STUDIES   IN   THE RADIATION CHEMISTRY   OF

DILUTE AQUEOUS SOLUTIONS OF SIMPLE GASES.

by

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A   Thesis   submitted for the   degree   of

Doctor of Philosophy

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September, 1962.

ABSTRACT.

Solutions of carbon monoxide (4.5×10^{-4}M) in 0.1N H_2SO_4 (oxygen-free) have been irradiated with γ-rays ($\sim 30,000$ rads/hr) and found to give hydrogen with G = 0.95; carbon dioxide G =2.6 ; formaldehyde G = 0.5 ; glyoxal G = 0.3 ; and formic acid G = 0.4. Hydrogen peroxide could not be detected. The results are interpreted in terms of a mechanism involving CHO and COOH radicals, some of the products being secondary. The effect of variations in acidity have been investigated, a striking observation being that formic acid is produced with G = 44 in alkaline solution. In the presence of ferrous ions ($2 \times 10^{-4} - 2 \times 10^{-3}$M Fe^{++}, 0.1N H_2SO_4) no ferric was produced, but in the presence of ferric ions ($2 \times 10^{-4} - 1 \times 10^{-3}$M Fe^{+++} 0.1N H_2SO_4) ferrous ions are produced with G = 6.40. The ratio of the rate constants for the reactions H + HCHO to H + CO (in 0.1N H_2SO_4) is 13.5 $\pm$ 3, of OH + CO to OH + Fe^{++} (in 0.1N H_2SO_4) is 3.9 $\pm$ 0.5 and of H + CO to H + H^+ + Fe^{++} (in 0.1N H_2SO_4) is 2.5 $\pm$ 0.3, all at 23°C.

The industrial implications of the irradiation of carbon monoxide by different radiation sources have been examined and it is concluded that using fission fragments in the irradiation of carbon monoxide and water vapour may be of some industrial importance. It is also suggested that some of the reactions between CHO and COOH radicals, which are discussed in the present study, may occur in the atmosphere of the planet Venus.

ACKNOWLEDGEMENTS

It is a pleasure to record my gratitute to Mr. G.R. Hall and Dr. A.J. Swallow for their supervision, guidance and encouragement throughout all the stages of the present work.

It is also a pleasure to thank Dr. E.S. Waight for permission to use the gas chromatography apparatus and the recording spectrophotometer.

I wish to acknowledge the award of a Shell Petroleum Company studentship for the period 1959 - 1962.

CONTENTS

Introduction :

The present work originated in some preliminary experiments on the γ-irradiation of oxygen-free aqueous solutions containing mixtures of carbon monoxide and acetylene. It was evident from the results of these experiments that the carbon monoxide entered into the free radical reactions produced under irradiation. Although acetylene in aqueous solutions had been studied recently by Weiss and co-workers(1), carbon monoxide had not been studied since the work of Fricke, Hart and Smith in 1938 (2), despite its simplicity, neutrality and industrial importance. It seemed advisable to know more about the carbon monoxide system itself before attempting the study of its mixtures. Accordingly carbon monoxide has been irradiated in acid, neutral and alkaline solutions and in the presence of ferrous or ferric ions. The results seem to be of interest from the theoretical and may be from the industrial points of view, as will be shown later.

Chapter I : Review of Previous Work.

This chapter deals with a review of the work done on the irradiation of some compounds connected with the present study, which is mainly concerned with the γ-irradiation of aqueous solutions of carbon monoxide.

High-energy radiation interacts with matter to form energetic electrons and ions. These electrons produce more ionization and excitation. The products of irradiation are formed from the subsequent reactions of these ionized and excited species. For ultraviolet radiation, the energy is absorbed by molecules in the medium to form excited molecules which may react to form the products.

(A). Irradiation in the gas phase.

(1) Carbon monoxide and mixtures.

In 1908, Cameron and Ramsay irradiated carbon monoxide with α-rays using radon (3). They reported three products, carbon dioxide, carbon and oxygen. Lind and Bardwell, in 1925, could not confirm the presence of oxygen, but did however find a third product, carbon suboxide (4). The overall stoichiometry appears to be :

$$6 \ CO \longrightarrow 2 \ CO_2 + C + C_3O_2$$
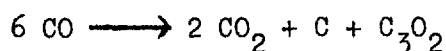
They found too that the ratio $- \Delta CO/+ \Delta CO_2 \simeq 3$ is consistent with the above equation. They established that the suboxide formed in the gas phase diffused to the glass wall and polymerized to a brownish adherent film. This suboxide was found to be

inert toward acid and alkali but was slowly oxidised by concentrated nitric acid. The suboxide was studied by electron micrographs (5) which revealed irregular and sometimes hexagonal clumps with a tendency to be joined by short necks as in the case of the polymer produced from acetylene irradiation. Evidence of growth in the gas phase was shown by the larger particules, falling to lowest positions in the containing vessel.

The ionic yield - $M(CO)/N(CO)$ reported by Lind and Bardwell diminished from 1.85 to a constant level of about 1.2 as the reaction continued. This drop in ionic yield was attributed to back reaction between CO_2 and one or both of the solid products. Confirmation was obtained by adding radon and CO_2 to an exhausted reaction vessel containing both products C and C_3O_2 polymer. The pressure rose slowly, CO was produced and CO_2 was consumed.

The possible back reactions could then be :

$$C + CO_2 \longrightarrow 2\ CO$$

$$C_3O_2 + CO_2 \longrightarrow 4\ CO$$

Another explanation of the falling yield of CO_2 would be charge transfer

$$CO^+ + CO_2 \longrightarrow CO + CO_2^+$$
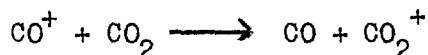
which would increase as CO_2 forms. The ionization potential of CO_2 (13.79 e.v.) is lower than that of CO (14.01 e.v.) and thus lends itself to that interpretation. In 1960,

direct evidence of the inhibitive role of CO_2 was obtained by using "Ascarite" to absorb CO_2 as rapidly as formed (6). The ionic yield - MCO/NCO remained constant at the initial value of 1.85. It seems that there are two processes which are operative for the formation of carbon dioxide i.e., ionization of CO and excitation. (6). At the beginning of the irradiation, both ionization and excitation of CO occurs. As CO_2 accumulates, CO^+ is removed by charge transfer with CO_2, and at higher doses only excitation operates.

More work was done on the irradiation of mixtures of carbon monoxide in the gas phase. In 1906, Löb irradiated moist carbon monoxide in the silent electric discharge. The products were hydrogen, carbon dioxide, formaldehyde, formic acid. After long irradiations, glycolaldehyde was produced as well. (7). No quantitative values were mentioned for the products. Thiele observed that carbon monoxide and oxygen unite less readily under ultraviolet irradiation than do hydrogen and oxygen. (8). Harteck and Kopsch reported a similar unreactivity of oxygen atoms, from a discharge tube, toward carbon monoxide. (9). Frankenburger, in 1930, irradiated carbon monoxide and hydrogen by ultraviolet rays with mercury as a sensitizer. (10). He identified formaldehyde and glyoxal as products by spectroscopic analysis.

The quantum efficiency for total aldehyde was about 1. The mechanism suggested involved the reactions :

$$Hg^* + H_2 \longrightarrow Hg + 2H$$

$$H + CO \longrightarrow CHO$$

$$CHO + CHO \longrightarrow HCHO + CO$$

$$CHO + CHO \longrightarrow CHO.CHO$$
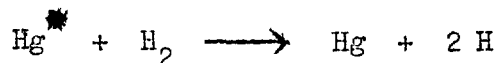
In a similar work, Farkas and Sachsse found hydrogen atoms (to) combine with carbon monoxide molecules in three body collisions to yield CHO radicals.(11). They calculated that one collision in every 3700 collisions produces one CHO radical (at room temperature).

When carbon monoxide and hydrogen were irradiated with α-radiation (Radon), a solid white product was formed which was insoluble in water. It was a non-crystalline and wax-like substance. (4). No test for an aldehyde, sugar or starch could be obtained. More recently, Douglas irradiated carbon monoxide and hydrogen in the presence of tritium. (12). The action of tritium β-particles on the mixture produced a solid white polymer, similar to that obtained in the case of α-particles, and other products in low yields such as formaldehyde, acetaldehyde, glyoxal, carbon dioxide, water and glycol. The reaction products were measured by mass-spectrography, formaldehyde being formed in the highest yields, G =0.025. In 1959, Moseley, Truswell and Edwards made

preliminary experiments on the interaction of CO with H_2 in the reactor BEPO at Harwell $($ (13). The gases in different proportions, confined at atmospheric pressure in sealed silica tubes, were exposed to fission fragments from $^{235}U_3O_8$ deposited as a thin film on the inside of platinum cylinders contained in the tube. Small quantities of CO_2, HCHO and CH_4 were obtained in low yield dependent on the ratio CO/H_2. CO_2 was always the predominant product and increased with the proportion of CO in the mixture. (GCO_2 = 0.22 - 1.80). A platinum shield to stop fission fragments showed that neutrons and γ-rays produced no reaction.

The reaction of carbon monoxide and chlorine under ultraviolet irradiation is a very well studied reaction (14), (15) and (16). Phosgene is produced, through a chain reaction, with a very high yield. The chlorine molecule dissociates under the irradiation to form chlorine atoms which can react with CO to form COCl radicals. These react with Cl_2 to form phosgene:

$$Cl_2 \xrightarrow{\ h\nu\ } Cl + Cl$$

$$CO + Cl \longrightarrow COCl$$

$$COCl + Cl_2 \longrightarrow COCl_2 + Cl$$
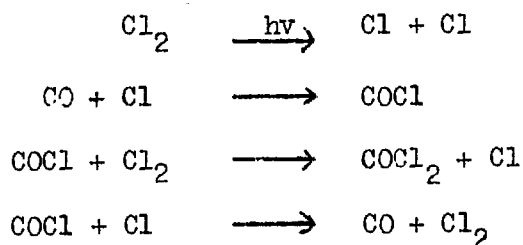
$$COCl + Cl \longrightarrow CO + Cl_2$$

Burns and Dainton calculated that the frequency factor, A, for the addition reaction $CO + Cl \longrightarrow COCl = 10^{8.8} l.mol^{-1}sec^{-1}$. (16) and that the activation energy is very low.

(2) Irradiation of acetylene and its mixtures.

By the action of the α-particles of radon mixed with
acetylene, the predominant product is a polymer resembling
cuprene. This polymer is a yellowish finely divided powder,
which neither melts nor sublimes, is insoluble in all known
solvents and shows no pattern in X-ray spectrography ((17) and
(18). Not much is known about its structure, molecular weight
and other properties, except that it will burn when ignited
in air with the bright white flame characteristic of gaseous
acetylene and that it consists mainly of large round particles
joined together by rods (5). In air, at ordinary temperature,
cuprene takes up oxygen up to 25 per cent of its weight in
six months without any change in its appearance or inert
character. In vacuum at about 300°C. it begins to char. The
reported yield - MC_2H_2/NC_2H_2 = 20. The liberation of hydrogen
in the course of the α-reaction is significant and may have
an important bearing on the mechanism of the reaction. The
fact that the hydrogen evolution is very low at the beginning
of the reaction and increases at higher doses without attainment
of a steady state, indicates two things (a) that the hydrogen
is produced by α-ray bombardment of solid cuprene already formed
rather than from C_2H_2 gas, and (b) that hydrogen does not
hydrogenate either gaseous C_2H_2 or solid cuprene under α-radiation.

Mund and Rosenblum found that with α-rays, 20 per cent of the C_2H_2 forms benzene while 80 per cent forms cuprene[(19)]. This was confirmed later by Rosenblum, (20), and Dorfman and Shipko (21).

Dorfman and Shipko found that the formation of benzene besides cuprene happens also in the irradiation of acetylene with the β-particles from tritium[(22)]. They postulated two independent mechanisms for the two reactions : trimerization induced by excited C_2H_2 giving C_6H_6, and polymerization induced by a free radical to give cuprene. The radical C_2H formed by the equation :

$$C_2H_2 \longrightarrow C_2H + H$$
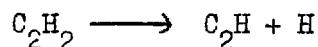
appears probable. The H atom so produced may conceivably produce hydrogen gas by reaction with acetylene (hydrogen abstraction) but, since hydrogen gas was not produced in the early stages of the irradiation as mentioned before, Dorfman therefore assumed that H atoms must add to acetylene : H + $C_2H_2 \longrightarrow C_2H_3$ and that both C_2H and C_2H_3 radicals promote the formation of cuprene. That H atoms are liberated from C_2H_2 by α-rays is shown by isotopic exchange in a mixture of C_2H_2 and C_2D_2. The study of polymerization of C_2H_2 induced by ionization and excitation was further pursued by Dorfman and Wahl (23) using a 0.8 Mev electron beam. The disappearance of C_2H_2 was measured manometrically, the appearance of C_6H_6

by ultraviolet light absorption at 253 mμ. They confirmed the earlier results of the benzene and cuprene formation. It seems that the mechanism proposed by Dorfman, of the reactions of acetylene polymerization under irradiation leading in parallel reactions to benzene and cuprene, is probable. However, the steps to form cuprene from the free radicals C_2H and C_2H_3 are still an open question, since the exact structure of cuprene is unknown.

Any attempt to elucidate the formation of cuprene from acetylene and solve its structure must be consistent with the following experimental facts : (23).

(1) - $N(C_2H_2)/N(C_2H_2) = 20$

(2) Products cuprene and benzene are primarily formed from acetylene in the ratio $\neq$ 16 $C_2H_2 (\longrightarrow$ cuprene) to $\neq$ 4 $C_2H_2 (\longrightarrow$ benzene).

(3) Oxygen (from air) adds to cuprene at any later time to the extent of 29.1 wt. per cent.

In 1960, Jones polymerized acetylene by irradiation with 1 Mev electrons and examined the infra-red spectrum of the fresh polymer cuprene (24). He found that the infra-red absorption spectrum of cuprene is of aromatic character. From this fact and from other physical properties such as insolubility, infusibility and non-volatility, he suggested that cuprene is a three-dimensional network of benzenoid rings joined by short, conjugated aliphatic chains. The aliphatic double bonds

would account for the affinity of cuprene for oxygen at ordinary temperature.

Bartok and Lucchesi irradiated mixtures of acetylene and propane in a nuclear reactor (25). A chain reaction was induced under this mixed nuclear radiation, which is of interest since one major product, 3-methyl-1-butene, is of industrial importance in the manufacture of synthetic rubber (26). Irradiations were performed in a static system using a cylindrical vessel made from stainless steel. The vessel was heated electrically and was immersed in a "swimming pool" nuclear reactor. The mixtures of acetylene and propane in the ratio ~ 1:9 were at a pressure of 10-15 atm. and at 250° - $400^{o}C$. The products were analysed by gas chromatography. Low molecular weight products included methane, ethane, ethylene, propane and other heavier unidentified products, which deposited in the reaction vessel. The dosimetry was determined using methane as a chemical dosimeter and measuring the hydrogen yield taking GH_2 = 5.7. $G\left(- C_2H_2\right)$= 59 at a dose rate of 17×10^6 rad/hr. and is inversely proportional to the square root of the intensity. This suggests that the alkylation chain reaction is terminated by binary radical recombinations in the vapour phase. The G value for 3-methyl-1-butene is 12 at a dose rate of 17×10^6 rads/hr. The following mechanism

was postulated for the chain reaction :

$$C_3H_8 \xrightarrow{I} n - C_3H_7\cdot + S - C_3H_7\cdot$$

$$n\text{-}C_3H_7\cdot + C_3H_8 \longrightarrow C_3H_8 + S - C_3H_7\cdot$$

$$S\text{-}C_3H_7\cdot + C_2H_2 \longrightarrow C - \overset{\overset{\displaystyle C}{|}}{C} - C = C\cdot$$

$$C - \overset{\overset{\displaystyle C}{|}}{C} - C = C\cdot + C - C - C \longrightarrow$$

$$C - \overset{\overset{\displaystyle C}{|}}{C} - C = C + C - \overset{\displaystyle \cdot}{C} - C$$

$$R + R \longrightarrow RR$$
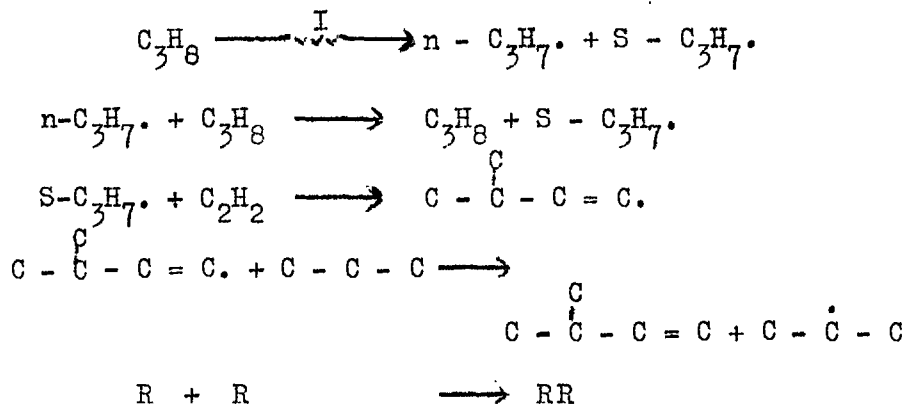
The above reaction scheme was made to fit the experimental observations, so that only 3-methyl-1-butene is formed as a product of the chain reaction. Applying the steady state treatment to the above mechanism, Bartok and Lucchesi derived some kinetic rate equations from which they calculated the activation energy of the addition of isopropyl radicals to acetylene to be 6 K.cal.

(B). Irradiation in aqueous solutions.

   (1) Free radical theory of water radiolysis.

      This theory was put forward, for the first time, in 1914 by Debierne who suggested that irradiation may split water into free atoms and free radicals (27). In 1929, Risse tried to explain the behaviour of ferrous sulphate solutions under irradiation (28). He was familiar with the indirect action of water and also with the result that the ferric ion yield was lowered by about 50% in the absence of air.

To explain this result he assumed the following reactions :

$$2 H_2O \xrightarrow{\quad\quad} 2 H + 2 OH$$

$$OH + OH \xrightarrow{\quad\quad} H_2O_2$$

$$H + H \xrightarrow{\quad\quad} H_2$$
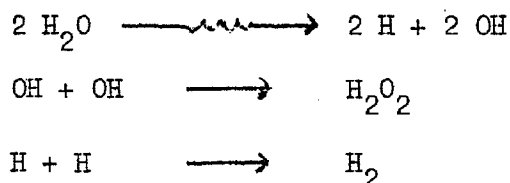
Hydrogen peroxide then oxidised the ferrous ion. With oxygen present, twice as much peroxide was formed because of the reaction :

$$2 H + O_2 \xrightarrow{\quad\quad} H_2O_2$$

Although this is not the mechanism as accepted now, yet it was of great scientific insight considering the early date of this work. The final acceptance of the free radical theory may be said to date from 1944, when Weiss showed that very many of the known effects of radiation on aqueous solutions could be explained in terms of the primary decomposition of water into hydrogen atoms and hydroxyl radicals∕ (29). He showed that the hydroxyl radical is responsible for oxidation reactions and hydrogen atom for the reduction ones. For example, in ferrous ion solutions, in the presence of oxygen, he suggested the following reactions :

$$OH + Fe^{++} \xrightarrow{\quad\quad} Fe^{+++} + OH^-$$

$$H + O_2 \xrightarrow{\quad\quad} HO_2$$

$$Fe^{++} + HO_2 \xrightarrow{\quad\quad} Fe^{+++} + HO_2^-$$

$$HO_2^- + H^+ \xrightarrow{\quad\quad} H_2O_2$$

$$Fe^{++} + H_2O_2 \xrightarrow{\quad\quad} Fe^{+++} + OH^- + OH$$
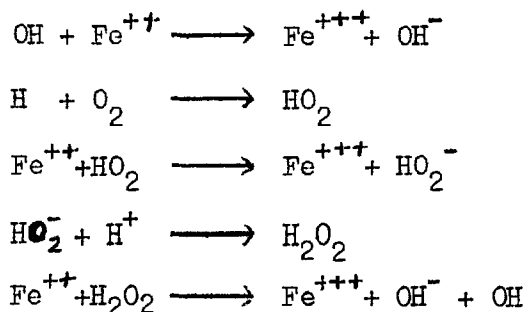
which is the accepted mechanism to-day. In 1948, Allen

suggested for the first time that molecular yields, H_2 and H_2O_2,

from water radiolysis, are formed in the regions of high free

radical concentration (30).

    The fact that X- and γ-rays are found experimentally to

cause practically no net effect on pure water irradiated in a

filled vessel from which hydrogen cannot escape was explained by

Allen to be due to the rapid removal of hydrogen and hydrogen

peroxide through the chain reaction :

$$OH + H_2 \longrightarrow H_2O + H$$

$$H + H_2O_2 \longrightarrow H_2O + OH$$
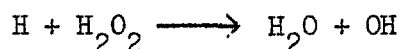
This explanation of the free radical and molecular yields

production in water under irradiation laid the basic foundation

of the radiation chemistry of aqueous solutions.

    (2) Effects of γ-irradiation on water.

    The overall process, which starts with the bombardment of

the water by γ-rays and terminates with the re-establishment

of thermodynamic equilibrium in that system, can be divided into

three stages :

a) Physical stage

    In this stage, the energy is transferred from the high

energy radiation to the system. The main mechanism of energy

loss is by Compton scattering, in which the photon transfers

part of its energy to an electron. The energy distribution of

Compton electrons depends on the energy of the incident photons.
For example, for 1 M.e.v. photons, the Compton electron has a
mean value of 0.45 M.e.v. (31). The main effect of the absorption
of high energy photons (1.17 and 1.33 M.e.v. in Co-60), is thus the
production of energetic electrons which proceed to dissipate their
energy in the water. Those molecules very close to the track will
be ionized and their associated secondary electrons will have
sufficient energy to ionize other molecules i.e., they will produce
spurs. The most remote molecules will merely be electronically
excited.

b) The physico-chemical stage.

In about 10^{-10} sec. the parent + ^{ve} ion is dissociated
according to

$$H_2O^+ \; + \; H_2O \; \longrightarrow \; H_3O^+ + OH$$

Any excited water molecules may dissociate according to

$$H_2O^* \; \longrightarrow \; H + OH$$
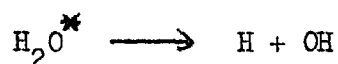
The track can be visualised as a string of beads (i.e. spurs) and
the principal effect of variation in Linear Energy Transfer is
taken to be the alteration in the average distance between the
spurs. The fate of the secondary electron is still not clear.
There are two different views regarding this. The first due to
Magee and Samuel assumes that these electrons lose energy in
inelastic collisions at the rate of 4% per collision, and hence
the distance travelled by a 10 e.v. secondary electron, till it

is thermalised, will be about 25°A. (32). At this distance the
electrostatic energy between the electron and the positive parent
ion exceeds the mean kinetic energy of the electron, and therefore
it is drawn back to the parent ion. This charge neutralisation
will produce an excited water molecule which is assumed to dissociate
into an H atom and an hydroxyl radical which will be thus formed
close to the original ionized molecule. The second hypothesis,
suggested by Lea, Gray and Platzman, is that the electron loses its
energy by causing vibration of the bond dipoles and rotation of
water molecules (31), (33) and (34). The dipole vibration loss
brings the energy of the electron down to about 0.2 e.v. in about
10^{-12} sec. at a distance larger than 50°A from the parent ion. At
this stage it will be surrounded by water molecules. It then
continues to lose energy by excitation of rotation of water
molecules, until it is thermalised in about 10^{-11} sec. Since that
is the relaxation time of water, the electron cannot be recaptured
by the parent ion, becomes solvated, and produces a hydrogen atom
according to

$$(e^-)_{aq} + water \longrightarrow H + OH^-_{aq}$$
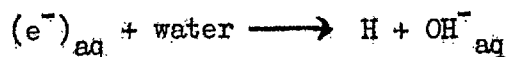
Consequently, according to this model, the H and OH which result
from a given primary ionization are quite far apart from one another.
However, the net effect of both theories is the production of H
atoms and OH radicals.

However, from recent work in the irradiation of aqueous solutions, there is mounting evidence for the participation of $(H_2O)^-$ radicals in solute reactions in the bulk of the solution, which gives support to the model of Lea, Gray and Platzman, with the modification that the solvated electron is stable enough to react with solutes and not with water to form H atom. Thus Barr and Allen (35) obtained evidence that there are two forms of H atom which show different velocity constants with H_2O_2; the form in neutral water being much more reactive with H_2O_2 than the form obtained from the reaction $H_2 + OH \longrightarrow H_2O + H$. Similar work by Allan and Scholes (36), Weiss (37), and Hayon and Weiss (38) showed similar conclusions about the existence of two forms of H atom : a basic form which exists in neutral solution $(H_2O)^-$, its acidic form being H atom, or H atom in neutral solution and its acidic form being H_2^+, the latter form being suggested by Rigg, Stein and Weiss (39).

