S. Dainton, J.K. Dishman, and D. Smithies, Trans. Faraday Soc., 62, 8 (1966)

5. E. Hayon, J. Phys. Chem., 68, 1242 (1964)

6. C.E. Burchill and I.S. Ginns, unpublished results, University of Manitoba (1969)

7. E.S. Huyser, C.D.Bredewig, and R.M. Van Scoy, J. Am. Chem. Soc., 86, 4148 (1969)

8. W.M. Garrison, Rad. Res. Supp., 4, 158 (1964)

9. P.J. Kozak and H. Gesser, J. Chem. Soc., 448 (1960)

10. R.K. Brinton, Can. J. Chem., 38, 1339 (1960)

11. P.C. Gray and J.C.J. Thynne, Trans, Faraday Soc., 59, 2275 (1963)

12. P.C. Gray, A. Jones, and J.C.J. Thynne, Trans. Faraday Soc., 61, 474 (1965)

13. G.G. Jayson, G. Scholes, and J. Weiss, J. Chem. Soc., 1358 (1957)

14. W.M. Garrison, Curr. Top. in Rad. Res., 4, 43 (1968)

15. J.W. Purdie, J. Am. Chem. Soc., 89, 226 (1967)

16. J.E.Packer and R.V.Winchester, Chem. Commun.,14, 826 (1968)

17. H.A.J.B.Battaerd and G.W.Tregear, Rev. Pure and Appl. Chem., 16, 83 (1966)

18. A.O.Allen, C.J.Hochanadel, J.A.Ghormley, and T.W.Davis, J. Chem. Phys., 56, 575 (1962)

19. F.D.Snell and C.T.Snell, "Colorimetric Methods of Ananysis" vol. II A, Van Nostrand, Princeton, New Jersey, p. 734, (1959)

20. S.Berntsson, Anal. Chem., 28, 1337 (1956)

21. F.D.Snell and C.T.Snell, "Colorimetric Methods of Analysis" vol. III, Van Nostrand, Princeton, New Jersey, p. 815, (1959)

22. E.B.Besselievre, "The Treatment of Industrial Wastes", McGraw Hill,(1969)

23. H.E.Babbitt and E.R.Baumann, "Sewerage and Sewage Treatment", Wiley and Sons (1967)

24. H.G.Payrow, "Sanitary Engineering", International Text Book Co., Scranton, Pennsylvania (1941)

25. E.W.Steel, "Water Supply and Sewerage", McGraw Hill (1960)

26. G.Hickling, Master of Science Thesis, University of Manitoba (1968)