Recently it has been found that the reducing species in neutral water has a charge (-1) which gives direct support to the form H_2O^- in neutral solution((40), (41) and (42). So it may be concluded that, although the formulas of the free radicals are generally written H and OH, the exact nature of the species may vary with particular condition. The H atom may exist as $(H_2O)^-$ or H or H_2^+. Hart, Gordon and Hutchinson suggested that OH radical may be present as O^-, OH or in its acidic form as $(H_2O)^+$ (43) and (44).

It seems possible that this behaviour of the different forms of H and OH may be valid too for other radicals, as will be suggested later (see Discussion).

c) The Chemical Stage.

After conversion into free radicals, but before appreciable diffusion has occurred, the spurs may contain several pairs of hydrogen and hydroxyl free radicals (Samuel and Magee model). Hydrogen and hydrogen peroxide are postulated to be formed by the pair-wise recombination of hydrogen and hydroxyl free radicals according to :

$$H + H \longrightarrow H_2$$
$$OH + OH \longrightarrow H_2O_2$$
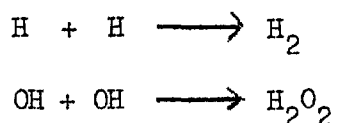
On the basis of this theory, approximately one half of the free radicals react to form water.

$$H + OH \longrightarrow H_2O$$
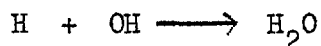
The radical-diffusion model of Samuel and Magee accounts satisfactorily for the production of H_2 and H_2O_2 (28), (45) and (46). The radical reactions to form molecular products occur during diffusion within 10^{-7} sec. of the time of passage of the photon. If the solute species are present at concentrations above 10^{-6} M, hydrogen and hydroxyl radicals escaping the previous reactions may react with the solute. These reactions occur in the volume of the liquid appreciably outside the original ionization sphere.

Only at solute concentrations above about 10^{-2}M does the solute begin to interefere seriously with the molecular yields of hydrogen and hydrogen peroxide. It may be noted here that if the initial radical distribution corresponds to the unsymmetrical one given by Lea, Gray and Platzman, the chance of forming hydrogen by the reaction $H + H \longrightarrow H_2$ would be negligible, as the H atoms are produced at a distance from each other. The fact is that both H_2 and H_2O_2 are formed in comparable amounts and vary with solute concentrations in a manner suggesting formation by analogous combination reactions. The dependence of molecular yields on a scavenger concentration was first studied by Sworski (47), (48) and (49). He found that for γ-irradiation GH_2O_2 was depressed approximately in proportion to $[KBr]^{1/3}$. Expressed in general form

$$G(R) = G(R)^0 - A(S)^n$$

where $G(R)$ is the molecular yield at scavenger concentration (S). A is a constant and the exponent n is about .33 for γ-irradiation. The equation has been found to hold for depression of both $GH_2O_2^{W}$ and GH_2^{W} by several solutes (50), (51) and (52).

(3) Irradiation of aqueous solutions of carbon monoxide.

In 1938 Fricke, Hart and Smith irradiated air free solutions of carbon monoxide with X-rays (110 kV). This was a part of one of the first comprehensive studies on the irradiation of aqueous solutions, which also included alcohols, aldehydes, ketones and acids (2). The dose rate used varied from 3000 - 120000 r/hr.
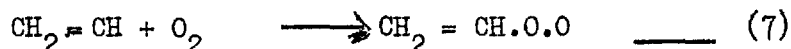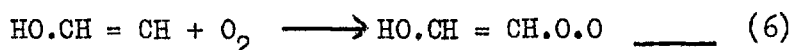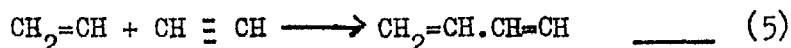
The gases produced were analysed by means of a Van Slyke apparatus.
In the carbon monoxide experiments, the gas was prepared from the
reaction of warm sulphuric acid with formic acid. Hydrogen, carbon
dioxide and formaldehyde were produced. Formaldehyde was tested
for by Hehner's method (53). The amounts could be estimated to an
accuracy of 1×10^{-5} moles/litre. The initial reaction rates (per 1000 r) were
$3.9 \mu M$ CO, $2.4 \mu M$ CO_2, $1.0 \mu M$ H_2, and $0.3 \mu M$ HCHO at pH = 3.5. This
equals to $G(-CO) = 3.5$, $G(CO_2) = 2.2$, $G(H_2) = 0.9$ and $G(HCHO) = .27$.
(54). The effect of the rays appeared to be independent of the
concentration of carbon monoxide, in the range $1 \times 10^{-5} - 8 \times 10^{-4} M$ CO.
A few experiments were carried out to determine the effect of the
pH in the reaction. There was no great change in the range of
pH = 1 to 7, although possibly the reaction rate increased with
decreasing pH. However, the measurements were not accurate enough
to make sure of the form of the relationship. In alkaline solution
the character of the reaction changed. The hydrogen and carbon
dioxide production decreased while the carbon monoxide consumption
greatly increased. They suggested that the principal reaction was
the combination of carbon monoxide with water to produce formic acid.
At that time Fricke, Hart and Smith considered activated water as
the species responsible for the reactions. The water seemed to be
converted under irradiation to this activated form, which was
chemically reactive but stable enough to diffuse through the
solution and react with solute molecule (55). The free radical

theory of water decomposition under irradiation was not yet generally accepted at that time.

Beside the work of Fricke, Hart and Smith, it seems that there is no other study reported about the irradiation of carbon monoxide aqueous solutions, except a brief mention by Johnson and Jerome Weiss in 1954 (56). They irradiated carbon monoxide ($\sim$5x10^{-4}M) in 0.8N sulphuric acid. They found that the rate of carbon dioxide formation was 38.3 $\overset{+}{-}$ $^{/.8}$ μM/1000 sec. at a dose rate equal to 234.5μ M Fe^{++} oxidised/1000 sec. These values correspond to GCO_2= 2.53 $\overset{+}{-}$ 0.11. No other products were determined in this study.

(4) Irradiation of aqueous solutions of acetylene.

Weiss and co-workers irradiated acetylene in aqueous solutions in the absence and in the presence of oxygen (1). In the absence of oxygen, they obtained a yellow-white solid polymer and several different aldehydes such as formaldehyde, acetaldehyde and croton-aldehyde. Glycolaldehyde was also produced but the observed yields were irreproducible. The yields were G(acetaldehyde) = 0.2, G croton-aldehyde = 0.2 and G(glycolaldehyde) = 0.2. In the presence of oxygen, the only aldehyde formed was glyoxal, with G value varied with acidity from G = 14 at pH = 1.2 to G = 7 at pH = 9. To explain their results they suggested the following mechanism :

$$CH \equiv CH + \bullet H \longrightarrow HO. CH = CH \qquad \_\_\_\_ \quad (1)$$

$$CH \equiv CH + H \longrightarrow CH_2 = CH \qquad \_\_\_\_ \quad (2)$$

$$H + O_2 \longrightarrow HO_2 \qquad \_\_\_\_ \quad (3)$$

$$HO.CH = CH + CH \equiv CH \longrightarrow HO.CH = CH.CH = CH \quad \_\_\_\_ \quad (4)$$

$$CH_2 = CH + CH \equiv CH \longrightarrow CH_2 = CH.CH = CH \quad \_\_\_\_ \quad (5)$$

$$HO.CH = CH + O_2 \longrightarrow HO.CH = CH.O.O \quad \_\_\_\_ \quad (6)$$

$$CH_2 = CH + O_2 \longrightarrow CH_2 = CH.O.O \quad \_\_\_\_ \quad (7)$$

$$HO.CH = CH.O.O \longrightarrow CHO.CHO + OH \quad \_\_\_\_ \quad (8)$$
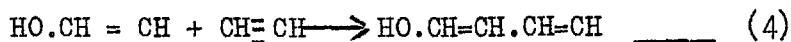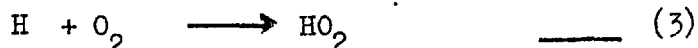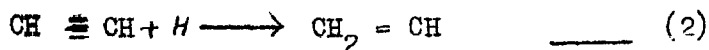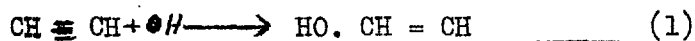
In the case of irradiations carried out in the absence of oxygen, the polymeric product may be the end of reactions (4) and (5).

(5) <u>Irradiation of aqueous solutions of formic acid.</u>

In 1934, aqueous solutions of formic acid were studied with X-rays by Fricke and Hart (57). In acid solutions and at concentrations of millimolar or less, and in the absence of air, the formic acid was found to decompose into equimolar quantities of hydrogen and carbon dioxide :

$$HCOOH \longrightarrow H_2 + CO_2$$

The yield for hydrogen and carbon dioxide being 3.2×10^{-6} moles/ litre/1000 r. and independent of dose rate, corresponding to $G = 3.3$. No hydrogen peroxide appeared. At concentrations of 10 M and above, the hydrogen yield remained constant but the carbon dioxide markedly increased. At pH above 3 the yields of H_2 and CO_2 both dropped off, the latter more rapidly, with the result that at pH 8 and above, no CO_2 was formed. The hydrogen yield

levelled off in alkaline solutions at about half its value in acid solutions. The reaction in alkaline solutions was conjectured to give oxalate as a product, whereas the reaction at high concentrations in acid was assumed to give formaldehyde, but actual determination of these products was not attempted.

In their later study of 1938, Fricke, Hart and Smith confirmed these findings and showed that the yield of the reaction is independent of the concentration in the range $10^{-4} - 10^{-2}$ M formic acid. (2).

Later, in 1951, Hart took up the subject again using γ-rays (58). He found that the oxidation of dilute aqueous solutions of formic acid, in the absence of air, by γ-rays follows the same course as for X-rays; equimolar amounts of hydrogen and carbon dioxide are produced at formic acid concentrations of 10^{-3} and 10^{-2} M in 0.001 N sulphuric acid. The addition of hydrogen peroxide to the formic acid systems results in a marked acceleration of the carbon dioxide production; a maximum increase in rate of 55-fold corresponding to $GCO_2 = 175$ was found experimentally at 7.4×10^{-4}M hydrogen peroxide in 10^{-2} M formic acid solutions (in 10^{-3}N sulphuric acid). Thereafter in the range up to 10^{-2} M hydrogen peroxide, concentration of formic acid and sulphuric acid being constant, the rate of carbon dioxide production decreased with increasing hydrogen peroxide concentration. Hydrogen peroxide decomposition was found to increase as the dose rate decreased according to $I^{-\frac{1}{2}}$.

These results are indicative of a chain reaction and explains why hydrogen peroxide is not produced in absence of oxygen. Hart postulated that the propagation steps are :

$$OH + HCOOH \longrightarrow H_2O + COOH$$

$$COOH + H_2O_2 \longrightarrow H_2O + CO_2 + OH$$
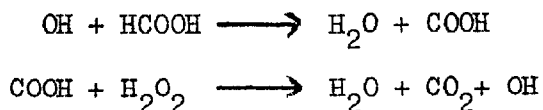
From the above propagation steps, it is seen that the hydroxyl and carboxyl free radicals alternate in the hydrogen peroxide sensitised reaction. The decrease in carbon dioxide production with increasing hydrogen peroxide concentration indicates that the chain terminating step involves the hydroxyl and hydrogen peroxide. In contrast to the marked acceleration in rate of carbon dioxide development as hydrogen peroxide is added to formic acid, hydrogen production remains substantially constant until after the maximum rate of carbon dioxide production has been reached. Thereafter a gradual decrease in hydrogen production occurs. This drop in hydrogen yield was suggested to be due to the competition between formic acid and hydrogen peroxide for the H atom according to

$$H + H_2O_2 \longrightarrow H_2O + OH$$
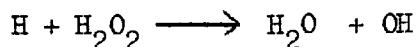
Oxygen was found to play an important role as inhibitor for the formic acid - hydrogen peroxide reaction. Oxygen seemed to be converted to hydrogen peroxide, as indicated by the fact that one hydrogen peroxide molecule was formed per one molecule of oxygen. After consumption of the oxygen, the characteristic rapid reaction of hydrogen peroxide with formic acid took place.

The foregoing facts were accounted for by the following mechanism :

$$H_2O \longrightarrow\!\!\!\!\sim\!\!\sim\!\!\sim\!\!\longrightarrow H^W, OH^W, H_2^W, H_2O_2^W.$$

$$H + HCOOH \longrightarrow H_2 + HCOO$$

$$OH + HCOOH \longrightarrow H_2O + HCOO$$

$$HCOO + HCOO \longrightarrow HCOOH + CO_2$$

$$HCOO + H_2O_2 \longrightarrow H_2O + CO_2 + OH$$
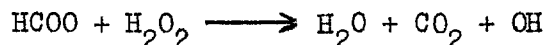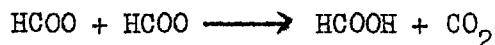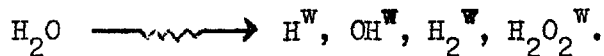
In the irradiation of formic acid solutions (without the addition of hydrogen peroxide) the above scheme predicts that the yield for formic acid decomposition should be

$$G(-HCOOH) = G(CO_2) = G(H_2) = G\ H_2O_2^W + \tfrac{1}{2}(GH^W + GOH^W) = GH_2^W$$

$+ GH^W = 3.2$ at pH 3 which is not very much different from the value expected for this pH. From this study, Hart was not able to determine which hydrogen atom in formic acid reacts with the H atom. This question was answered by the irradiation of deutero-formic acid, DCOOH (59). Hydrogen evolved from a solution of this compound was found to contain about 65% of HD. The 35% of normal hydrogen could arise partly as molecular hydrogen from water radiolysis and partly from contamination of the DCOOH with some ordinary formic acid. Later this experiment was repeated by Baxendale and Smithies who obtained similar results (60). This shows that H atoms from water radiolysis reacts with the hydrogen atoms attached to the carbon to form COOH radicals :

$$H + HCOOH \longrightarrow H_2 + COOH$$

and <u>not</u> : $\quad H + HCOOH \longrightarrow H_2 + HCOO$

When oxygen is present, H atoms reacts with oxygen in preference to formic acid

$$H + O_2 \longrightarrow HO_2$$

Chain propagation is terminated by

$$COOH + O_2 \longrightarrow CO_2 + HO_2$$

The hydroxy peroxy radicals are removed by

$$HO_2 + HO_2 \longrightarrow H_2O_2 + O_2$$

This explains the inhibitory action of oxygen on the chain formation of carbon dioxide in the irradiation of formic acid and hydrogen peroxide mixtures in aqueous solutions.

In 1952, Hart studied the γ-ray oxidation of ferrous sulphate solution in the presence of air and formic acid (61). He found that this oxidation proceeds by a chain reaction. $G(Fe^{+++})$ increased from 15.5 in the Fricke dosimeter to 230 in a solution containing $5 \times 10^{-4} M$ Fe^{++}, 0.8 N H_2SO_4 and 0.1 M formic acid and saturated with oxygen. The reaction was found to depend on the concentrations of ferrous sulphate, formic acid and oxygen, the main product being carbon dioxide. To explain the experimental results, Hart suggested the following mechanism :

$$H_2O \xrightarrow{\hspace{1cm}} H, OH, H_2, H_2O_2 \qquad (1)$$

$$OH + HCOOH \longrightarrow H_2O + HCOO \qquad (2)$$

$$HCOO + O_2 \longrightarrow HO_2 + CO_2 \qquad (3)$$

$$H + HCOOH \longrightarrow H_2 + HCOO \qquad (4)$$

$$Fe^{++} + HO_2 \longrightarrow Fe^{+++} + HO_2^- \qquad (5)$$

$$HO_2^- + H^+ \longrightarrow H_2O_2 \qquad (6)$$

$$Fe^{++} + H_2O_2 \longrightarrow Fe^{+++} + OH^- + OH \qquad (7)$$

$$Fe^{+++} + HCOO \longrightarrow Fe^{++} + H^+ + CO_2 \qquad (8)$$

$$HCOO + H^+ + Fe^{++} \longrightarrow Fe^{+++} + HCOOH \qquad (9)$$

$$Fe^{++} + OH \longrightarrow Fe^{+++} + OH^- \qquad (10)$$

$$Fe^{+++} + HO_2 \longrightarrow Fe^{++} + H^+ + O_2 \qquad (11)$$
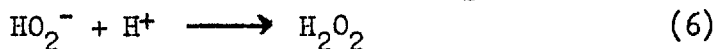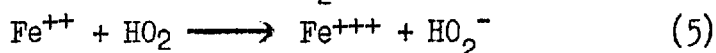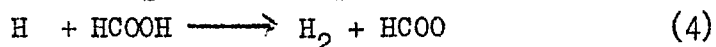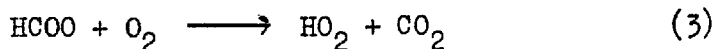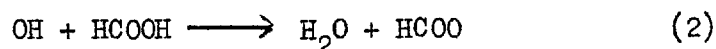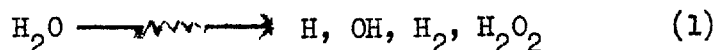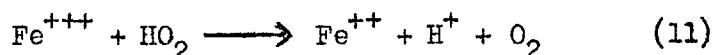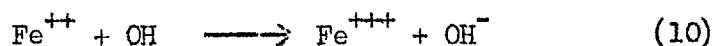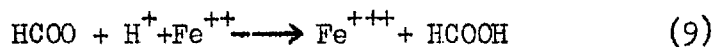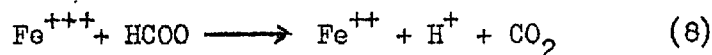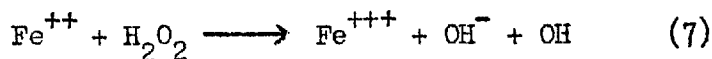
The initiation reactions of the chain are (1), (2) and (4), the propagation reactions are (2), (3), (5), (6) and (7), and the termination reactions are (8), (9), (10) and (11). The experimental results agreed well with the above mechanism.

It may be noted that the chain oxidation of aerated ferrous ion can also be produced by other organic compounds such as hydrocarbons (62) and alcohols (63) through the formation of peroxides. That is the reason for the susceptibility of the Fricke dosimeter to organic impurities. Chloride ion diminishes this effect and, at sufficiently high concentrations of (Cl^-), the original $G(Fe^{+++})$ of 15.5 is restored. The reaction

$$OH + Cl^- \longrightarrow OH^- + Cl$$

produces the Cl atom which is a much weaker oxidising agent than the hydroxyl radical and does not readily attack organic molecules in a ferrous sulphate solution.

In 1954, Hart studied extensively the effect of pH and oxygen on the γ-irradiation of formic acid solutions (64) and (65).

The mechanism of this system is the following :

$$H_2O \xrightarrow{} H, \; OH, \; H_2, \; H_2O_2$$

$$OH + HCOOH \longrightarrow H_2O + COOH$$

$$H + HCOOH \longrightarrow H_2 + COOH$$

$$H + O_2 \longrightarrow HO_2$$

$$COOH + O_2 \longrightarrow HO_2 + CO_2$$

$$HO_2 + HO_2 \longrightarrow H_2O_2 + O_2$$
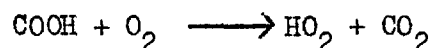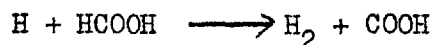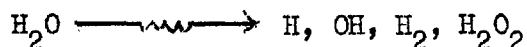
Hydrogen, hydrogen peroxide and carbon dioxide are produced. The yield of hydrogen decreases and that of peroxide increases as the oxygen concentration is increased in the formic acid solution, and at sufficiently high oxygen concentrations, only the molecular hydrogen yield from water radiolysis remains. At high concentration of oxygen, when all H atoms react with oxygen, this mechanism predicts the basic radiation yields of water : GH^W, GOH^W, GH_2^W and $GH_2O_2^W$

$$2G(-O_2) - G(CO_2) = GH^W$$

$$G(CO_2) = GOH^W$$

$$G(H_2) = GH_2^W$$

$$G(H_2O_2) = GH_2O_2^W + \tfrac{1}{2}(GH^W + GOH^W)$$

$$= GH_2^W + GH^W$$

At the standard conditions of pH around 2 and formic acid concentration 1 to 10 mM, the results were in very good agreement with those expected. Values of $GH_2^W = 0.4$, $GH_2O_2^W = 0.8$, $GOH^W = 2.6$, $GH^W = 3.4$ were obtained and agree well with values expected for this pH. As the oxygen concentration was decreased, the hydrogen yield rose

as expected from the competition equation. The rate constants for the reaction of H with O_2 and with HCOOH were found to be in the ratio of about 540 : 1 (at 10^{-2}M formic acid and pH = 3.12). When the concentration of formic acid increased to 1M, the hydrogen yield decreased, instead of increasing according to the above mechanism. The apparent ratio of rate constants for II reacting with oxygen and formic acid increased to the value of 6245 : 1 (at 1M formic and pH = 1.83). This shows that at this high concentration of formic aicd, there must be some other mechanism than the one above. Hart suggested that at this high concentration of formic acid, electron capture by formic acid is competing with electron capture by water. He postulated the following processes

$$H_2O \xrightarrow{\quad\sim\hspace{-2pt}\sim\hspace{-2pt}\sim\quad} H_2O^+ + e \qquad \underline{\qquad} (1)$$

$$H_2O^+ \xrightarrow{\qquad} H^+ + OH \qquad \underline{\qquad} (2)$$

$$H_2O + e \xrightarrow{\qquad} H_2O^- \qquad \underline{\qquad} (3)$$

$$HCOOH + e \xrightarrow{\qquad} HCOOH^- \qquad \underline{\qquad} (4)$$

$$H_2O^- \xrightarrow{\qquad} II + OH^- \qquad \underline{\qquad} (5)$$
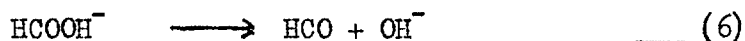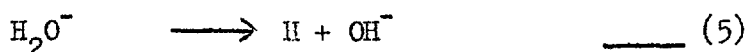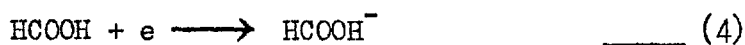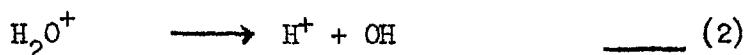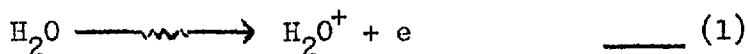
$$HCOOH^- \xrightarrow{\qquad} HCO + OH^- \qquad \underline{\qquad} (6)$$

In view of the competition for electrons between reactions (3) and (4), fewer hydrogen atoms are produced in reaction (5) thus leading to lower hydrogen produced via H + HCOOH $\longrightarrow H_2$ + COOH. The formyl radical, HCO, must lead to a product other than hydrogen. Hart suggested that formaldehyde may be formed according to :

$$HCO + HCOOH \xrightarrow{\qquad} HCHO + COOH$$

but no actual determination of formaldehyde was done.

In 1955, Hart studied the aqueous formic acid - ferric sulphate system (66). Ferric ion was reduced to ferrous ion. At low ratio of $\frac{\text{formic acid}}{\text{ferric ion}}$ the stoichiometry is expressed by

$$2\ Fe^{+++} + HCOOH \longrightarrow 2\ Fe^{++} + 2\ H^{+} + CO_2$$
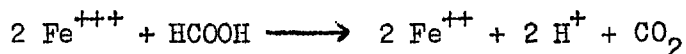
and at higher ratios of these reactants is expressed by :

$$2\ Fe^{+++} + 2\ HCOOH \longrightarrow 2\ Fe^{++} + 2\ CO_2 + H_2 + 2\ H^{+}$$
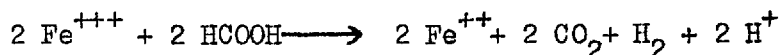
The mechanism proposed by Hart is the following :

$$H_2O \xrightarrow{\quad\sim\!\!\sim\!\!\sim\quad} H,\ OH,\ H_2,\ H_2O_2$$

$$OH + HCOOH \longrightarrow H_2O + COOH$$

$$H + HCOOH \longrightarrow H_2 + COOH$$

$$COOH + Fe^{+++} \longrightarrow Fe^{++} + H^{+} + CO_2$$

$$H + Fe^{+++} \longrightarrow Fe^{++} + H^{+}$$

$$Fe^{++} + H_2O_2 \longrightarrow Fe^{+++} + OH + OH^{-}$$
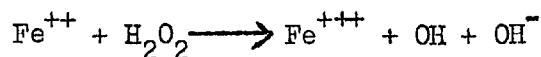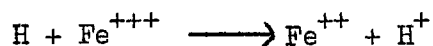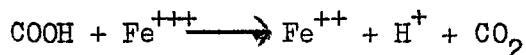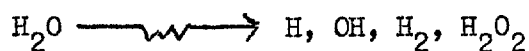
From the above scheme the sum of the free radical yields from water radiolysis can be measured :

$$GFe^{++} = GH^{W} + GOH^{W}$$

In 1960, Smithies and Hart studied the effect of high formic acid concentration in γ-irradiated aqueous solutions in the absence of oxygen (67). The concentrations used ranged from 1 to 26.6 M (pure) formic acid. Carbon dioxide, carbon monoxide and hydrogen were the sole gaseous products and formaldehyde was supposed to be a reactive intermediate. $G(CO_2)$ reached values as high as 12, increased as $(HCOOH)^{\frac{1}{2}}$ at high dose rates, and as $(\text{dose rate})^{-\frac{1}{2}}$ at constant concentration.

These results indicate a chain reaction. The chain reaction was found to have little effect on $G(CO)$ and $G(H_2)$. Possible propagation steps are suggested to be the following :

$$COOH + HCOOH \longrightarrow CO_2 + H_2O + CHO$$
$$CHO + HCOOH \longrightarrow HCHO + COOH$$
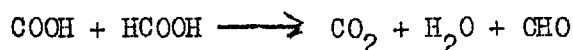
A trimolecular termination step consistent with the observed dependence on formic acid concentration is :

$$2\ COOH + HCOOH \longrightarrow CO_2 + 2\ HCOOH$$
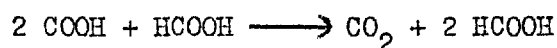
They found that $G(H_2)$ decreased from 3.2, as the formic acid concentration was increased up to 5 M, and then remained substantially unchanged up to 26.6 M, pure formic acid, at a G of 2.2. The decrease of $G(H_2)$ was suggested to be due to the electron captured by formic acid as discussed before (65) or due to the following reaction put forward by Garrison and co-workers (68) :

$$H + HCOOH \;\rightleftarrows\; HC\underset{OH}{\overset{OH}{<}}$$
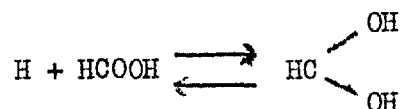
by which H atoms forms $CH(OH_2)$ radicals instead of H_2 via the reaction $H + HCOOH \longrightarrow H_2 + COOH$. This $CH(OH_2)$ radical may react with HCOOH to form HCHO. According to this scheme $G(H_2)$ tends to zero at high formic acid concentration and is replaced by formaldehyde. However, in 26.6 M formic acid $G(H_2) = 2.2$ which indicates that the process is more complicated at this very high concentration of formic acid. To overcome this difficulty Smithies and Hart suggested that other reactions are operating in 5M formic acid and above.

Electron impact studies on formic acid have shown that the following reactions happen in the gas phase (69) and (70). :

$$HCOOH + e \longrightarrow HCOO^+ + H + 2 e^-$$

$$HCOOH^+ + (M) \longrightarrow HCOO^+ + H$$
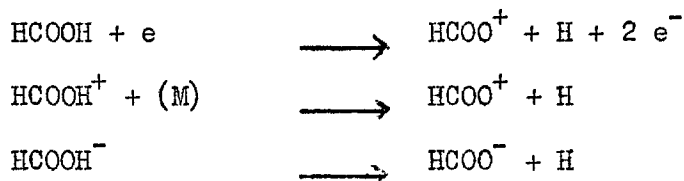
$$HCOOH^- \longrightarrow HCOO^- + H$$

In view of the appreciable excess energy available or possible in these hydrogen atom producing reactions, Smithies and Hart suggested that the reaction $H + HCOOH \longrightarrow H_2 + COOH$ is favoured relative to the reaction $H + HCOOH \longleftarrow CH(OH)_2$ by hot hydrogen atoms. In concentrated formic acid solutions (5 M and more) moderation of the excess energy is by formic acid from which hydrogen atoms can be extracted. With increasing water content, formic acid moderation is replaced by water moderation which does not lead to hydrogen production. The effect of the hot hydrogen atom then becomes negligible, and the H atom reacts according to $H + HCOOH \longrightarrow CH(OH)_2$. In other words, the reaction $H + HCOOH \longrightarrow H_2 + COOH$ occurs at very low formic acid concentration and at very high concentration.

G(CO) was found to rise rapidly in the concentration range from 0.01 to 1.0 M and then more gradually until a yield of 1.25 was reached in 26.6 M formic acid. G(CO) was independent of dose rate and, to explain its formation, Smithies and Hart proposed that the subexcitation electrons react with formic acid, as its concentration increases, and that the excited formic acid leads to carbon monoxide possibly through intermediate free radical reactions. The reduction

in G(CO) by ferric sulphate and benzo-quinone is in accord with the
formation of carbon monoxide from free radical precursors. To
explain the independence on dose rate, they suggested that the
carbon monoxide arises by radical - radical reaction within the
expanding spherical spur. Formaldehyde was found to build up to
very low steady state concentrations in the irradiated formic acid
solutions. When they initially added 10^{-3} M formaldehyde to 5 M
formic acid, formaldehyde was removed with a yield of G = 6.15.
Neither $G(CO_2)$ nor $G(H_2)$ were altered to any appreciable extent
under these conditions. Without supporting evidence, they postulated
the reactions :

$$COOH + HCHO \longrightarrow CO_2 + CH_2OH$$
$$CH_2OH + HCOOH \longrightarrow CH_3OH + COOH$$
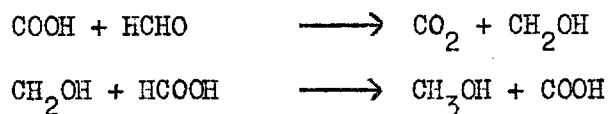
The presence of methanol was not verified in these solutions.

Garrison, Bennett and Cole found that in the irradiation with
beams of protons or helium ions from a cyclotron, a number of
additional reaction products appeared in formic acid solutions (68).
Most of these did not appear when neutrons from the cyclotron target
served as the radiation source. The difference arises from the
effect of radiation intensity, which was several hundredfold higher
in the irradiated zone for particle beams than for neutrons. The
products and their G values are : glyoxalic acid, 0.30; mesoxalic
acid, 0.2; oxalic acid, 0.13; tartronic acid, 0.06; glycolic
acid, 0.03; tartaric acid, 0.006; formaldehyde, 0.002 and glyoxal, 0.12.

To account for the experimental facts, they suggested that the mechanism which happens in the irradiated formic acid solutions (0.25 N) by neutrons is the same as that for γ-rays :

$$H_2O \xrightarrow{\hspace{2cm}} H, \; OH, \; H_2, \; H_2O_2$$

$$OH + HCOOH \longrightarrow H_2O + COOH$$

$$H + HCOOH \longrightarrow H_2 + COOH$$

$$H_2O_2 + COOH \longrightarrow H_2O + CO_2 + OH$$

$$2 \; COOH \longrightarrow HCOOH + CO_2$$
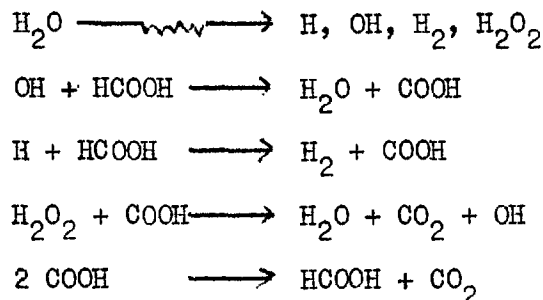
With 10 M.e.v. protons or 40 M.e.v. helium ions other reactions, in addition to those above, happen within the beam volume element which has a much higher radical concentration compared to the bulk of the solution :

$$H + COOH \longrightarrow H_2 + CO_2$$

$$OH + COOH \longrightarrow H_2O + CO_2$$

$$H + HCOOH \underset{\longleftarrow}{\longrightarrow} HC(OH)_2$$

$$2 \; COOH \longrightarrow (COOH)_2$$
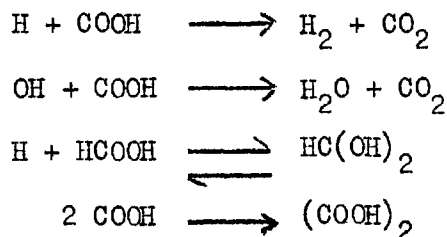
In neutron irradiation they found H_2O_2 was not produced while in the charged-particle irradiations $GH_2O_2 = 0.3 - 0.4$. They explained this result by the fact that radical combination reactions (e.g., $OH + COOH \longrightarrow H_2O + CO_2$) would compete effectively with the chain reaction which results in the disappearance of H_2O_2, and so H_2O_2 can be produced in the charged-particle irradiations. To explain that no oxalic acid was formed in the neutron irradiation while it was produced in the particle beam runs, they suggested that in neutron

(or γ) irradiations, the COOH radical reacts with the HCOOH to form
the HCOO radical :

$$COOH + HCOOH \longrightarrow HCOOH + HCOO$$

and these radicals would react by disproportionation :

$$HCOO + HCOO \longrightarrow HCOOH + CO_2$$
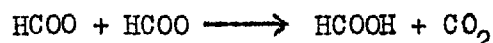
While in the particle beam the COOH radical, because of its high
concentration in the beam volume element, will react according to:

$$COOH + COOH \longrightarrow (COOH)_2$$

i.e., it would not have enough time to isomerise to the form HCOO
by reacting with formic acid.

In the beam particle irradiation experiments, the yield of
glyoxalic acid and glyoxal was explained to be due to the following
reactions :

$$H \cdot C(OH)_2 + COOH \longrightarrow CHO.COOH + H_2O$$

$$H.C(OH)_2 + H.C(OH)_2 \longrightarrow CHO.CHO + 2 H_2O$$
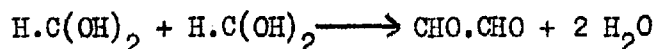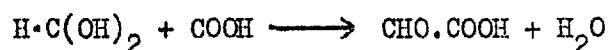
In the neutron (or γ-rays) irradiations, as the radical concentrations
are lower, $HC(OH)_2$ is not formed and H atom reacts preferentially to
form hydrogen via H + HCOOH $\longrightarrow$ H_2 + COOH. With the same argument
they explained the formation of glycolic acid :

$$CHO.COOH + H \longrightarrow CHOH.COOH$$

$$CHOH.COOH + COOH \longrightarrow CH_2OH.COOH + CO_2$$

In alkaline solutions of formic acid (sodium formate) at pH~12,
irradiated with neutrons, they found the chief product to be oxalate
and glyoxalate. This is in agreement with the finding of Hardwick

who irradiated 0.1 M sodium formate with an electron beam (3 M.e.v.)
(71). He found G oxalic acid = 1.35, G glyoxalic acid =0.64,
$G(H_2)$ = 1.18 and G(formaldehyde) = 0.17. No hydrogen peroxide was
found by Hardwick in the irradiated solutions.

To explain his results he assumed the following reactions :

$$H + HCOOH \rightleftharpoons HC(OH)_2$$

$$H + HC(OH)_2 \longrightarrow H_2 + HCOOH$$

$$\longrightarrow H_2O + HCHO$$

$$H + H_2O_2 \longrightarrow H_2O + OH$$

$$OH + HCOOH \longrightarrow H_2O + COOH$$

$$COOH + COOH \longrightarrow (COOH)_2$$

$$COOH + HC(OH)_2 \longrightarrow 2 HCOOH$$

$$\longrightarrow CHO.COOH + H_2O$$
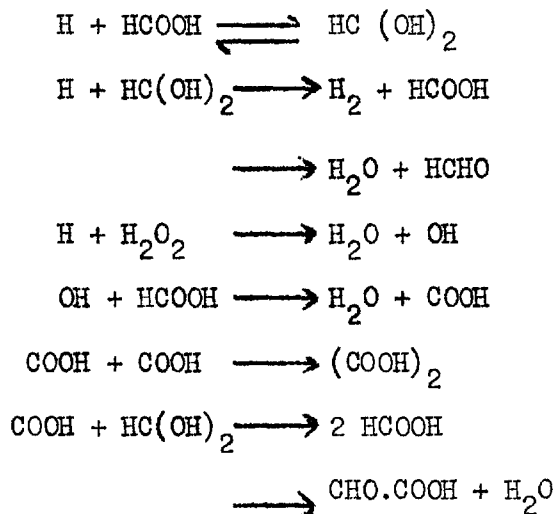
Under irradiation the pH of the solution rose from about 7 to a
value of about 11. However, the irradiated solution having a high
pH, suggests that the solvated electron $(H_2O)^-$ may play an
important part in the reactions, as mentioned before/ (35), (36)
and (37).

Recently, Hart studied the effect of the addition of
perdisulphuric acid to γ-irradiated formic acid solutions (72).
$G(CO_2)$ as high as 600 was found which suggested a chain reaction.
He found that $G(CO_2)$ increases with the square root of the formic

acid concentration and with decreasing dose rate according to $(I)^{-\frac{1}{2}}$. At constant formic acid and perdisulphuric acid concentrations, $G(CO_2)$ also increases rapidly as the pH increases from 0.52 ($GCO_2 = 60$) to 5.1 ($G(CO_2) = 600$), but subsequently decreases at pH's in the range from 5.1 to 7 and again in the range from 9 to 11. The suggested mechanism is the following :

$$H_2O \longrightarrow\!\!\!\wedge\!\!\wedge\!\!\wedge\!\longrightarrow H,\ OH,\ H_2,\ H_2O_2$$

$$H + HCOOH \longrightarrow H_2 + COOH$$

$$OH + HCOOH \longrightarrow H_2O + COOH$$

$$COOH + S_2O_8 \longrightarrow CO_2 + HSO_4^- + SO_4^-$$

$$SO_4^- + HCOOH \longrightarrow HSO_4^- + COOH$$

$$2SO_4^- + HCOOH \longrightarrow S_2O_8^{--} + HCOOH$$
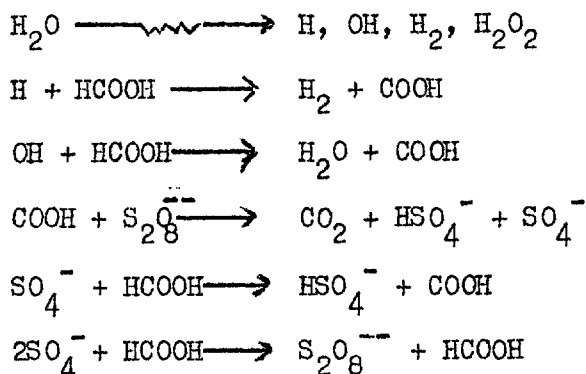
To explain the effect of pH, Hart suggested that the ionised form $HCOO^-$ is more reactive than the neutral molecule. At pH 5.1, formic acid is completely ionised and so the reaction

$$SO_4^- + HCOO^- \longrightarrow HSO_4^- + COO^-$$

can take place faster than in the case of the neutral molecule (low pH). To account for the decrease of GCO_2 between pH 5.1 and 7 he assumed the equilibrium :

$$COOH \rightleftharpoons COO^- + H^+$$
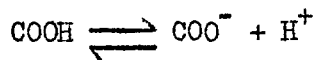
Above pH 5.1, he suggests that the COOH radical will be mostly as COO^- radical ion which is not as reactive as COOH and may dimerize :

$$2\ COO^- \longrightarrow (COO^-)_2$$
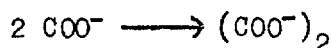
forming oxalic acid. The further decrease beyond pH 9 may be due to the equilibrium $\quad OH \rightleftharpoons O^- + H^+$
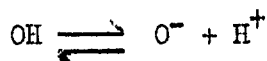
with O^- as the new species instead of OH.

(6) Irradiation of aqueous solutions of formaldehyde

When dilute solutions of formaldehyde are irradiated with X-rays at pH = 4, equal yields of hydrogen and formic acid are obtained with a G=3.1 (2). The hydrogen yield decreased as pH increased. Hart and Platzman suggest the following mechanism to explain these results: (73)

$$H + HCHO \longrightarrow H_2 + CHO \qquad (1)$$
$$H + HCHO \longrightarrow CH_2OH \qquad (2)$$
$$OH + CHO \longrightarrow HCOOH \qquad (3)$$
$$CHO + H_2O_2 \longrightarrow HCOOH + OH \qquad (4)$$
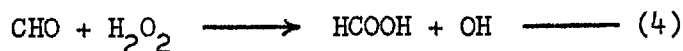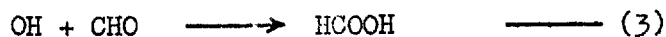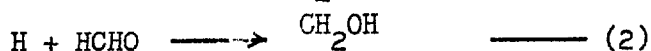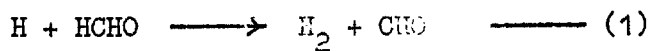
They suggested reaction (2) because $G(H_2) = 3.1$ is less than $G(H)^W + G(H_2)^W \simeq 4$, the hydrogen yield if all the hydrogen atoms reacted according to (1). As $G(HCOOH)$ is = 3.1, and as reaction (4) can produce $G(HCOOH) = G(H_2O_2)^W \simeq 0.8$, they had to postulate reaction (3) to account for the high yield of formic acid. However, radical-radical reactions, such as reaction (3), are not likely to happen when formaldehyde is present which can react with OH radicals. As an alternative mechanism which may account for the formation of formic acid with such high yield, specially in alkaline solutions, we may suggest the following:

$$H + HCHO \longrightarrow H_2 + CHO \qquad \text{——— (1)}$$

$$H + HCHO \longrightarrow CH_2OH \qquad \text{——— (2)}$$

$$OH + HCHO \longrightarrow H_2O + CHO \qquad \text{- - - - (2a)}$$

$$CHO + H_2O_2 \longrightarrow HCOOH + OH \qquad \text{——— (3)}$$

$$CHO \rightleftarrows CO^- + H^+ \qquad \text{——— (4)}$$

$$CO^- + H_2O \longrightarrow (HCOOH)^- \qquad \text{——— (5)}$$

$$(HCOOH)^- \longrightarrow HCOO^- + H \qquad \text{——— (6)}$$

$$\text{or } (HCOOH)^- + H_2O \rightleftarrows HCOOH + (H_2O)^- \qquad \text{——— (7)}$$
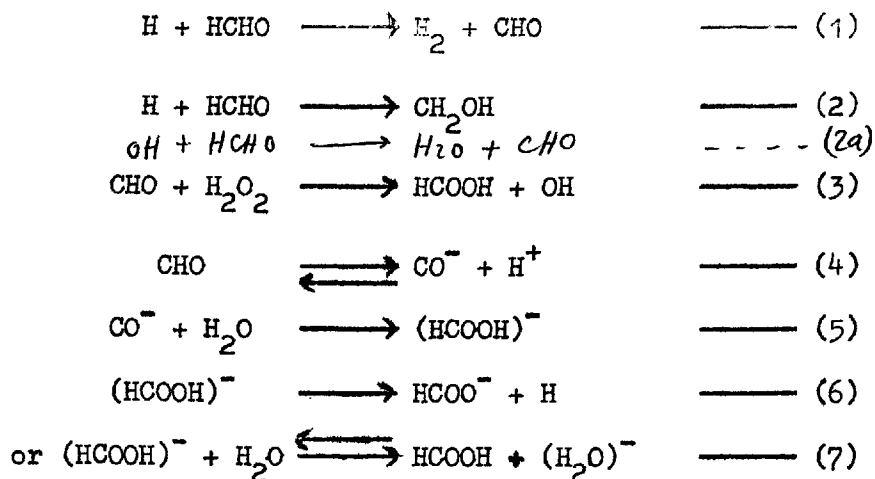
This mechanism is similar to that suggested for the chain formation of formic acid in irradiated alkaline carbon monoxide solutions (see discussion).

(7) Irradiation of aqueous solutions of methyl alcohol

X-irradiation of dilute aqueous solutions of methanol yields hydrogen, ethylene glycol and a little formaldehyde $GH_2 = 4$ at pH = 1 and approaches the molecular yield as the pH increases. The suggested mechanism is the following: (2) and (74)

$$H + CH_3OH \longrightarrow H_2 + CH_2OH \qquad \text{——— (1)}$$

$$OH + CH_3OH \longrightarrow H_2O + CH_2OH \qquad \text{——— (2)}$$

$$CH_2OH + CH_2OH \longrightarrow CH_2OH \cdot CH_2OH \qquad \text{——— (3)}$$

$$CH_2OH + H_2O_2 \longrightarrow HCHO + H_2O + OH \qquad \text{——— (4)}$$
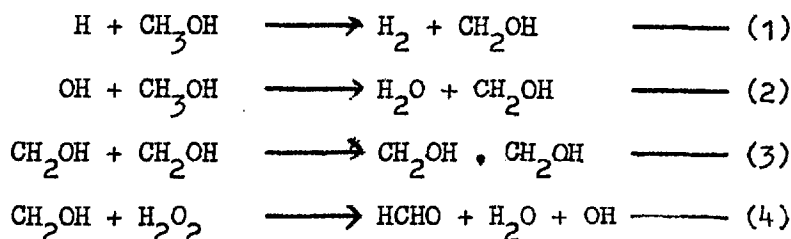
The lower yield of hydrogen at higher pH, as in the case of formaldehyde solutions, may be due to the reaction:

$$H + OH^- \rightleftarrows (H_2O)^-$$
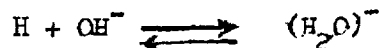
being shifted to the right. This would suppress H-abstraction

(reaction (1)) in favour of some reaction (not producing

hydrogen) of the hydrated electrons with the alcohols. It may

be noted that the reaction

$$CH_2OH + CH_2OH \longrightarrow CH_3OH + HCHO$$
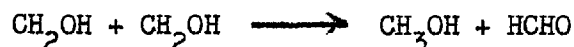
is not likely to happen in dilute methyl alcohol solutions, as

shown by Mcdonell and Gordon (75) who irradiated concentrated

methyl alcohol aqueous solutions with Υ-rays, from 0.3 M to

$\sim$30 M (pure) methyl alcohol. They found that formaldehyde and

ethylene glycol were produced under irradiation. The formaldehyde

yield increased as the methyl alcohol concentration was increased,

to a value of G $\simeq$ 1.2 in pure methyl alcohol. The ethylene glycol

yield remained constant at G = 3 as the methyl alcohol concentra-

tion was increased. From these data, they concluded that formal-

dehyde formation is a high activation energy process which can

occur only in the small highly energized regions of the spur where

the methyl alcohol molecule is excited and decomposed according to:

$$CH_3OH^* \longrightarrow CH_2OH^* + H^*$$
$$CH_2OH^* + CH_2OH^* \longrightarrow CH_3OH + HCHO$$
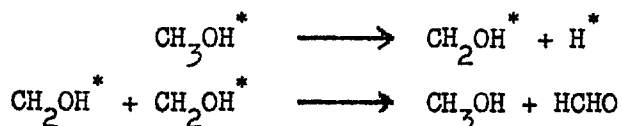
according to this mechanism, as the concentration of methyl alcohol

is increased, more excited methyl alcohol molecules are formed and

are transformed to formaldehyde. On the other hand, ethylene

glycol is formed in the bulk of the solution according to:

$$H + CH_3OH \longrightarrow H_2 + CH_2OH$$

$$OH + CH_3OH \longrightarrow H_2O + CH_2OH$$

$$CH_2OH + CH_2OH \longrightarrow CH_2OH \cdot CH_2OH$$
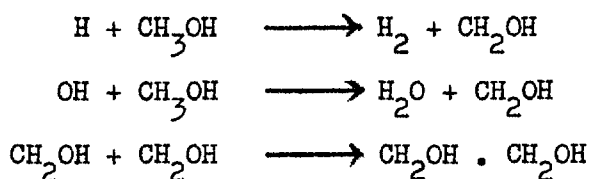
thus ethylene glycol formation is independent of methyl alcohol concentration.

Baxendale and Hughes irradiated dilute aqueous solutions of methanol, in the presence of ferric ions and in the absence of oxygen, with X-rays (76) and (77). Ferrous ions and formaldehyde were produced. They suggested the following mechanism:

$$H + CH_3OH \longrightarrow H_2 + CH_2OH$$

$$H + Fe^{+++} \longrightarrow H^+ + Fe^{++}$$

$$OH + CH_3OH \longrightarrow CH_2OH + H_2O$$

$$CH_2OH + Fe^{+++} \longrightarrow HCHO + Fe^{++} + H^+$$

$$Fe^{++} + H_2O_2 \longrightarrow Fe^{+++} + OH^- + OH$$
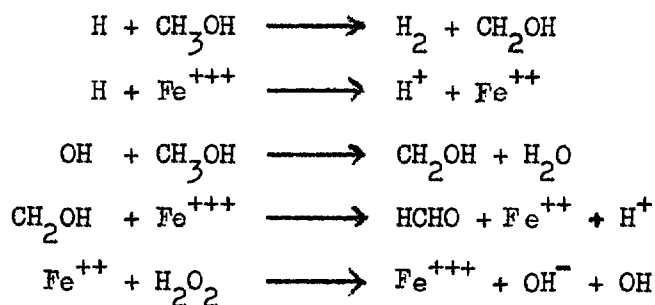
Under conditions where the ratio CH_3OH/Fe^{+++} is high, the above mechanism leads to:

$$G(H_2) = G(H_2)^W + G(H)^W$$

$$G(HCHO) = G(H)^W + G(OH)^W + G(H_2O_2)^W$$

$$G(Fe^{+++}) = G(H)^W + G(OH)^W$$

at high Fe^{+++}/CH_3OH ratio, $G(H_2)$ approaches $G(H_2)^W$, and so they could obtain all the radical and molecular yields of water radio-lysis with X-rays (50 kv). Table (1) presents yields measured in this way for H_2O containing 0.1 N sulphuric acid.

Table (1)

X-rays (50 kv) basic yields in H_2O (0.1 N sulphuric acid)(76)

$G(H)^W$	3.29
$G(OH)^W$	2.83
$G(H_2)^W$	0.64
$G(H_2O_2)^W$	0.87

For comparison, the following are the basic yields of Υ-irradiation found by Johnson and Weiss in their study of ceric ions (0.1 - 0.8 N sulphuric acid) (78).

Table (2)

Υ-rays (Co-60) basic yields in water (0.1 - 0.8 N H_2SO_4)(78)

$G(H)^W$	3.65
$G(OH)^W$	2.85
$G(H_2)^W$	0.40
$G(H_2O_2)^W$	0.80

The molecular yields for X-rays are found to be somewhat higher than those of Υ-rays (Co-60). This is due to the higher value of linear energy transfer in the X-ray irradiation compared to that in the Υ-irradiation with the result that more radicals are formed in

the spur and thus more hydrogen and hydrogen peroxide are produced (consistent with the Samuel-Magee model). Table (3) shows the L.E.T. of X- and Y-radiations.

Table (3)

L.E.T. of X- and Y-radiations in water (79)

Radiation	L.E.T. (ev per A°)
Co Y-rays	0.02
250 kvp X-rays	0.10
10 kvp X-rays	0.20

(8) Irradiation of aqueous solutions of carbon dioxide:

Getoff, Scholes and Weiss irradiated deareated aqueous solutions of carbon dioxide (10^{-2}M) with Y-rays (80). They found that the products of irradiation are hydrogen, formaldehyde, acetaldehyde, formic acid, oxalic acid and glycol. In the presence of ferrous ions (10^{-3}M) small amounts of carbon monoxide (G~0.1) were found. They concluded from the presence of carbon monoxide that it can be an intermediate in the radiolysis of carbon dioxide solutions and that in the presence of ferrous ions, the carbon monoxide is protected from oxidation by the OH radical which reacts with the ferrous ions present in excess. At pH=4, $G(H_2)$ = 0.74, $G(HCHO)$ = 0.85, $G(HCOOH)$ = 0.17. No data was given for the other products. The yields of hydrogen, formaldehyde and formic

acid decreased as the pH increased. To explain the results,
they suggest that carbon dioxide is reduced by solvated electrons
or by H atoms to form carbon monoxide or COOH radicals. The CO,
being very reactive, is further reduced by hydrogen atoms to give
CHO radicals. These CHO radicals can account for the formaldehyde
production. The formation of formic acid may proceed from the
disproportionation of two COOH radicals. No mechanism was given
for the production of the other products.

Garrison and Rollefson irradiated carbon dioxide in aqueous
solutions (0.005 - 0.1 M) with 35 M.e.v. helium ions in presence of
0.1 N sulphuric acid and 1 M ferrous sulphate (81). The principal
products formed are ferric ion and hydrogen and lower yields of
formic acid, formaldehyde, oxalic acid and methyl alcohol. They
suggested that radical-radical reactions may happen but no
detailed mechanism was given to account for all these products.

(9) Irradiation of aqueous solutions of ferrous and ferric ions

Ferrous ion in aerated acid solution (the Fricke dosimeter)
is oxidised to ferric ion   under irradiation. It is one of the
most thoroughly investigated reactions in radiation chemistry,
e.g. (82), (83), (84) and (85). The ferric ion yield is G = 15.5
for γ-irradiation and less for radiation of higher L.E.T. In
γ-irradiation, the yield is independent of ferrous ion concentration
from 10^{-4} - 10^{-2} M and of oxygen concentration from 10^{-6} - 10^{-3} M.

It is also independent of dose-rate within wide limits. However,
at very high dose-rates, e.g. 10^6 rads/sec., efficient stirring
may be required to replenish the ferrous ion exhausted in the
irradiated zone. In these air-saturated solutions the maximum
dose which can be used is about 40,000 rads, when the oxygen in
the solution is used up. The reaction mechanism for these
solutions was mentioned before (p.12), from which $G(Fe^{+++}) =$
$2GH_2O_2^W + GOH^W + 3GH^W = 15.5.$

In the absence of air, $G(Fe^{++})$ is lower and equal to
$2GH_2O_2^W + GOH^W + GH^W = 7.8$ (86). In order to interpret this
result, it is necessary to assume that H atoms oxidise ferrous ions
in an acid medium. The mechanism of this oxidation reaction is
still controversial. It may be written as $H + H^+ + Fe^{++} \longrightarrow$
$Fe^{+++} + H_2$ which requires three-body collision, but the process may
be facilitated by the formation of the radical ion H_2^+($H + H^+ \longrightarrow$
H_2^+) followed by electron transfer (39):

$$H_2^+ + Fe^{++} \longrightarrow H_2 + Fe^{+++}$$
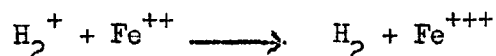
Another hypothesis regarding this oxidation is that H atom reacts
with the water of hydration forming part of the environment of the
ferrous ion (87):

$$Fe^{++}(H_2O) + H \longrightarrow FeOH^{++} + H_2$$
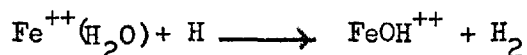
Recently, Czapski, Jortner and Stein oxidised ferrous ions in the
absence of air using hydrogen atoms produced from a high frequency

discharge, (88) and (89). To explain their results, they suggest that there are two possible alternative pathways for the mechanism of this oxidation. One involves the relatively slow reaction of H atoms with H^+ to form H_2^+ as mentioned before. This mechanism is operative in solutions such as of I^- (90). The other alternative is that when metal cations such as Fe^{++} are present. The metal ion may react directly with hydrogen atoms to form a hydride. This hydride complex may react with H^+ yielding molecular hydrogen:

$$Fe^{++}aq + H \rightleftharpoons FeH^{++}aq$$

$$FeH^{++}aq + H^+aq \longrightarrow Fe^{+++}aq + H_2$$
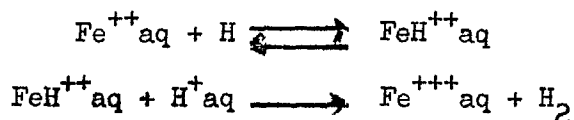
In the case of ferric ion in acid solutions, in the absence of air, no reduction of Fe^{+++} occurs under γ-irradiation, (86) and (91).

(C)   Reaction of carbon monoxide with hydroxyl radicals
       (Fenton reagent)

In 1957, Dainton and Hardwick studied the reactivity of hydroxyl radicals, produced from Fenton reagent, with carbon monoxide (92). The reaction mixture contained ferrous ions, sulphuric acid (or perchloric acid), hydrogen peroxide, dissolved oxygen and carbon monoxide. The method depends on the fact that OH radicals react with carbon monoxide, in competition with Fe^{++}, to form COOH radicals which produce HO_2 radicals. The HO_2 radicals can oxidise more ferrous ions than those oxidised by the OH radicals.

From the excess of ferric ion produced in the presence of carbon monoxide over that produced in its absence, they calculated the ratio of rate constants $\dfrac{k(OH + CO)}{k(OH + Fe^{++})}$. They suggested the following mechanism for this system:

$$Fe^{++} + H_2O_2 \longrightarrow Fe^{+++} + OH^- + OH \quad \text{———— (1)}$$

$$OH + Fe^{++} \longrightarrow Fe^{+++} + OH^- \quad \text{———— (2)}$$

$$OH + CO \longrightarrow COOH \quad \text{———— (3)}$$

$$COOH \longrightarrow CO_2 + H \quad \text{———— (4)}$$

$$H + O_2 \longrightarrow HO_2 \quad \text{———— (5)}$$

$$COOH + O_2 \longrightarrow CO_2 + HO_2 \quad \text{———— (6)}$$

$$HO_2 + Fe^{++} \longrightarrow Fe^{+++} + HO_2^- \quad \text{———— (7)}$$

$$HO_2^- + H^+ \longrightarrow H_2O_2 \quad \text{———— (8)}$$
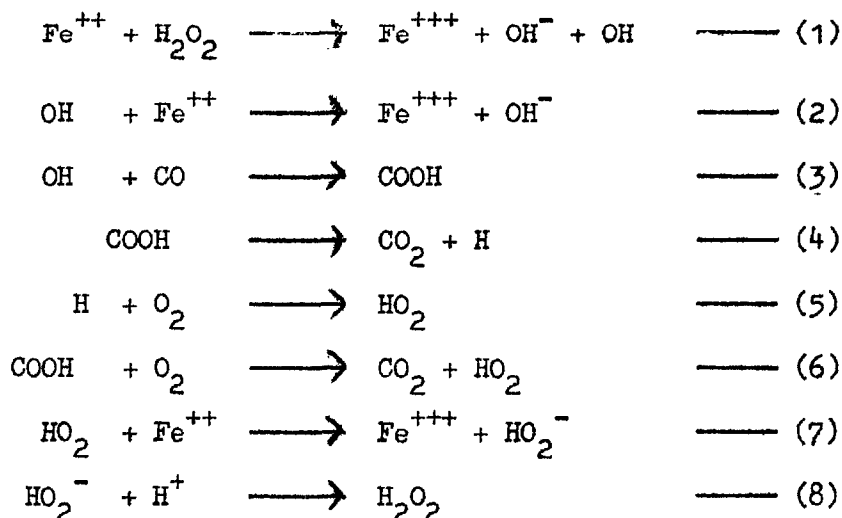
They concluded from kinetic considerations that reaction (3) is a bimolecular addition of OH radical and CO, similar to that of Cl atom and carbon monoxide, and not an oxygen atom transfer reaction, e.g. $CO + OH \longrightarrow CO_2 + H$. However, the fate of the COOH radical was not certain. They suggested that the COOH radical may slowly rearrange to $CO_2 + H$ according to reaction (4) or may stay as such (reaction (3)). From the above scheme, both reactions will eventually produce $CO_2 + HO_2$ through reactions (5) or (6), and so either suggestion will explain their quantitative results.

Daintor and Hardwick found the ratio $\dfrac{k(OH + CO)}{k(OH + Fe^{++})}$ = 2.6 in 0.2 N $HClO_4$ at $20^{\circ}C$ and 2.14 in 0.8 N H_2SO_4 at $25^{\circ}C$.

Hardwick, in a similar study, found that the same ratio of rate constants is 3.79 in 0.1 N perchloric acid at 20°C (93).

Chapter II.   Experimental Methods:

(A) Preparation of solutions:

Ordinary distilled $\overset{water}{\wedge}$ was redistilled from alkaline potassium permanganate and then once more.   The pH of this water was about 5.7.   This value is due to carbon dioxide of the air and its concentration in the water can be calculated as follows:

$$CO_2 + H_2O \rightleftharpoons H_2CO_3 \rightleftharpoons (H)^+ + (HCO_3)^-$$
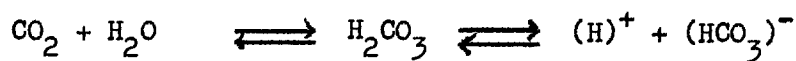
$$\frac{(H)^+ (HCO_3)^-}{(H_2CO_3)} = K, = 4.31 \times 10^{-7} \text{ at } 18^\bullet C \quad (94)$$

pH of triple distilled water (found) = $5.7 = \log \frac{1}{H^+}$

$$\therefore \quad (H)^+ = 1.99 \times 10^{-6} \text{ M}$$

$$\text{and } (HCO_3)^- = 1.99 \times 10^{-6} \text{ M}$$

$$\text{and } \therefore (H_2CO_3) = \frac{1.99 \times 10^{-6} \times 1.99 \times 10^{-6}}{4.31 \times 10^{-7}} = 0.92 \times 10^{-5} \text{ M} \begin{pmatrix} \text{at} \\ \text{equilibrium} \end{pmatrix}$$

(H_2CO_3) of original solution before dissociation = 0.92×10^{-5}

$$+ 1.99 \times 10^{-6}$$

$$= 1.12 \times 10^{-5} \text{ M.}$$

This value of 1.12×10^{-5} M can be checked directly from the solubility of carbon dioxide from the atmosphere in water at room temperature ($23^\circ C$).   This equals 0.243 C.C carbon dioxide. (N.T.P.)/litre (95), $\therefore$ concentration of carbon dioxide in water

$$= \frac{0.243}{1000 \times 22.4}$$

$$= 1.09 \times 10^{-5} \text{ M.}$$

That shows that a carbon monoxide solution of 4.5×10^{-4} M is about 50 times more concentrated than that of carbon dioxide in triply distilled water. The carbon dioxide will be reduced still further by deaeration, especially in acidic solutions. Thus the reactions in the irradiated solutions will be due to carbon monoxide, and other compounds if present, and not to carbon dioxide. Solutions of lower pH were obtained by adding sulphuric acid and of higher pH by adding sodium hydroxide. The alkaline solutions were freed from carbon dioxide by boiling the water before adding filtered concentrated sodium hydroxide (96). The procedure was to dissolve 7g of sodium hydroxide in 7 m.l of water and the viscous liquid was filtered through an asbestos mat in a Gooch crucible, with aid of suction. The filtrate was collected in a small dry test tube. The residue was not washed. 4 m.l of the clear filtrate was diluted to one litre with freshly boiled water. Ferrous ammonium sulphate and iron alum in 0.1 N sulphuric acid were used for experiments with ferrous and ferric ions respectively. All chemicals used in the present work were "Analar" grade obtained from Hopkin and Williams Limited, or British Drug Houses Limited.

(B) <u>Carbon monoxide purification:</u>

Carbon monoxide, stated to be 99% pure, was obtained from a cylinder (I.C.I.). The impurities which may be found in carbon monoxide cylinders are: iron carbonyl, carbon dioxide, oxygen and hydrogen. The following method was used to eliminate these

impurities, except in the case of hydrogen, which no attempt was made to remove.

(a) Iron carbonyl may be produced in carbon monoxide cylinders on storage. The concentrations present in commercial cylinders range from 0.16 - 0.18 mg/litre (97). This is readily removed by passing through a liquid oxygen trap.

(b) Carbon dioxide was also removed by passing through the liquid oxygen trap.

(c) Oxygen was removed by passing the gas through an alkaline sodium hydrosulphite solution followed by an alkaline pyrogallol solution, both solutions being in a gas bubbler. The alkaline sodium hydrosulphite solution was made by dissolving 16g sodium hydrosulphite, 6.6g sodium hydroxide and 2g sodium anthraquinone β sulphonate in 100 m.l water. The latter compound acts as a sensitizer for the absorption of oxygen by the sodium hydrosulphite, and at the same time as an indicator for the exhaustion of the solution, (it turns from brownish red to dull brown). The alkaline pyrogallol solution was made by dissolving 10g pyrogallol in 50 m.l of water and 95g sodium hydroxide in 150 m.l of water and mixing the two solutions (98). The hydrosulphite solution has the advantage of changing its colour as the solution is exhausted while no change in colour occurs in the pyrogallol solution. The pyrogallol solution has the advantage of rapid absorption of oxygen without the use of sensitizer.

Analysis of samples of gases purified in this way showed that they contained no carbon dioxide or oxygen. However, the purified gas contained about 0.5% of hydrogen. This hydrogen should not interfere with the free radical reactions in the irradiated solutions as its concentration would be about $\frac{1}{200}$ that of carbon monoxide, their solubilities in water being about the same. It is also known that the reactivity of OH radicals with CO is about 16 times as fast as that of OH with H_2 (92). H atoms can react only with carbon monoxide.

(C) <u>Acetylene purification:</u>

In the beginning of this study, some preliminary work was done on mixtures of carbon monoxide and acetylene in deaerated aqueous solutions. The acetylene was obtained from a cylinder (British Oxygen Company) and purified according to the method of Kistiakowsky (99). The impurities found in acetylene cylinders are: acetone, oxygen, carbon dioxide and hydrogen sulphide. The gas was passed through a series of wash bottles which contained in order: (1) saturated sodium bisulphite solution which absorbs the acetone with liberation of SO_2; (2) 0.2 N iodine in aqueous potassium iodide solution which eliminates SO_2 and liberates iodine gas; (3) saturated aqueous sodium thiosulphate solution which absorbs iodine gas; (4) alkaline sodium hydrosulphite with sodium anthaquinone β-sulphonate as indicator, prepared as described before, to eliminate oxygen; (5) 10% aqueous potassium hydroxide solution to absorb carbon dioxide and hydrogen sulphide.

(D) <u>Deaeration and preparation of the solution</u>:

Fig. (1) is an outline of the apparatus. (r) is the reaction vessel which is a 250 m.l round bottom flask. This could be connected to a vacuum line through a tap (1) and a ground joint (2). 100 m.l quantities of solution were deaerated by freezing the solution in (r), using a dry ice-acetone mixture, then evacuating to less than 10^{-4} mm. Hg. using a mercury diffusion pump backed by an oil pump. Tap (1) was then closed and the solution was thawed by immersing in warm water while shaking. The freezing, evacuating, and thawing were repeated once more. This procedure was sufficient to free the water from air and carbon dioxide. After the second thawing, (r) was immersed in cold water to allow the solution to reach room temperature before adding the gases. Tap (7) was closed and carbon monoxide was then added from the 2 litre storage flask (S1) to the solution, the reaction vessel being shaken to equilibrate the solution with the gas phase. The final hydrostatic pressure was measured on a manometer (m) and was 400 mm. Hg. in the case of carbon monoxide runs. The pressure of water vapour at room temperature (23°C) is about 20 mm. Hg. so that the net carbon monoxide pressure was thus 380 mm. Hg. The corresponding carbon monoxide concentration in water at 23°C would be 4.5×10^{-4} M (100). It was assumed that the concentration would be the same in other solutions. In case of mixtures of carbon monoxide and acetylene, tap (4) was closed after filling (r)

OUTLINE OF THE APPARATUS
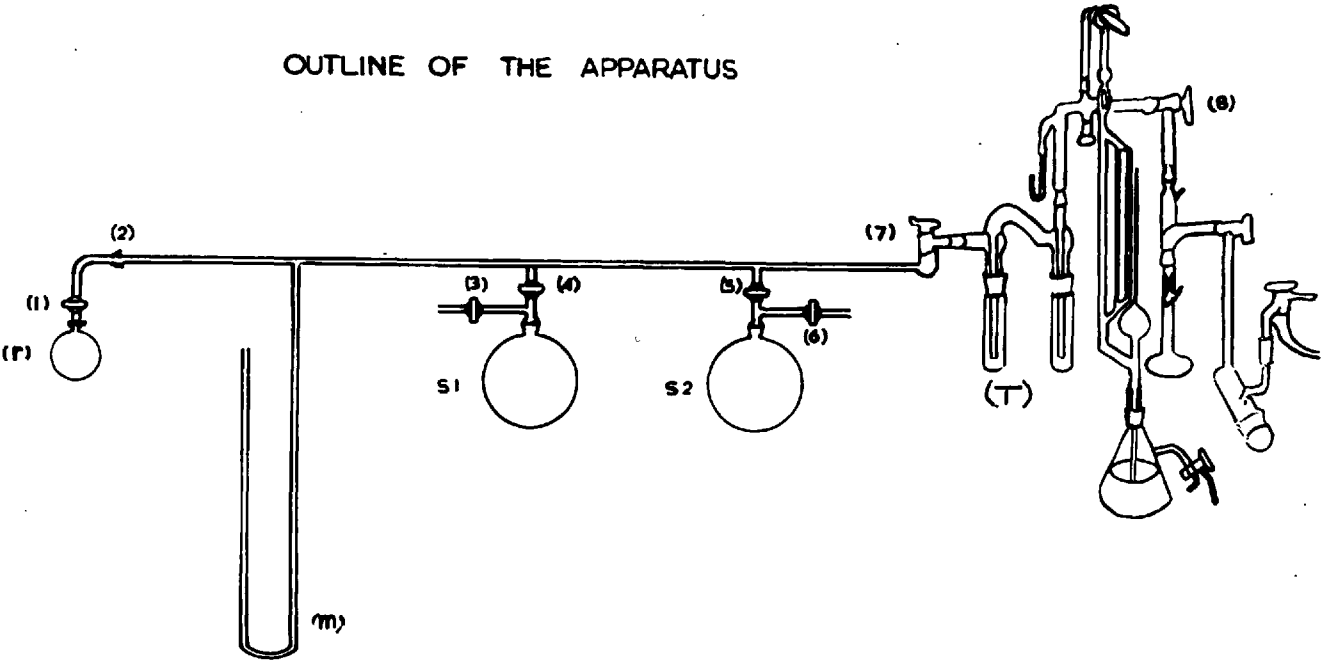
FIG. (1)

with carbon monoxide to 400 mm. Hg. and acetylene was introduced
to the reaction vessel from the 2 litre storage flask (S_2) till the
total pressure was 600 mm. Hg.   The net acetylene pressure was
then 200 mm. Hg.   This corresponds to 1.20×10^{-2} M acetylene,
i.e. about 25 times the concentration of carbon monoxide.

(E)   Irradiation of solution and description of Cobalt-60 source:

          After filling the gases, tap (1) was closed and the reaction
vessel was disconnected from the evacuation line through the
joint (2).   The solution was then irradiated with γ-rays from a
kilo-curie cobalt-60 source (101).   The source is a cylindrical
capsule 6 inches by 0.56 inches diameter, which is prepared by
neutron irradiation of the parent material cobalt-59, in a nuclear
reactor.   The source can be withdrawn to a safe position when
samples are being assembled within the irradiation space.   The
source is moved between the safe and exposed positions by a
flexible cable running through a S-shaped guide tube and operated
by an electric motor.   The source is located about 5 inches from
the bottom of the guide tube when in the exposed position.
Concrete of about 5 feet thickness is used for radiation shielding.
The source could provide dose-rates of up to 1 Megarads/hour.

(F)   Dose Rate Determination:

          Doses were determined with the Fricke dosimeter (in 0.1 N
sulphuric acid).   Approximately 10^{-3} M ferrous sulphate solution
was prepared by dissolving the following reagents in one litre of

distilled water:

$$\left(NH_4\right)_2 SO_4 \cdot FeSO_4 \cdot 6H_2O \qquad\qquad 0.40 \text{ gm}$$

$$Na\, Cl \qquad\qquad 0.06 \text{ gm}$$

$$H_2SO_4 \qquad\qquad 3.00 \text{ m.l}$$

100 m.l of this solution was transferred to the reaction vessel
(in presence of air) and placed near the cobalt-60 source.
The solution was irradiated to receive about 10,000 rads.
The Fricke dosimeter gives satisfactory results in the range
4,000 - 40,000 rads, i.e. until all the available oxygen is used
up. The optical density of ferric ions produced was measured
at 304 mμ in 1 cm. cell. Fig (2) shows the absorption curve
for a dosimetry solution irradiated for 9,000 rads. The dose
rate was determined as follows, assuming the G value for ferrous
ion oxidised to ferric ion = 15.5 molecules per 100 e.v (102)

$$\text{Optical density} = E \times c \times l$$

$$\text{where } E = \text{molar extinction coefficient}$$

$$C = \text{concentration of solution (moles/litre)}$$

$$l = \text{thickness of solution.}$$

$$\text{in 1 cm. cell } l = 1$$

$$\therefore \qquad c = \frac{O.D}{E} \times 6.025 \times 10^{23} \text{ molecules/litre}$$

$$\text{and absorbed dose} = \frac{O.D}{E} \times \frac{6.025}{15.5} \times 10^{23} \times \frac{100}{1000} \text{ e.v/g in water}$$

$$\text{but 1 rad} = 6.24 \times 10^{13} \text{ e.v/g}$$

$$\therefore \quad \text{dose} = \frac{O.D}{E} \times \frac{6.025 \times 10^{22}}{15.5 \times 6.24 \, c \, 10^{13}}$$

SPECTRACORD
FERROUS SULPHATE DOSIMETRY
DOSE = 9000 RADS.

FIG. (2)

O.D 1 cm

60.
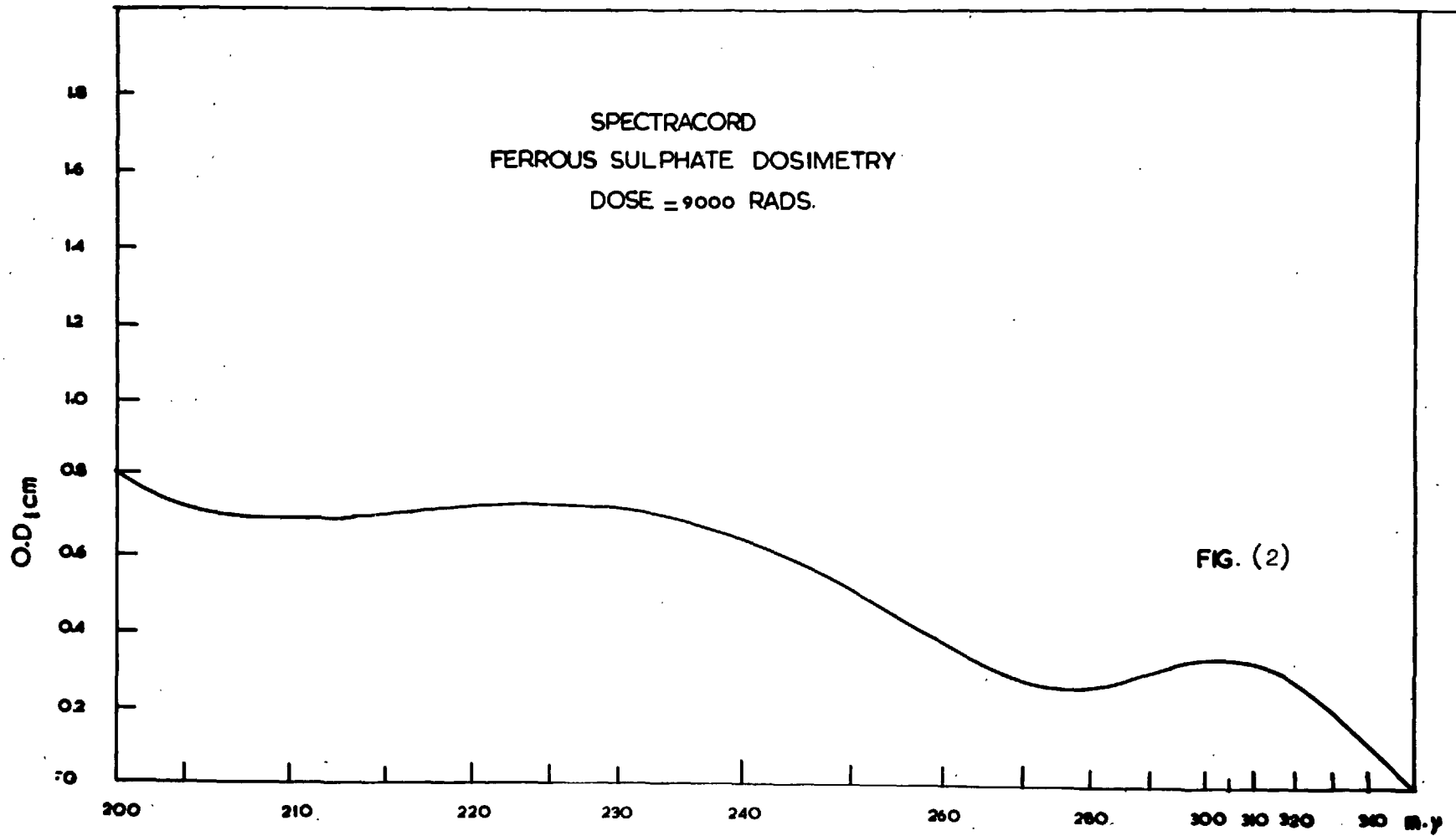
The optical density decreases 0.7% per degree above $20^{\circ}C$ (103)

$$\therefore O.D_{20^{\circ}C} = O.D_{T^{\circ}C} (1 - 0.007t)$$

where $t = T - 20$

$T = $ temp. of sample in C°.

Using values reported by Haybittle, Saunders and Swallow (102)

$E = 2115$ at $20^{\circ}C$ and 0.1 N sulphuric acid.

$$\therefore \text{Dose} = 2.94 \times 10^{4} (1 - 0.007t) \times O.D_{T^{\circ}C} \text{ rads.}$$

Knowing the time of irradiation, the dose rate can be readily
calculated.   Dose rates used in the present work were in the
region of 26,000 - 30,000 rads/hr.   This corresponded to a
horizontal distance of about 6 inches from the source (centre of
the reaction vessel to centre of the source guide tube) and about
6 inches from the surface of the solution in the reaction vessel
to the bottom of the guide tube.   At this location the dose rate
was found not to be sensitive to any possible small vertical
variations in the source position.

(G) <u>Identification and determination of products:</u>

The products of irradiation tested for were the following:
(1) hydrogen, (2) carbon dioxide, (3) hydrogen peroxide,
(4) aldehydes, (5) ethylene glycol, (6) acids.

<u>(1) Hydrogen:</u>

Hydrogen was identified and determined by gas chromatography
according to the method of Ray (104).   Activated charcoal
(Sutcliffe and Speakman No. 207B) of 60 - 100 mesh granular was

heated in an oven for 4 hours at 140°C. This charcoal was used

to fill two 3 ft. columns of 6 mm. bore glass tube. The two

columns were connected in series and placed in the gas chroma-

tography apparatus (Griffin and George V.P.C. Mark II., using

a katharometer detector). The apparatus was operated at room

temperature (23°C) and the carrier gas was nitrogen which is the

best gas for the determination of hydrogen using a thermal

conductivity detector (105). The bridge current was 100 m.A, the

sensitivity was maximum at 50, and the chart speed was 6 inches/hr.

The initial pressure of nitrogen was atmospheric, outlet pressure

650 mm. Hg. and flow rate 2 litres/hr. Under these conditions

the retention time for hydrogen was found to be 2 minutes and the

peak was quite sharp, needle like, indicating easy and complete

removal of the hydrogen from the charcoal. For quantitative

determinations two calibration curves were made:

(a) The first calibration curve was done to see if the

hydrogen was quantitatively separated from a mixture of hydrogen

in large volume of nitrogen when the volume of the mixture was

varied. This was done because as the quantity of hydrogen produced

under irradiation was low, it was necessary to collect a large

volume of the gas phase. The mixture of hydrogen in nitrogen was

made in a 2 litre bulb, the total pressure being one atmosphere.

The hydrogen was about 2%, determined as the ratio of the partial

pressures of hydrogen and nitrogen as measured on a mercury manometer.

A gas burette was used to collect a known volume of the mixture and was connected to the top of the charcoal column through a glass tube. This glass tubing was evacuated, and the gas was injected into the column. Fig. (3) shows the calibration curve of hydrogen in the mixture. It shows that hydrogen was quantitavely separated even when using volumes of the mixture as large as 20 m.l at atmospheric pressure.

(b) Another calibration curve was made to determine exactly the percentage of hydrogen in the mixture used in (a). This was done by injecting known volumes of hydrogen at one atmosphere directly into the top of the charcoal column using a micro syringe. Fig. (3) shows this calibration curve. By comparing the two calibration curves at a certain peak, say 100 mm., it was possible to calculate the percentage of hydrogen in the mixture. At that peak of 100 mm., the corresponding volume of the mixture is 12.5 c.c (1 atm.) and the corresponding volume of hydrogen is 0.25 c.c (1 atm.) from which the hydrogen in the mixture $= 0.25 \times \dfrac{100}{12.5}$

$= 2\%.$.

For quantitative determination of the hydrogen in the irradiated solutions, the reaction vessel was shaken well, connected to the gas burette, and a measured volume of gas at one atmosphere was collected. The gas was then injected into the column as described before. It may be noted that the amount of hydrogen gas in solution is negligible at the very low partial pressure of hydrogen in the gas phase.(Appendix (1)).

CALIBRATION CURVE OF HYDROGEN

BY GAS CHROMATOGRAPHY

PRESSURE 760 mm.Hg.
TEMP. 23 °C

FIG. (3)
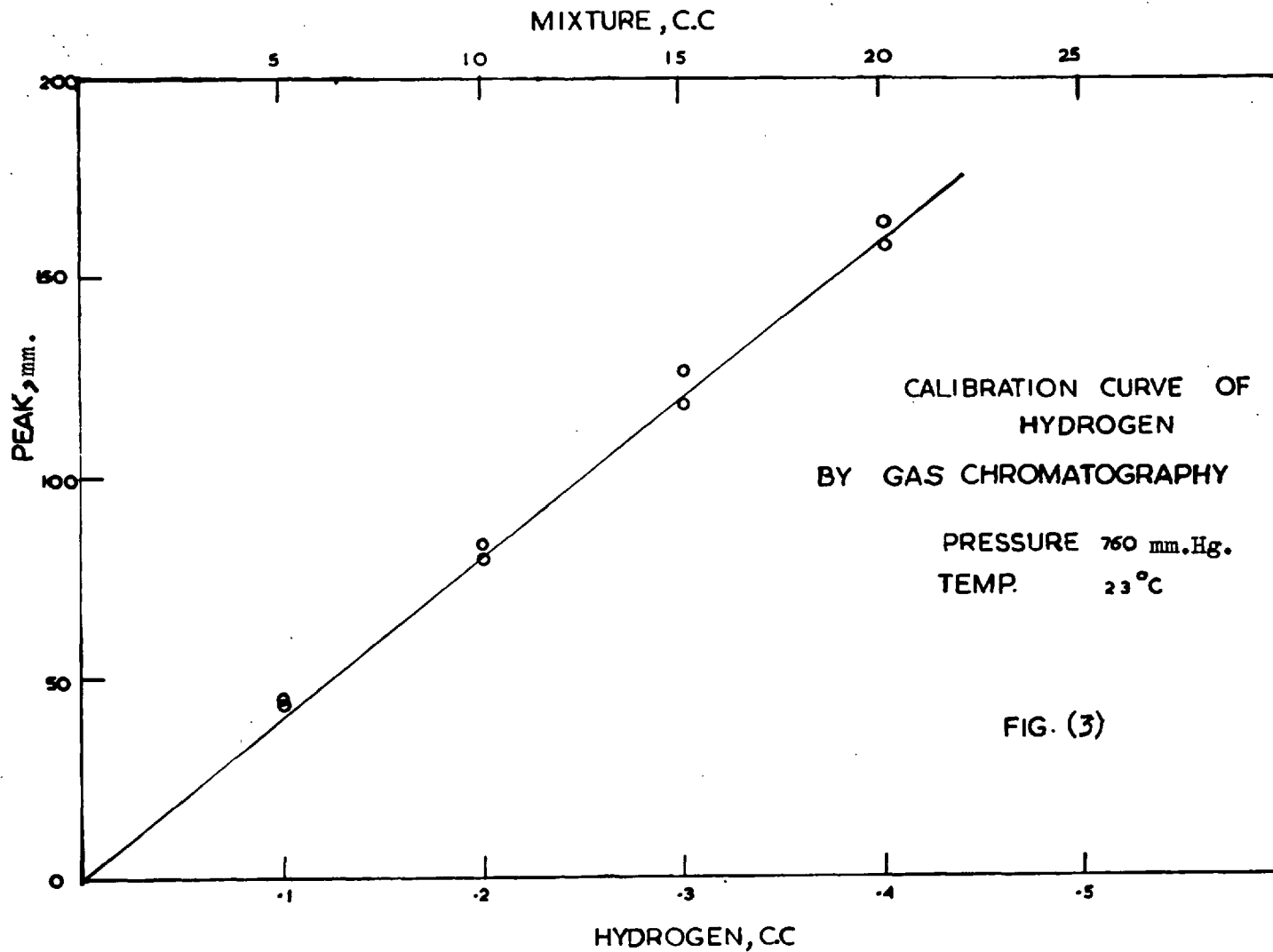
It was found that carbon monoxide would not interfere with the hydrogen as the retention time of carbon monoxide was 5 minutes and showed on the opposite side of the base line. This is due to the difference in the thermal conductivity of hydrogen and carbon monoxide with regard to nitrogen as shown in Table (4).

<div align="center">

Table (4)

Gas	Thermal Conductivity* (106)
Hydrogen	4.16
Nitrogen	0.58
Carbon monoxide	0.56

</div>

This table shows also that the gas chromatography detector should be much more sensitive for hydrogen than for carbon monoxide owing to the big difference in thermal conductivities between hydrogen and nitrogen, and the small difference between carbon monoxide and nitrogen. A correction was always made for the hydrogen in the unirradiated carbon monoxide by running a blank.

(2) Carbon dioxide

Carbon dioxide could not be determined using the gas chromatography method discussed above. Carbon dioxide showed a broad peak using the charcoal column at room temperature. This was

---

*Given as calories transmitted per second through a layer of gas 1 cm. thick and (1 meter)^2 in area when the temperature gradient in the gas is 1°C per cm.

mainly due to the irreversible absorption of carbon dioxide on

the charcoal. Another method was tried using a silica gel

column and helium gas as a carrier gas (107). This method -

showed a better peak, but the limit of detection was about 10^{-4}

moles CO_2, which is not suitable for the purpose of this work

where   the expected CO_2 was in the range 10^{-6} - 10^{-5} moles.

A method for detection and determination of carbon dioxide using

a Macleod gauge, as described by Baldwin (108), was developed.

The method depends on the fact that a trap cooled with liquid

nitrogen is suitable for the quantitative condensation of carbon

dioxide. Other gases such as hydrogen and carbon monoxide, will

not condense at liquid nitrogen temperature ($-195^{\circ}C$) if their partial

pressure is kept below atmospheric and continuous evacuation is

applied on the trap. For the calibration of the carbon dioxide on

a Macleod gauge, known volumes of 3% carbon dioxide in nitrogen

was introduced from the reaction vessel (r) to the evacuated trap (T)

of Macleod gauge, immersed in liquid nitrogen, in small portions.

The pump evacuated the uncondensed gases and the carbon dioxide was

completely condensed in the trap. The Macleod gauge was then

closed at both ends, tap (7) and tap (8), and the liquid nitrogen

was removed from the trap and warmed up to room temperature.   The

carbon dioxide pressure was then determined on the Macleod gauge.

Any traces of water vapour had to be completely eliminated before

introducing the gas mixture to the trap. This was done by

immersing (r) in a dry ice-acetone bath. Fig. (4) shows the calibration of carbon dioxide on the Macleod gauge. To check the validity of the procedure, the following experiments were done:

(a) Carbon monoxide from the cylinder which was purified by the previously mentioned method should not theoretically contain any carbon dioxide, as the liquid oxygen trap should condense it completely. Using the Macleod method, CO_2 could not be found in the carbon monoxide obtained by this method of purification.

(b) Triple distilled water prepared from alkaline potassium permanganate solution should contain 0.243 c.c. CO_2/litre water (see above). The CO_2 content of this water was found to be 0.236 c.c. of CO_2/litre water using the Macleod gauge method.

(c) The initial G value of CO_2 from the irradiation of 0.01M formic acid and 0.01M ferric sulphate in 0.1N H_2SO_4 was found to be 4.20 using the Macleod gauge method. Hart found the value of 3.88 using Van Slyke apparatus (66).

To apply this method to the irradiation solutions, the reaction vessel was shaken well, connected to the evacuation line and then immersed in dry ice-acetone mixture. The gases were then introduced slowly to the evacuated trap immersed in liquid nitrogen. Tap (1) was then closed and the solution in (r) was thawed in hot water while shaking, frozen again in dry ice-acetone mixture and evacuated once more. The carbon dioxide was then measured on the calibrated Macleod gauge as described before. Using this method it was possible to measure carbon dioxide in amounts as low as 10^{-6} moles.

CALIBRATION CURVE OF CO_2
MACLEOD GAUGE METHOD

MIXTURE: 3% CO_2 IN N_2
PRESSURE: 760 mm. Hg
TEMP. : 23 °C

FIG.(4)
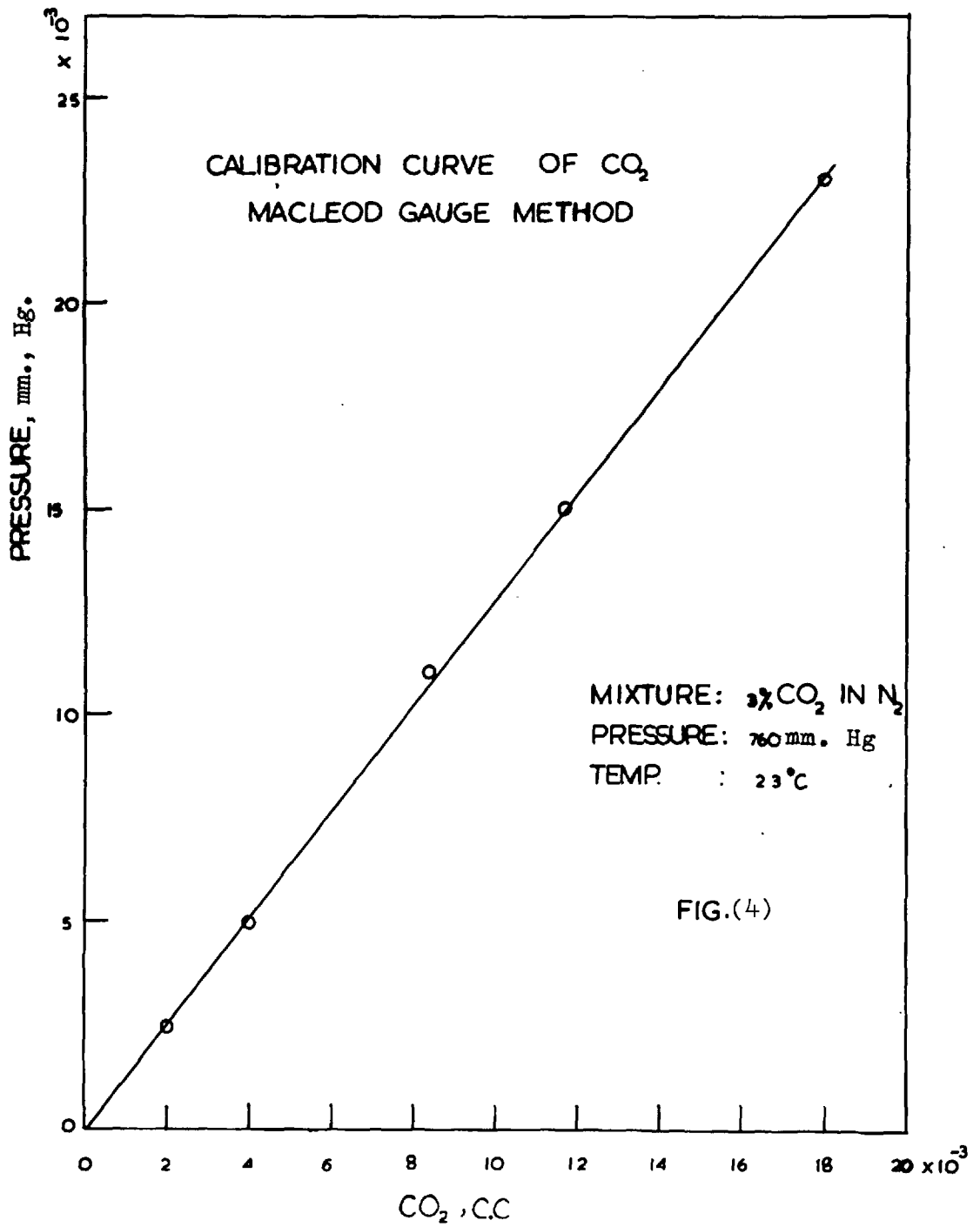
(3) Hydrogen Peroxide:

Three methods were used to detect hydrogen peroxide:

(a) The titanium sulphate method (109). The reagent is made by adding 20 m.l of concentrated sulphuric acid to 2 m.l of 10% titanium sulphate and making up to 100 m.l with water. 1 m.l of the reagent is added to 3 m.l of the tested solution: a yellowish colour develops if hydrogen peroxide is present, and the absorption-is at 410 mμ. This method is not very sensitive (about 10^{-4} M hydrogen peroxide) and can be applied in neutral and acidic solutions. This method will detect hydrogen peroxide but not hydroperoxides.

(b) The iodide method (110) and (58) which can only be applied in neutral or slightly acidic solutions. Under these conditions the iodide ion can be oxidised by H_2O_2 to I_3^-. The reagent is made of two solutions (1) 10 m.l of 1% ammonium molybdate, 1g of sodium hydroxide, 33g of potassium iodide, and diluted to 500 m.l of water; (2) 10g of potassium acid phthalate in 500 m.l of water. Equal volumes of (1) and (2) are mixed just before use. 5 m.l of the mixture is added to 1 m.l of the tested solution and the absorption of I_3^- is measured at 350 mμ. The method is fairly sensitive (about 10^{-5} M) and will detect both hydrogen peroxide and other hydroperoxides if present.

(c) Ferrous thiocyanate method (111). The reagent is made up by dissolving 5g ammonium thiocyanate and 5g ferrous sulphate in 100 m.l

of water containing 1 m.l of concentrated sulphuric acid.   The

solution is freed from the red colour by shaking with amyl alcohol.

The analysis is carried out by adding to 3 m.l of the tested

solution 1 m.l of the reagent.   If hydrogen peroxide or other

hydroperoxides are present, a red colour develops instantaneously

which has a maximum absorption at 450 mμ.   The method is applied

in acid solutions and is quite sensitive (10^{-6} M).

(4) <u>Aldehydes</u>.

Aldehydes were identified by paper chromatography of their 2:4 dinitrophenyl hydrazones according to the method of Schmitt(112). 20 ml. of 0.25% 2:4 dinitrophenyl hydrazine in 30% perchloric acid were added to the irradiated solutions and the hydrazones formed were extracted into carbon tetrachloride, concentrated under vacuum and then applied to the paper (Whatman No.1). The solvent system was dibutyl ether - dimethyl formamide - tetrahydrofuran in the ratio of 85 to 15 to 4. The ascent method was used and the run took about 4 hours. The location of the spots was aided by the use of a spray of alcoholic sodium hydroxide (0.1N). Aldehydes were quantitatively determined according to the method of Johnson and Scholes (113) in which they determined microquantities of acetaldehyde as its 2:4 dinitrophenyl - hydrazone. Their procedure was extended in the present work to include other aldehydes. The reagents used were the following :

a)   The hydrazine reagent was prepared by dissolving 0.25 g 2:4 dinitrophenyl hydrazine in 100 ml. of 30% V/V perchloric acid. This acid has the advantage, over other acids such as hydrochloric acid and sulphuric acid, that the hydrazine is much more soluble, that carbon tetrachloride extracts less of the unchanged reagent and that the reagent is more stable (in a dark stoppered container) than if it is prepared in other acids (113) and (114). However, experience from the present work showed that it is better to

prepare the hydrazine reagent freshly daily in order to obtain reproducible blanks.

b)   Alcoholic sodium hydroxide solution was prepared by dissolving 0.4 g sodium hydroxide in 100 ml. of absolute alcohol.

c)   Carbon tetrachloride was washed three times with water. This was enough to eliminate interfering substances, and appreciably reduced the blank.

The method depends on the formation of 2:4 dinitrophenyl hydrazone by the addition of the hydrazine reagent to the aqueous solution, followed by quantitative extraction into carbon tetrachloride. The addition of alcoholic sodium hydroxide to the carbon tetrachloride extracts produces a wine-red colour in the case of acetaldehyde (and other simple aldehydes such as formaldehyde) and a violet-bluish colour in the case of dialdehydes such as glyoxal or glycolaldehyde. This intense colour is presumably due to the formation of the resonating quinoidal ion (115) :

$$R - CH = N - NH \quad \text{—}\langle\text{NO}_2\rangle\text{—} NO_2 \xrightarrow{\text{base}} R - CH{=}N{-}N = \langle\text{NO}_2\rangle{=}N \begin{smallmatrix} O^{\ominus} \\ O \end{smallmatrix}$$
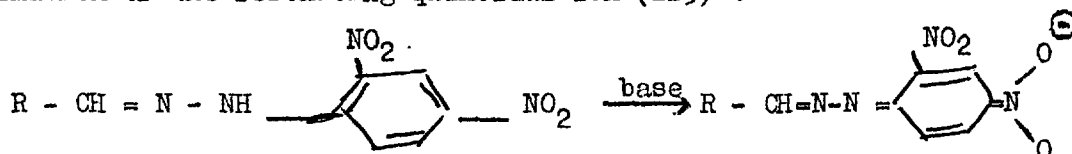
2:4 dinitrophenyl hydrazone   quinoidal ion

The procedure used for the determination of aldehydes in the irradiated solutions was to add 5 ml. of the hydrazine reagent to 20 ml. of the irradiated solution. The solution was set aside for 30 minutes at room temperature and was then extracted by shaking vigorously with

20 ml. of carbon tetrachloride for one minute. The aqueous layer

was extracted a second time with 5 ml. of carbon tetrachloride for

½ minute. The combined carbon tetrachloride extracts were then

transferred to a 50 ml. volumetric flask and 2 ml. of alcoholic

sodium hydroxide was added. Immediately ethanol was added up to

the mark and the optical density was measured within 10 minutes

after the addition of the alcoholic sodium hydroxide except in the

case of formaldehyde when the optical density diminished quite

rapidly and decay curves had to be done for its determination (see

below). Calibration curves of the optical density against

concentration were obtained for the following aldehydes :

(1) formaldehyde (2) acetaldehyde (3) acrylaldehyde (4) crotonaldehyde

(5) glyoxal (6) glycolaldehyde.

In all cases, the aldehyde 2:4 dinitrophenyl hydrazone was used as a

standard because of its crystalline form and stability. The 2:4

dinitrophenyl hydrazone was prepared by adding concentrated solution

of 2:4 dinitrophenyl hydrazine in perchloric acid (1 gm in 60 ml. of

30% acid) to a concentrated aqueous solution of the aldehyde. After

thirty minutes, water was added to precipitate the 2:4 dinitrophenyl

hydrazone. The precipitate was filtered and washed thoroughly with

boiling water to remove traces of perchloric acid. The hydrazone

was crystallized from the appropriate solvent (Table (5)). It was

then dried in an oven at 100°C. to remove traces of solvent before

determining its melting point. In the case of nitrobenzene it was

washed with hot alcohol to remove the nitrobenzene before drying at 100°C.

Table (5).

Compound.	Solvent of cyrstallization.	M.P. C° (found) (corrected).	M.P. C° (116) (corrected).
Formaldehyde D.N.P.H.	Ethyl alcohol	126	125
Acetaldehyde D.N.P.H.	Ethyl alcohol	147	147 & 165
Acryaldehyde D.N.P.H.	Ethyl alcohol	166	168
Crotonaldehyde D.N.P.H.	Benzene-Pet.ether	192	190
Glyoxal D.N.P.H.	Nitrobenzene	320-325	328
Glycolaldehyde D.N.P.H.	Nitrobenzene	320-325	328

The standard solution was prepared by dissolving known amounts of the hydrazone in CCl_4 and proceeding as described before.

(1)   Formaldehyde 2:4 dinitrophenyl hydrazone in CCl_4 (alc.NaOH) was found to have a maximum absorption at 430 mμ. However, the colour faded rapidly, as mentioned before, which is characteristic for formaldehyde (117). Decay curves were done to establish the conditions for formaldehyde determination in the range of concentration expected i.e. $10^{-6} - 10^{-5}$ M. This was made possible by the use of a recording spectrophotometer (Spectra-Cord Model 4000, The Perkin-Elmer Corpn.) Fig.(5). It was found that the absorption decreased about 10% in $2\frac{1}{2}$ minutes. All formaldehyde was determined at $2\frac{1}{2}$ minutes and then corrected for decay using the curves. Figs.(6), (7), (8), (9) and (10) show the decay curves and calibration curve for formaldehyde. The method was at least 10 times as sensitive as the chromotropic acid method (118) which could not be used at the low concentrations found in this work.

SPECTACORD

FORMALDEHYDE   D.N.P.H   DECAY CURVES

9.5×10^{-6} M

zero time = addition of alcoholic NaOH

			min	sec
absorption at	1	after	2	10
	2		4	30
	3		7	10
	4		9	20
	5		11	40
	6		14	00
	7		16	18

FIG. (5)

FORMALDEHYDE HYDRAZONE (D.N.P.H)

DECAY CURVES

(1) 9.5 x 10⁻⁶ M
(2) 5.7 x 10⁻⁶ M
(3) 3.7 x 10⁻⁶ M

FIG. (6)

FORMALDEHYDE HYDRAZONE (D.N.P.H)
DECAY CURVE

38×10^{-6} M

$$\text{any point} = \frac{\text{o.d at specific time}}{\text{o.d at } 2\frac{1}{2} \text{ minutes}} \times 100$$

FIG.(7)

FORMALDEHYDE HYDRAZONE (D.N.P.H)
DECAY CURVE

5.7×10^{-6} M

any point = $\dfrac{\text{o.d at specific time}}{\text{o.d at } 2\frac{1}{2} \text{ minutes}} \times 100$

FIG. (8)

TIME, MINUTES

FORMALDEHYDE HYDRAZONE (D.N.P.H)
DECAY CURVE

9.5×10^{-6} M

any point $= \dfrac{\text{o.d at specific time}}{\text{o.d at } 2\frac{1}{2} \text{ minutes}} \times 100$

FIG. (9)

CALIBRATION CURVE
FORMALDEHYDE HYDRAZONE IN CCl_4 (A.L.C. NAOH)
VERSUS
O.D.$_{430}$ m.γ, 5 cm

FIG. (10)

(2)   Acetaldehyde 2:4 dinitrophenyl hydrazone exists in two forms which have different melting points depending on the method of its preparation. For example, the use of HCl in preparing the hydrazine reagent gave a product melting at 167°C. whereas the use of H_2SO_4 gave the form melting at 147°C. (119). The existence of the two forms was controversial for many years till it was proved by infra red analysis that they are two different forms (120) and are not due to any impurity as had been suggested before (121) and (122). The form obtained in the present work using perchloric acid in preparing the hydrazine reagent was the one with the lower melting point (see Table (5)). Acetaldehyde D.N.P.H. in CCl_4 (alc. NaOH) was found to have a maximum absorption at 430 mμ. The colour was stable for at least 10 minutes. Fig.(11) and Fig. (12).

(3)   Acrylaldehyde 2:4 dinitrophenyl hydrazone in CCl_4 (alc.NaOH) had a maximum absorption at 402 mμ and the colour was stable for at least 2 hours. Fig.(13) and (14).

(4)   Crotonaldehyde 2:4 dinitrophenyl hydrazone in CCl_4 (alc.NaOH) had a maximum absorption at 455 mμ and the colour was stable for at least 2 hours. Fig.(15) and (16).

(5)   Glyoxal reacts with 2:4 dinitrophenyl hydrazine to form an osazone according to the following equation :

$$CHO.CHO + 2\ C_6H_4(NO_2)_2NH.NH_2 \longrightarrow \begin{array}{l} CH: N.\ NH.\ C_6H_4\ (NO_2)_2 \\ | \\ CH: N.NH.\ C_6H_4\ (NO_2)_2 \end{array}$$

SPECTRACORD

ACETALDEHYDE HYDRAZONE (D.N.P.H) IN CCl₄ (ALC.NaOH)

3.6×10^{-5} M

FIG.(11).

CALIBRATION CURVE
ACETALDEHYDE HYDRAZONE IN CCl_4 (ALC.NAOH)
VERSUS
$O.D_{430 m.\gamma}$, 5cm.

FIG. (12)

CONCENTRATION, M
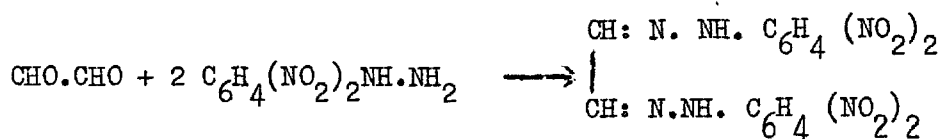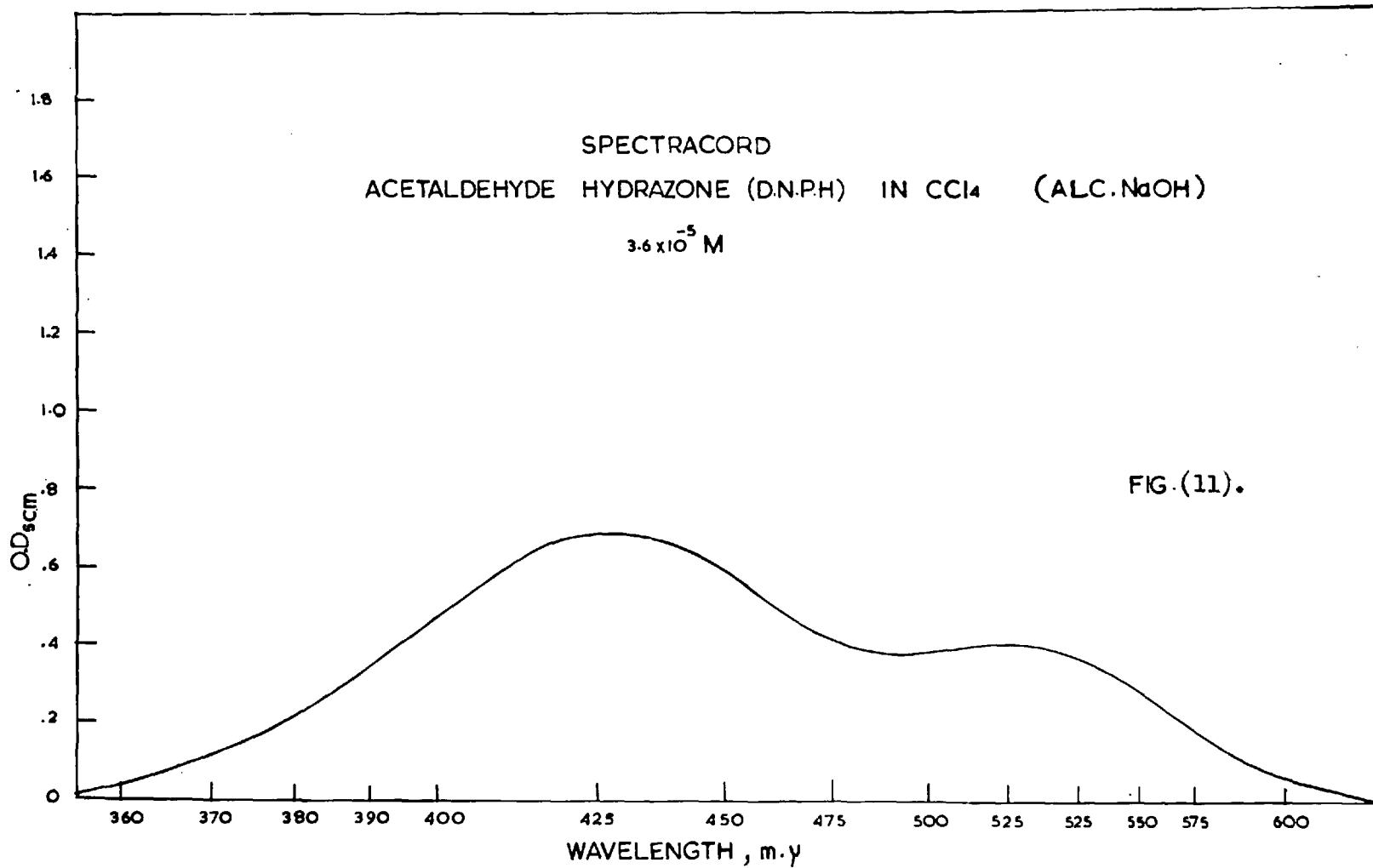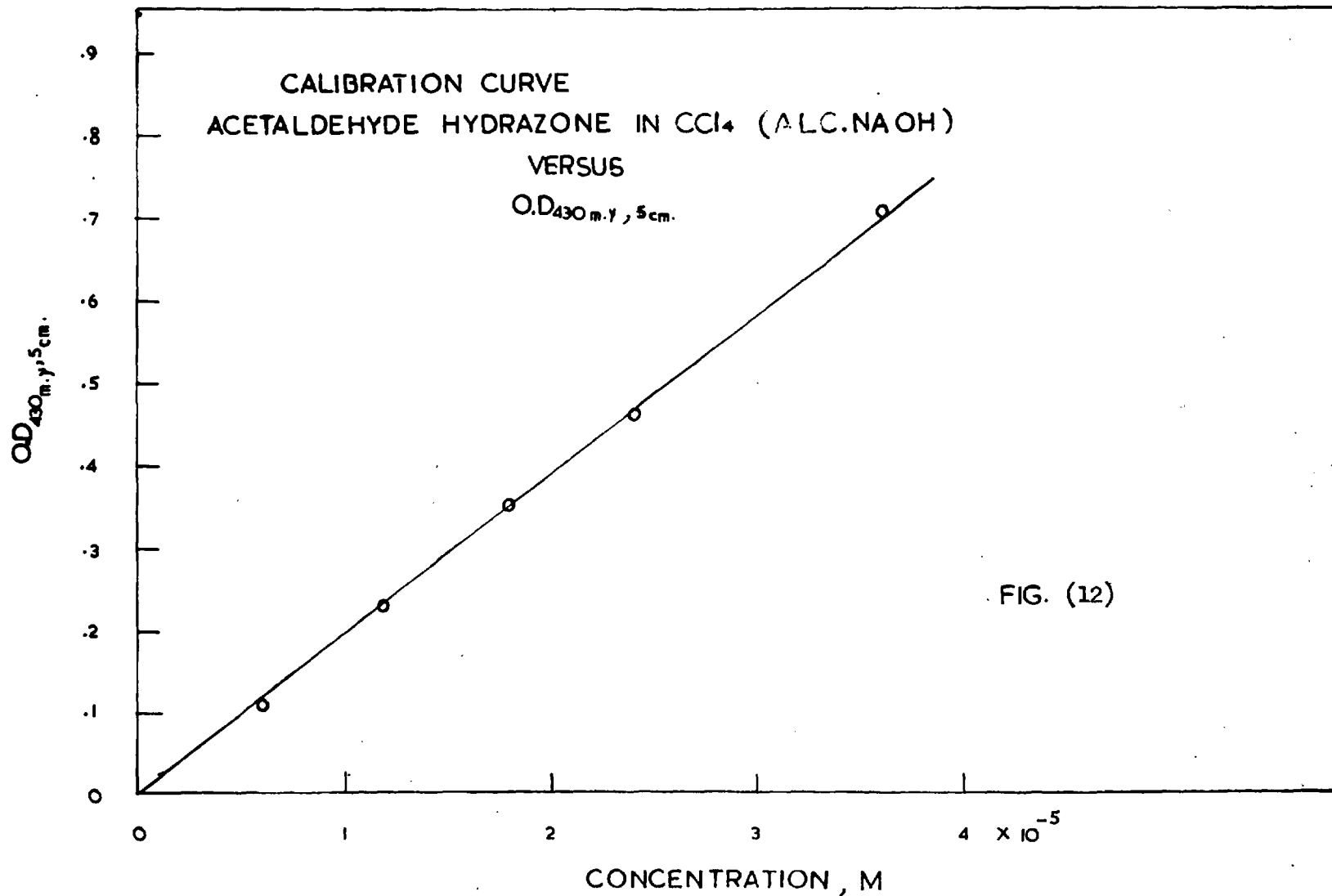
SPECTRACORD

ACRYLALDEHYDE D.N.P.H IN CCl₄ (ALC. NaOH)

4×10^{-5} M

FIG.(13)

CALIBRATION CURVE
ACRYLALDEHYDE HYDRAZONE IN CCl_4 (ALC. NaOH)
VERSUS
$O.D_{402 m \cdot \gamma}$, 5 cm.

FIG. (14)

SPECTRACORD

CROTONALDEHYDE HYDRAZONE IN CCl₄   (ALC.NaOH)

2.66×10^{-5} M

FIG. (15)

CALIBRATION CURVE
CROTONALDEHYDE HYDRAZONE IN CCl$_4$ (ALC.NaOH)
VERSUS
O.D$_{455m.\gamma}$, 1 CM.

FIG. (16)
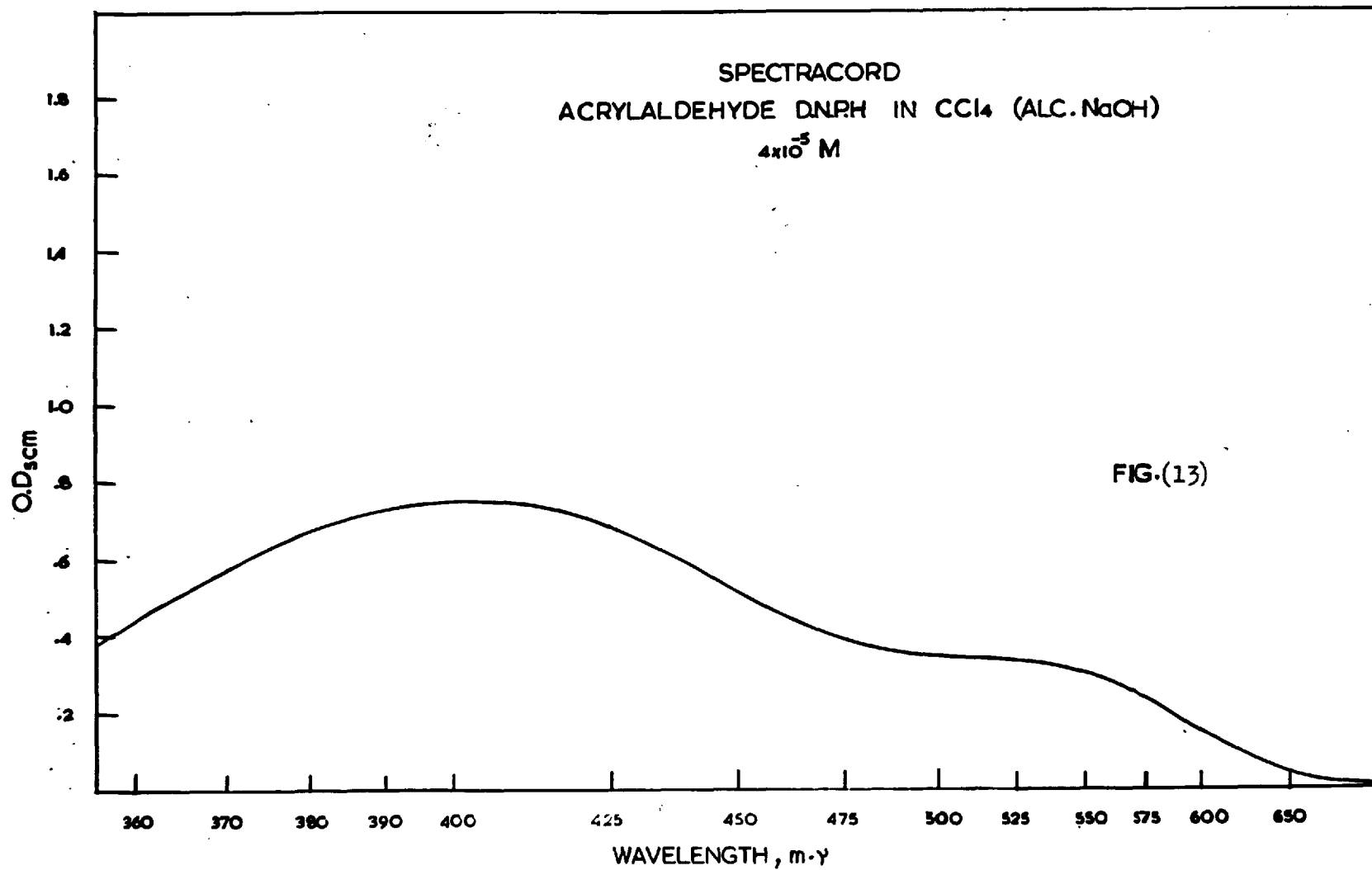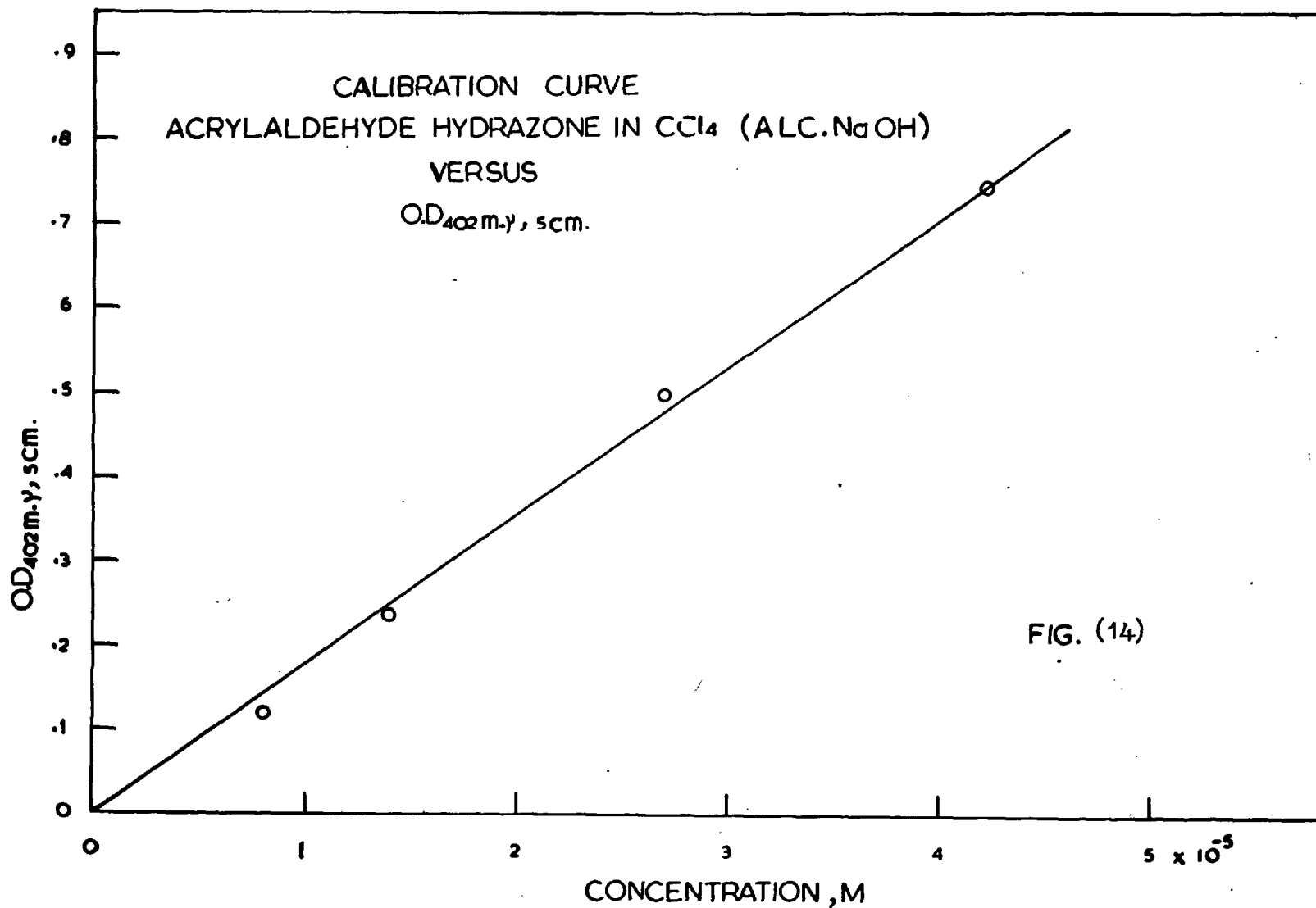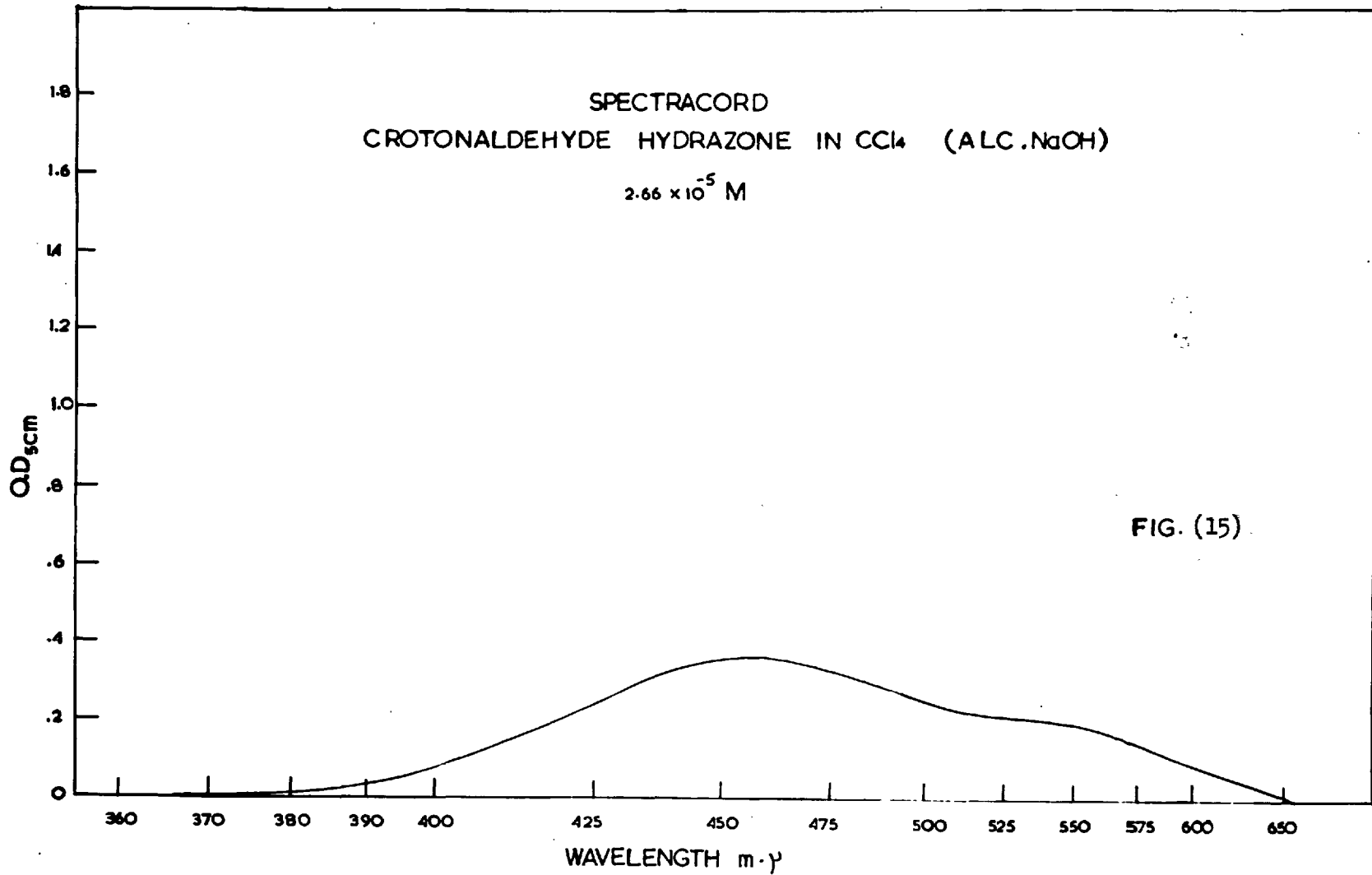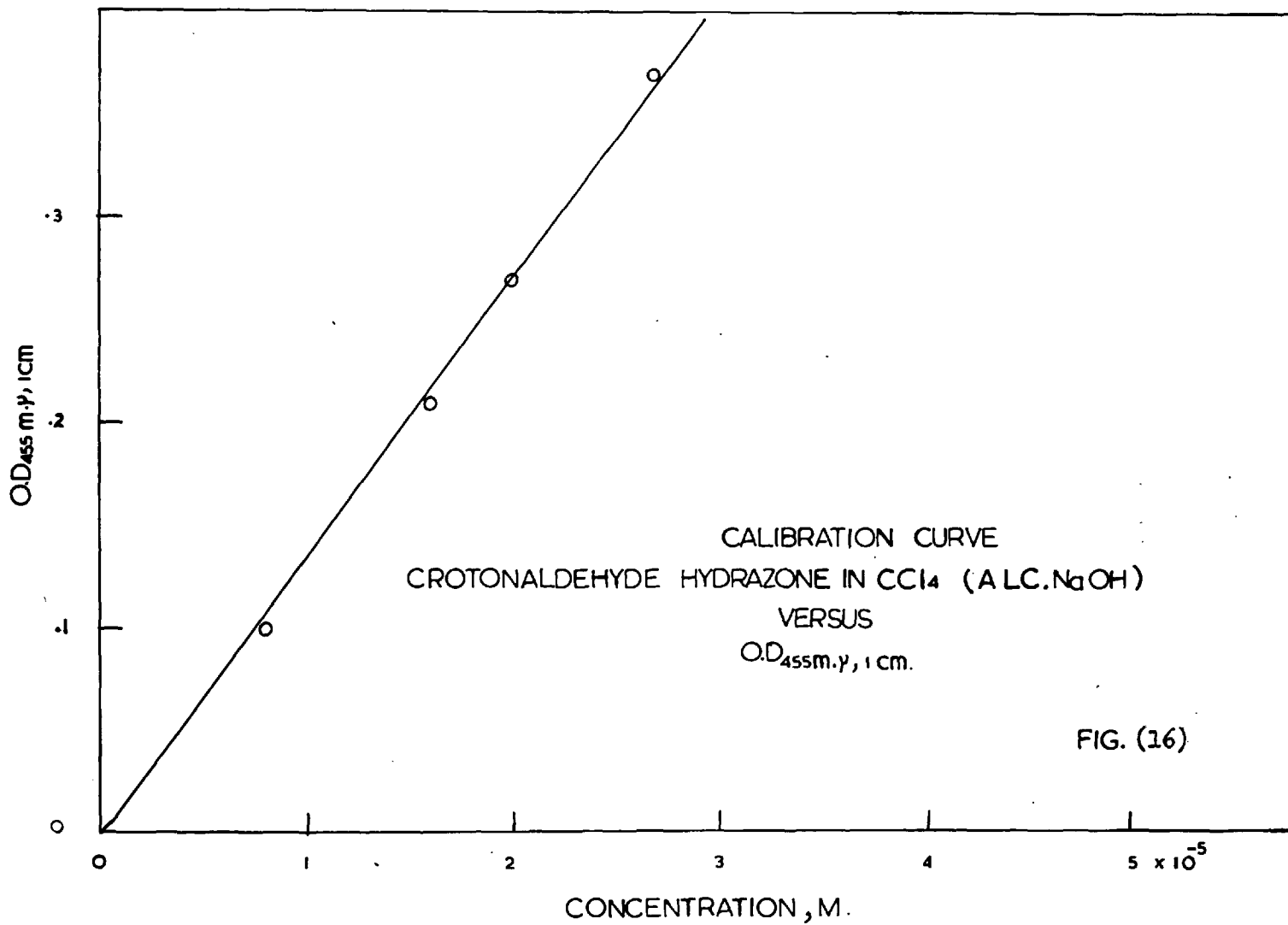
Glycolaldehyde reacts with 2:4 dinitrophenyl hydrazine to form the same osazone as that of glyoxal. However the mechanism of its formation is still an open question (123). Glyoxal and glycolaldehyde osazone in CCl_4 (alc.NaOH) showed identical spectra with a maximum absorption at 570 mμ and the colour was stable for at least 2 hours. Figs.(17), (18), (19) and (20).

Table (6) shows some properties of the hydrazones examined.

Table (6).

2:4 dinitrophenyl hydrazone in CCl_4(0.1 N alc. NaOH).

Compound.	Max.absorption (mμ)	E x 10^{-3}.
Formaldehyde	430	8
Acetaldehyde	430	3.9
Acrylaldehyde	402	3.6
Crotonaldehyde	455	14
Glyoxal	570	13.2
Glycolaldehyde	570	13.2

(5) Ethylene glycol.

Ethylene glycol was tested for by a modification of the method of Tompsett and Smith (124). The method developed was to oxidise ethylene glycol to formaldehyde with periodic acid, remove the aldehyde by distillation, and determine colorimetrically the formaldehyde as D.N.P.H. in alcoholic sodium hydroxide instead of with chromotropic acid as suggested in the original method.

SPECTRACORD

GLYOXAL DIHYDRAZONE IN CCl₄ (ALC. NaOH)

4.2×10^{-5} M.

FIG. (17)

WAVE LENGTH, m·γ

CALIBRATION CURVE.
GLYOXAL DIHYDRAZONE IN CCl4 (A L.C. NaOH)
VERSUS
$O.D_{570\,m\cdot\gamma,\,I\,CM}$

FIG. (18)

CONCENTRATION, M.

SPECTRACORD

GLYCOLALDEHYDE DIHYDRAZONE IN CCl_4 (ALC. NaOH)

4.2×10^{-5} M

FIG. (19)

WAVELENGTH , m·ɣ

CALIBRATION CURVE

GLYCOLALDEHYDE DIHYDRAZONE IN CCl₄ (ALC.NaOH)

VERSUS

O.D.570 m.ɣ, 1cm

FIG. (20)

CONCENTRATION, M.

92.

The periodic acid reagent (0.01 M) was prepared by dissolving 1.07g sodium periodate in 500 ml. 0.15 M sulphuric acid. The procedure was to add 5 ml. of periodic acid reagent to 25 ml. of a standard solution of ethylene glycol (10^{-5} M) in a distillation flask, then to add 1 ml. of concentrated sulphuric acid to the mixture. Steam was then introduced into the flask, and the vapours which contained any volatile aldehyde passed through a water condenser. The condensate was received in 5 ml. of the hydrazine reagent, and formaldehyde was determined as before. This determination showed that ethylene glycol was quantitatively oxidised to formaldehyde according to :

$$CH_2OH.\ CH_2OH + HIO_4 \longrightarrow 2\ HCHO + HIO_3 + H_2O$$
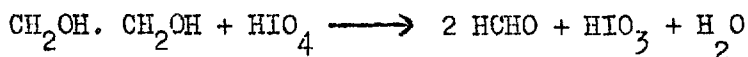
according to which one mole of ethylene glycol produces 2 moles of formaldehyde. However, other expected irradiation products such as glyoxal, glycolaldehyde and formic acid produced an aldehyde under the conditions of the test. Blank tests on these compounds using the periodic acid method showed that 1 mole of glyoxal produced 2 moles of aldehyde, 1 mole glycolaldehyde produced 1 mole of aldehyde, and 1 mole formic acid produced 1 mole of aldehyde. The nature of this aldehyde could not be identified with certainty but, since its 2:4 dinitrophenyl hydrazone in alcoholic sodium hydroxide absorbed at 430 mμ , it was probably formaldehyde or a mixture of formaldehyde with some other simple aldehyde. Because of this interference, the method could not be used for quantitative determination of ethylene glycol but only as an indirect indication of its presence, as will be discussed later.

(6) <u>Organic Acids.</u>

Paper chromatography was tried for the detection of organic acids using the method of Quale et al (125). The acids tested for were formic acid, oxalic acid, glyoxalic acid and glycolic acid, all as their ammonium salts. The solvent was prepared by adding 85 ml. of ethanol to 15 ml. of 0.1 N ammonia and the paper was Whatman No.4. At the low concentrations of acids used in our experiments, the B.D.H. Universal Indicator suggested in the method could only locate formic acid, although in Quale's work, using more concentrated spots, he was able to locate oxalic acid as well as formic acid. A more sensitive indicator was sought to locate oxalic acid and the other acids if they could be separated. Bromocresol green, Bromophenol, and 2-6 dichlorophenol were tried but the spots were not clearly identified and many times ghost spots appeared. Another indicator suggested by Pesez and Ferrora (126) was found to be promising. The indicator consisted of hydroxy-quinoline and zinc sulphate in water. Sprayed with this indicator, the spots showed fluorescence under U.V. light. This showed that using the above mentioned solvent, there was a good separation for the four acids. Unfortunately, the limit of sensitivity of this indicator was not low enough to be of value for the low concentrations of the irradiation products. Concentrating the irradiated solution by neutralisation to pH = 7 and evaporating did not help in reaching this limit. The method should prove of value if the organic acids are present in higher concentrations.

Other methods were then employed to detect the organic acids likely to be produced in the irradiated solutions. These were colour reactions specific for the acid tested for, without interference from the other acids if present. The irradiated solutions were neutralised with dilute sodium hydroxide to pH = 7 and concentrated by evaporation and then tested for the organic acids by the following methods :

a) Glyoxalic acid.

This was tested for by the method of Eegriwe (127). This depends on the fact that when glyoxalic acid and pyrogallol carboxylic acid are brought together in the presence of excess concentrated sulphuric acid, a blue colour develops. The procedure was to add a little solid pyrogalol carboxylic acid to one drop of the tested solution, in a micro test tube, and then 2 drops of concentrated sulphuric acid. The mixture was cooled by plunging the test tube into water and another 0.5 ml. additional sulphuric acid was added. The mixture was then kept for 30 minutes in warm water (40°C.). A light to dark blue colour indicates a positive response. Limit of identification is 1 γ glyoxalic acid (10^{-6}g) per drop.

b) Glycolic acid.

The method used to detect this acid was that of Calkins(128). The reagent used was 2:7 dihydroxynaphthalene (0.01g in 100 ml. concentrated sulphuric acid) which reacts with glycolic acid in

sulphuric acid medium to form a violet-red compound. Formaldehyde and other aldehydes which would interfere, were removed by forming hydrazone derivatives and extracting both reagent and derivatives with ethyl acetate as suggested by Garrison (129). The procedure was to add a drop of the test solution to 2 ml. of the reagent in a micro test tube and heat for 10 - 15 minutes in a water bath. The limit of identification is 0.2 γ glycolic acid/drop.

c) Oxalic acid.

This was tested for by thiobarbituric acid according to the method of Feigl (130). The procedure was to evaporate one drop of the test solution with 2 drops of concentrated ammonium hydroxide in a micro test tube. Some thiobarbituric acid was then added and the test tube was placed in a bath at $130^{\circ}C$. The temperature was then increased to $150^{\circ}C$. If oxalic acid was present, a red product, soluble in alcohol would be rapidly formed. Limit of identification is 1.6 γ' oxalic acid/drop.

d) Formic acid.

This acid was detected by the method of Feigl (131). When formic acid or an alkali formate is warmed with mercuric chloride in acetic acid - acetate buffered solution, white, crystalline mercurous chloride precipitates :

$$2 \, HgCl_2 + HCOO^- \longrightarrow Hg_2Cl_2 + CO_2 + 2 \, Cl^- + H^+$$
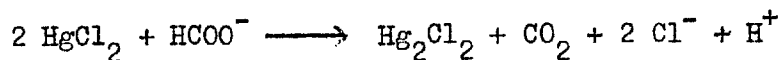
Small amounts of mercurous chloride can be detected by the reaction with ammonia (blackening due to finely divided mercury) :

$$Hg_2Cl_2 + 2 \, NH_3 \longrightarrow HgNH_2Cl + NH_4Cl + Hg$$
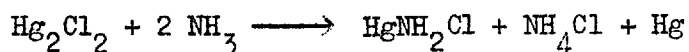
The procedure was to place a drop of the test solution in a micro crucible and add one drop of 10% mercuric chloride solution and one drop of buffer solution (1 gm.sodium acetate and 1 ml.glacial acetic acid per 100 ml. water). The mixture was brought to dryness in the oven at 100°C. (excluding light). The evaporation residue was then taken up in a drop of water and a drop of 0.1 N ammonia added. If formic acid was present, a black colour would appear. Limit of identification is 5 **γ** formic acid/drop.

For quantitative determination of formic acid the method of Grant was used (132). This depends on the reduction of formic acid by Mg and HCl to formaldehyde and its estimation by chromotropic acid. The method was developed using 30% perchloric acid which seemed to permit more efficient reduction of formic acid than hydrochloric acid, thus adding to the sensitivity of the method. The 2:4 dinitrophenyl hydrazine method to determine formaldehyde was used instead of the chromotropic acid method. The procedure was to add 0.5 c.c of the formic acid solution to a 10 cm. length of magnesium ribbon (kept in a desiccator containing sodium hydroxide pellets to minimise corrosion from air) in a test tube immersed in iced cold water. 0.50 ml. of 30% perchloric acid was added dropwise, taking 10 minutes to prevent any losses of formaldehyde due to a sudden rise in temperature from the heat of the reaction. The solution was then added to 1 ml. of hydrazine reagent, and the magnesium ribbon was washed twice with 5 ml.water and the wash water added to the hydrazine

reagent. After thirty minutes, the hydrazone formed was extracted twice with 10 ml. and 2 ml. CCl_4. To the CCl_4 extract, 1 ml. of alcoholic sodium hydroxide was added in a 25 ml. volumetric flask and ethyl alcohol was added to the mark. The absorption was measured at 430 mμ using 4 cm. cells, using the standard decay curves. Fig.(21) shows the calibration curve of formic acid using this procedure.

CALIBRATION CURVE OF FORMIC ACID
REDUCTION TO FORMALDEHYDE

FIG. (21)
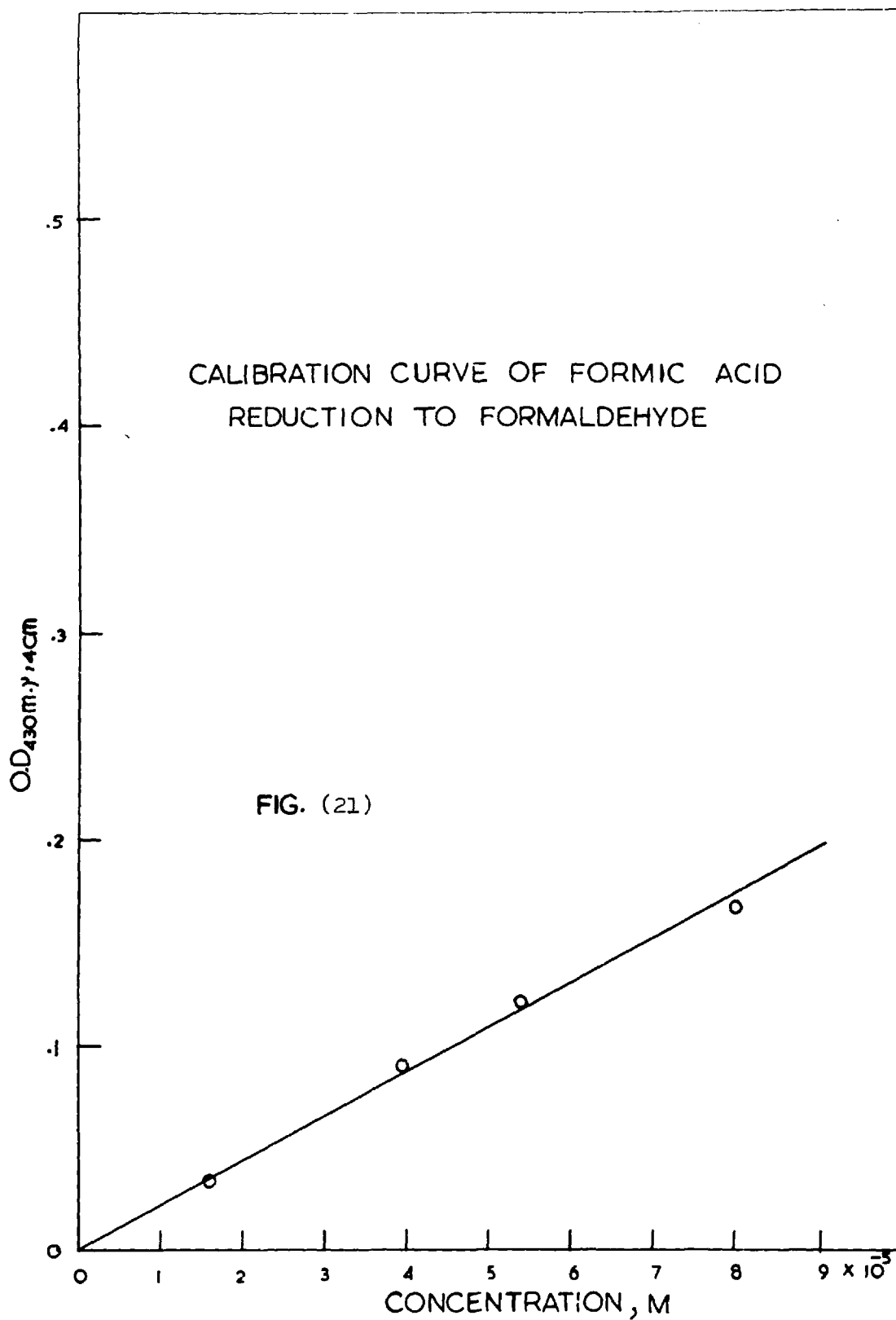
Chapter III   Results.

(A). <u>Mixtures of carbon monoxide and acetylene
in neutral solution.</u>

Deaerated solutions of acetylene in neutral water $(1.2 \times 10^{-2} M)$ were irradiated to a dose of 9000 rads. The irradiated solutions were tested for aldehydes by the 2:4 dinitrophenyl hydrazine method. The hydrazine reagent was added to the irradiated solution and the hydrazones formed were extracted into carbon tetrachloride. Fig.(22) shows the absorption spectra of the hydrazones in CCl_4 after the addition of alcoholic sodium hydroxide. It is noted that there are two broad peaks at about 430 mμ and about 570 mμ.. These should correspond to the products found by Weiss and co-workers using paper chromatography (1), i.e. acetaldehyde (maximum absorption, 430 mμ), crotonaldehyde (maximum absorption 455 mμ) and glycolaldehyde (maximum absorption 570 mμ).

Deaerated solutions of mixtures of acetylene $(1.2 \times 10^{-2} M)$ and carbon monoxide $(5 \times 10^{-4} M)$ were irradiated for 9000 rads. The hydrazones were extracted into carbon tetrachloride, and alcoholic sodium hydroxide was added as before. Fig.(23) shows the absorption spectra of the hydrazones in carbon tetrachloride after the addition of alcoholic sodium hydroxide. The same two broad peaks occur at about 430 mμ and about 570 m μ, showing that the same aldehydes may be found as in the case of acetylene alone. However, it is clear that the yield of total aldehydes produced is only about half that from acetylene alone.

FIG. (22)

SPECTRACORD

IRRADIATION OF C_2H_2 SOLUTION , D.N.P.H IN CCl_4 (A.L.C.NaOH)

C_2H_2 PRESSURE $=$ 20cm Hg

C_2H_2 CONC. $=$ 1.10×10^{-2} M

DOSE RATE $=$ 26000 RADS/HOUR

DOSE $=$ 9000 RADS

SPECTRACORD

IRRADIATION OF C_2H_2+CO SOLUTION , D.N.P.H IN CCl_4 (ALC.NaOH)

C_2H_2 CONC. $=$ 1.10×10^{-2} M

CO CONC. $=$ 4.50×10^{-4} M

DOSE RATE $=$ 26000 RADS/HOUR

DOSE $=$ 9000 RADS.

FIG. (23)
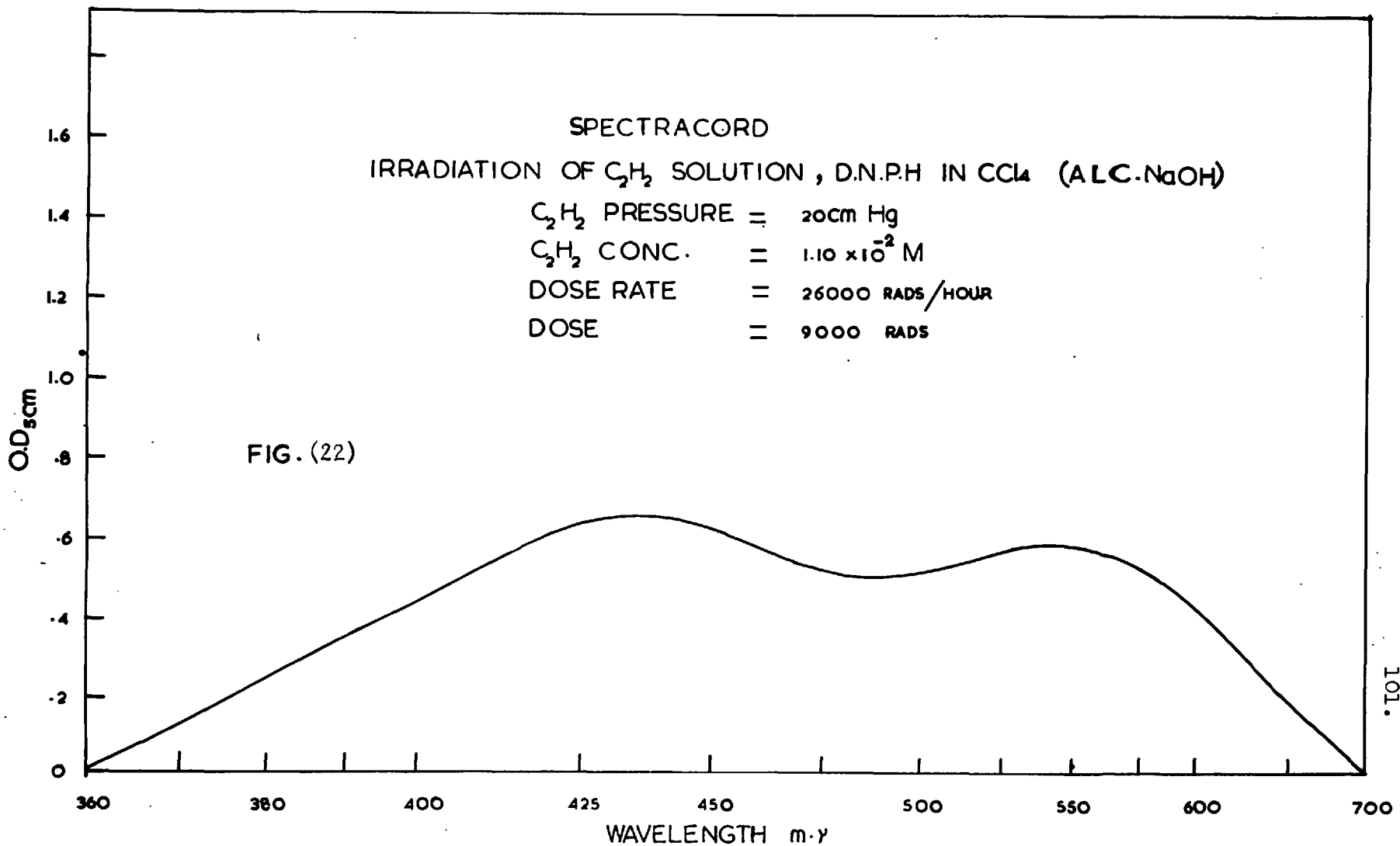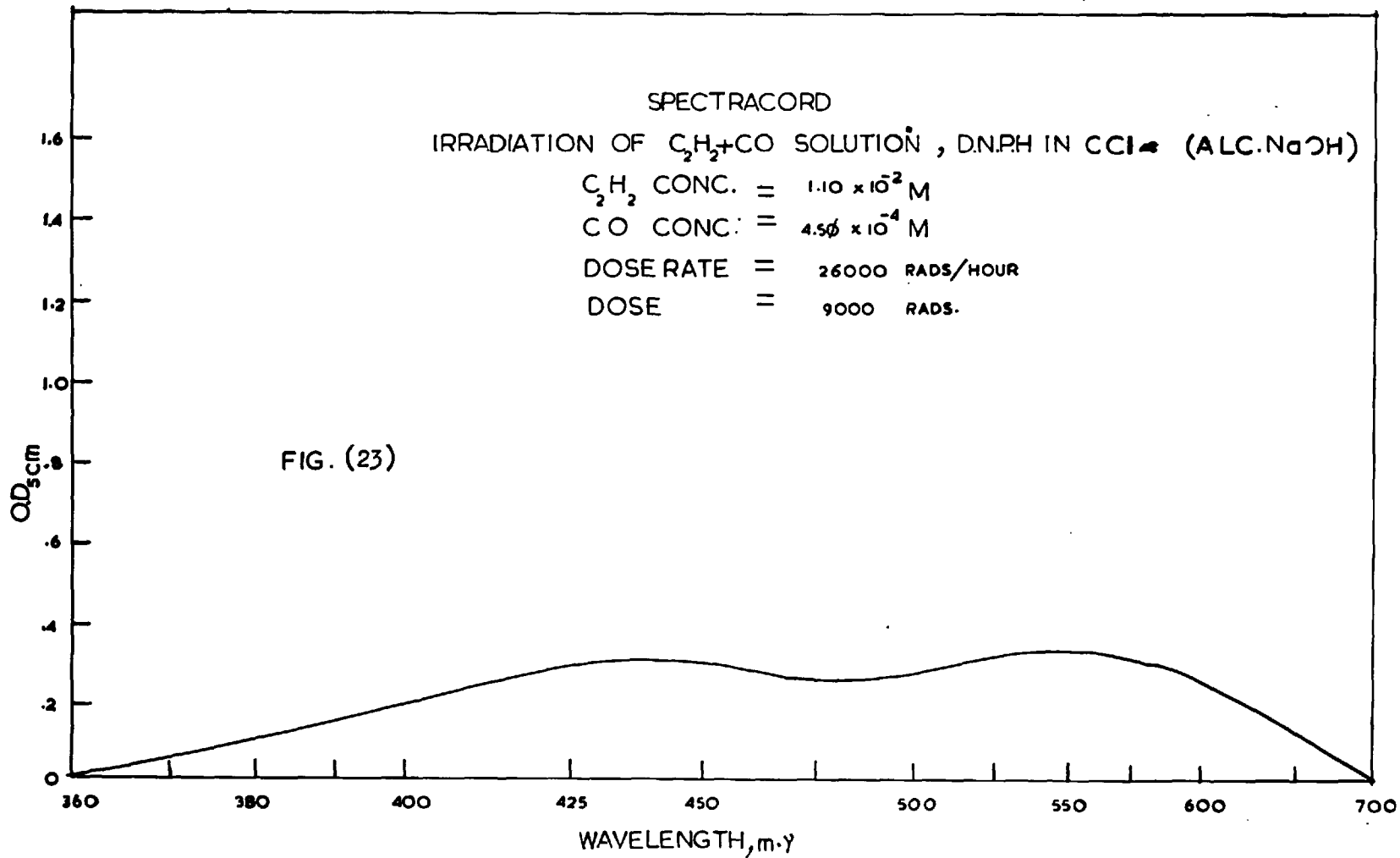
(B). Aqueous solutions of carbon monoxide.

The formation of hydrogen as a function of dose is shown in Fig.(24). The limited accuracy of the hydrogen determination at the lowest doses makes it difficult to assess values of the initial yields. However, it is clear that hydrogen is an important product, probably partly   a secondary product (see Discussion). The experimental values for the hydrogen yield obtained in the different irradiated solutions are shown in Table (7).

Table (7).

Hydrogen yields in irradiated CO-solutions.

Dose (rads).		26000			52000			78000	
Solution.	mm. H_2.	Vol-ume.	H_2 c.c.	mm. H_2	Vol-ume.	H_2 c.c.	mm. H_2	Vol-ume.	H_2 c.c.
		23°C, 1 atm	N.T.P.		23°C, 1 atm	N.T.P.		23°C, 1 atm	N.T.P.
0.1 N H_2SO_4	27	0.063	0.058	57	0.132	0.122	75	0.174	0.161
10^{-4}N H_2SO_4	13	0.029	0.027	27	0.063	0.058	42	0.095	0.09
Neutral.	12	0.028	0.026	24	0.055	0.051	36	0.083	0.077
2×10^{-4}M Fe^{++}	30	0.07	0.065	61	0.136	0.13	84	0.196	0.181
2×10^{-4}M Fe^{+++}	24	0.055	0.051	45	0.106	0.098	72	0.167	0.154
0.1 N NaOH	33	0.075	0.071	69	0.160	0.148	98	0.23	0.212

G-values at the lowest dose for which values can be given (26000 rads) have been calculated from the volume of the hydrogen gas produced.

HYDROGEN FORMATION VERSUS DOSE

DOSE RATE 26000 RADS/HOUR

G_{H_2}

(1) 0.1 N Na OH   1.2

(2) $2 \times 10^{-4} M Fe^{++}$ 1.1

(3) 0.1 N H_2SO_4 0.95

(4) $2 \times 10^{-4} M Fe^{+++}$ 0.86

(5) 10^{-4} N H_2SO_4 0.445

(6) NEUTRAL   0.440

FIGURE. (24)

DOSE, RADS.
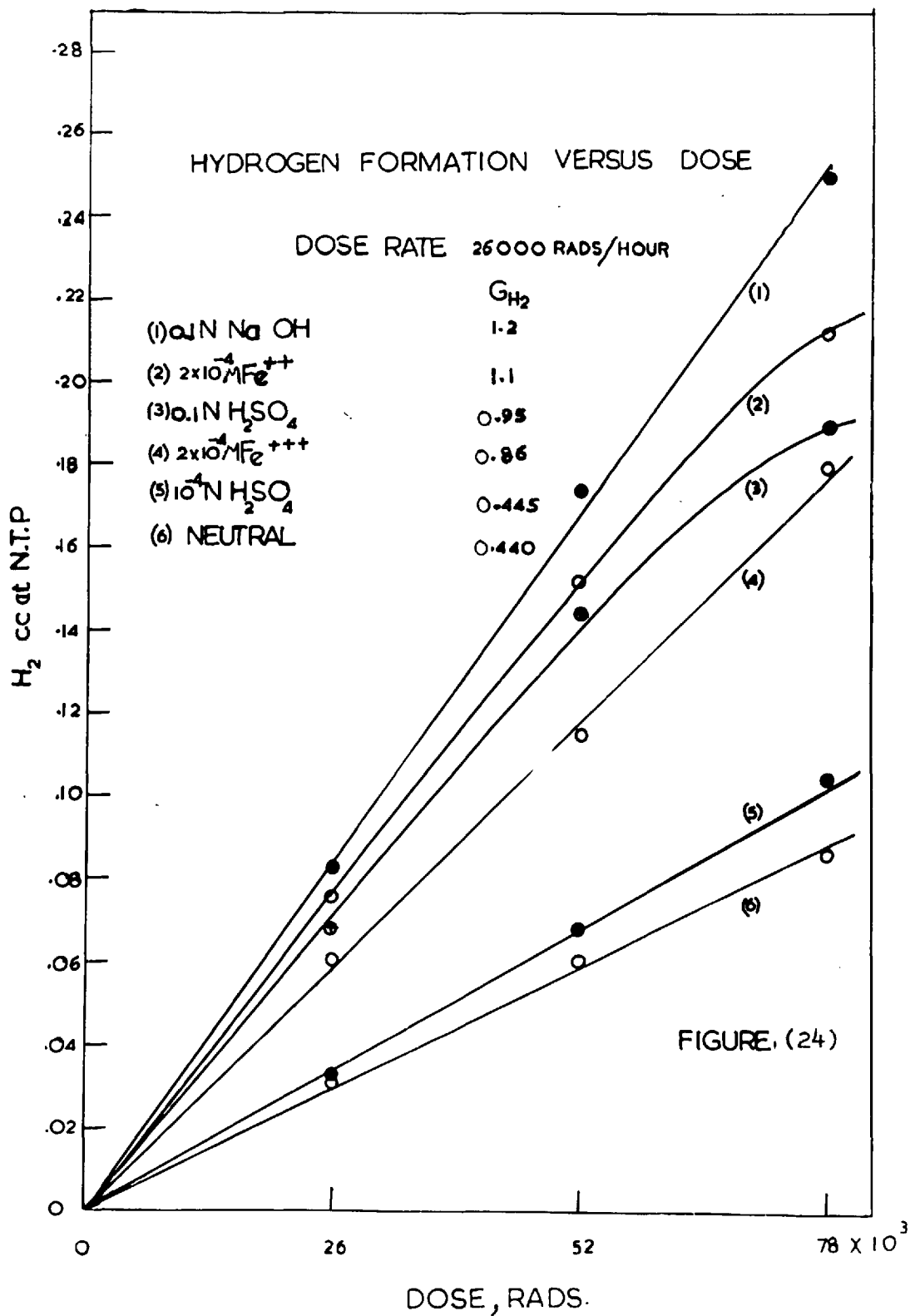
As an example of the method of calculation, we may consider the results for the 0.1 N H_2SO_4 solution irradiated for 26000 rads.

Height of hydrogen peak in chromatogram = 27mm.

From calibration curve Fig.(3) volume of hydrogen = 0.063 c.c. (at 23°C, 1 atm.)

Volume of hydrogen (N.T.P.) = $0.063 \times \dfrac{273}{296} = 0.058$ c.c.

molecules of hydrogen produced = $\dfrac{0.058}{22400} \times 6.03 \times 10^{23}$ molecules.

Energy input in 100g water = $26000 \times 6.24 \times 10^{13} \times 100$ e.v.

$G(H_2) = \dfrac{0.058 \times 6.03 \times 10^{23}}{22400 \times 26000 \times 6.24 \times 10^{13} \times 100} \times 100 = 0.95$

G-values of hydrogen calculated in this way are tabulated in Table (12). The values are significantly higher than the molecular yield from water in several cases. For pH 3.5, Fricke, Hart and Smith found the rate of hydrogen formation to be equal to 1.0 μ M per 1000 r (2), which corresponds to G = 0.9 (54).

The gas phase chromatography experiments also show no evidence for oxygen as an irradiation product. From the sensitivity of the method, the G-value for oxygen formation must be less than 0.1 and may be zero.

The experimental values of carbon dioxide yield obtained in the different irradiated solutions are shown in Table (18). The formation of carbon dioxide with increasing dose is shown in Fig.(25).

CO₂ FORMATION VERSUS DOSE

DOSE RATE 26000 RADS/HOUR

G_{CO_2}

(1) $2 \times 10^{-4}_M Fe^{++}$ 2.6

(2) $10^{-4} N H_2SO_4$ 2.65

(3) $0.1 N H_2SO_4$ 2.6

(4) NEUTRAL   2.75

(5) $2 \times 10^{-4}_M Fe^{+++}$ 3.5

FIGURE (25)

CO₂ cc at N.T.P
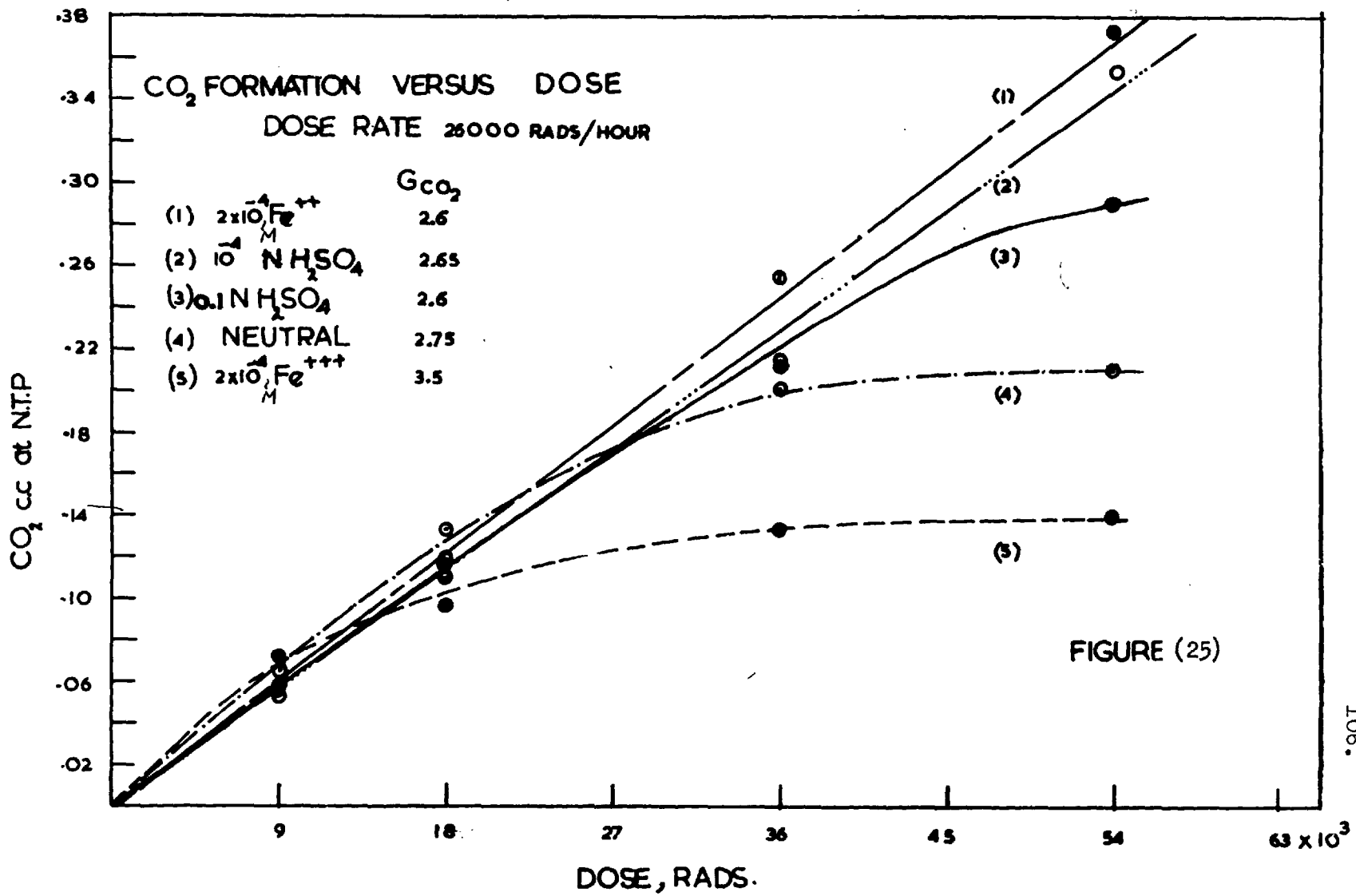
DOSE, RADS.

Table (8).

Carbon dioxide yields in irradiated . CO solutions.

Dose (rads) Solution.	9000			18000			36000			54000		
	Pressure mm. Hg.	c.c. 23°C 1 atm.	N.T.P.	Pressure mm. Hg.	c.c. 23°C 1 atm.	N.T.P.	Pressure mm. Hg.	c.c. 23°C 1 atm.	N.T.P.	Pressure mm. Hg.	c.c. 23°C 1 atm.	N.T.P.
0.1N H_2SO_4	0.075	0.058	0.054	0.142	0.11	0.100	0.278	0.215	0.198	0.375	0.29	0.268
10^{-4}N H_2SO_4	0.076	0.059	0.055	0.155	0.12	0.110	0.284	0.22	0.203	0.465	0.36	0.332
Neutral.	0.079	0.061	0.056	0.168	0.13	0.120	0.259	0.20	0.184	0.258	0.20	0.184
$2x10^{-4}$MFe^{++}	0.075	0.058	0.054	0.142	0.11	0.100	0.324	0.25	0.23	0.478	0.37	0.342
$2x10^{-3}$MFe^{++}	0.038	0.029	0.027	-	-	-	-	-	-	-	-	-
$2x10^{-4}$MFe^{+++}	0.103	0.078	0.072	0.116	0.09	0.083	0.074	0.135	0.124	0.181	0.14	0.129
$1x10^{-3}$MFe^{+++}	0.105	0.079	0.073	-	-	-	-	-	-	-	-	-

G-values at a dose of 9000 rads have been calculated for the different irradiated solutions from the volume of carbon dioxide evolved. An example of the procedure is as follows :

In 0.1 N sulphuric acid solution irradiated for 9000 rads pressure of CO_2 on Macleod gauge = 0.075 mm. Hg.

From calibration curve Fig.(4), value of CO_2 = 0.058 c.c. at 23°C, 1 atm.

Volume of CO_2 at N.T.P. $= 0.058 \times \dfrac{273}{296} = 0.054$ c.c.

molecules of CO_2 produced $= \dfrac{0.054}{22400} \times 6.03 \times 10^{23}$ molecules.

Energy input in 100g water $= 9000 \times 6.24 \times 10^{13} \times 100$ e.v.

$$G(CO_2) = \frac{0.054 \times 6.03 \times 10^{23}}{22400 \times 9000 \times 6.24 \times 10^{13} \times 100} \times 100 = 2.6$$

G-values of carbon dioxide for different solutions have been calculated in the same manner and are tabulated in Table (12). The yield of carbon dioxide does not vary very much with acidity, $G(CO_2)$ being 2.6 in 0.1N sulphuric acid and 2.75 in neutral water. No attempt was made to determine carbon dioxide or carbonate in 0.1N sodium hydroxide. In solutions containing ferrous ions, the carbon dioxide yield was dependent on ferrous concentration, being $G = 2.6$ in 2×10^{-4}M Fe^{++} and $G = 1.3$ in 2×10^{-3}M Fe^{++}. In solutions containing ferric ions the yield was $G(CO_2) = 3.5$ in 2×10^{-4}M Fe^{+++} and 3.55 in 1×10^{-3}M Fe^{++} which shows that the carbon dioxide yield is independent of the ferric ion concentration in this range.

For solutions of pH 3.5, Fricke, Hart and Smith found the initial carbon dioxide yield to be 2.45μM per 1000 r (2), which corresponds to $G = 2.2$ (54). For 0.8N sulphuric acid, Johnson and Weiss found $G(CO_2) = 2.53 \pm 0.11$ (56). All the determinations are therefore in reasonable agreement, remembering that Fricke, Hart and Smith used rather soft X-rays (110 kV) while Johnson and Weiss used hard X-rays, which should give results more similar to those from Co-60.

No hydrogen peroxide or other peroxides could be detected in any of the irradiated solutions, and therefore could not be formed with G greater than 0.05. The methods used to detect hydrogen peroxide were the titanium sulphate method, the iodide method, and

the thiocyanate method. At least two of these methods were used
to test for hydrogen peroxide in each of the examined solutions.

Detection of aldehydes in the irradiated solutions by the
2:4 dinitrophenyl hydrazine method showed that formaldehyde was
present. Proof of its formation was furnished by the rapid decay
of the absorption of its 2:4 dinitrophenyl hydrazone in CCl_4 (in
the presence of alcoholic sodium hydroxide) at 430 mμ . The
optical density decreased about 50% in 15 minutes, which is specific
for formaldehyde (117) and Fig.(5). Paper chromatography confirmed
the existence of formaldehyde and showed the existence of a dialde-
hyde in the irradiated solutions. This dialdehyde could be glyoxal
or glycolaldehyde since both give the same 2:4 dinitrophenyl hydrazone.
The spot gave a bluish-purple colour when sprayed with alcoholic
sodium hydroxide, a further proof of dialdehyde. The method of
Dechary et al (133) could not help in distinguishing between glyoxal
and glycolaldehyde because of the low concentration formed. However,
from the shape of the concentration of the dialdehyde vs. dose curve
Fig.(26), it seems likely that the dialdehyde is a primary product.
This would be consistent with the formation of glyoxal by dimerization
of CHO radicals, whereas glycolaldehyde could only be a secondary
product. The spectra of the 2:4 dinitrophenyl hydrazones from an
irradiated neutral carbon monoxide solution, in CCl_4 and in the
presence of alcoholic sodium hydroxide, is shown in Fig. (27).

DIALDEHYDE FORMATION VERSUS DOSE
DOSE RATE 26000 RADS/HOUR

FIG.(26)

$G_{DIALDEHYDE}$

(1) 0.1 N H_2SO_4 0.30
(2) 10^{-4} N H_2SO_4 0.24
(3) 0.1 N NaOH   0.07
(4) NEUTRAL   0.07
(5) 2×10^{-4} M Fe^{+++} 0.06
(6) 2×10^{-4} M Fe^{++} 0.06

DIALDEHYDE , M.

DOSE , RADS.

SPECTRACORD

IRRADIATION OF CO SOLUTION, D.N.P.H IN CCl₄ (ALC. NaOH)

CO CONC. $= 4.5\emptyset \times 10^{-4}$ M

CO PRESSURE $= 40$ cm Hg

DOSE RATE $= 26000$ RADS/HOUR

DOSE $= 9000$ RADS

FIG.(27)

O.D.$_{5cm}$
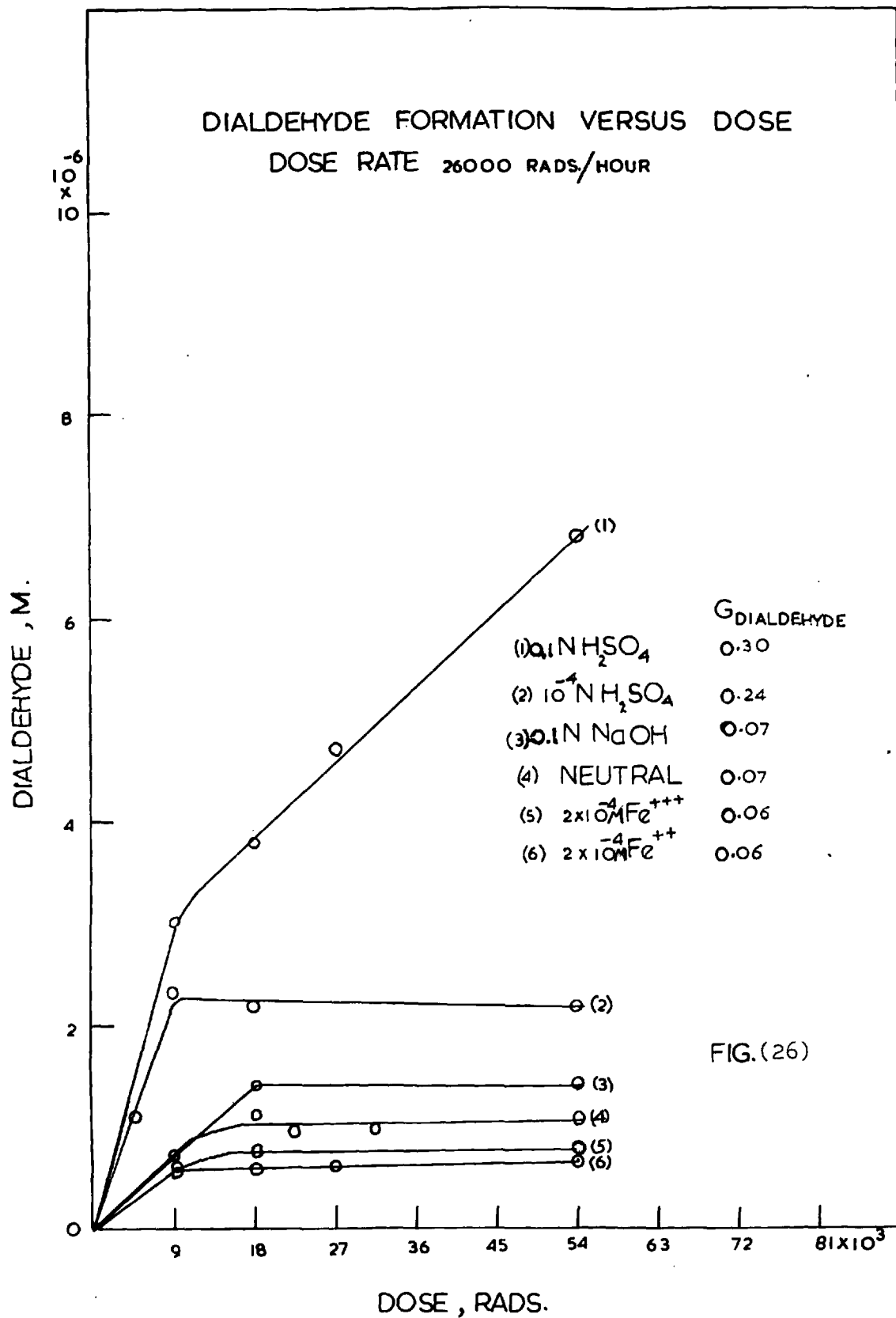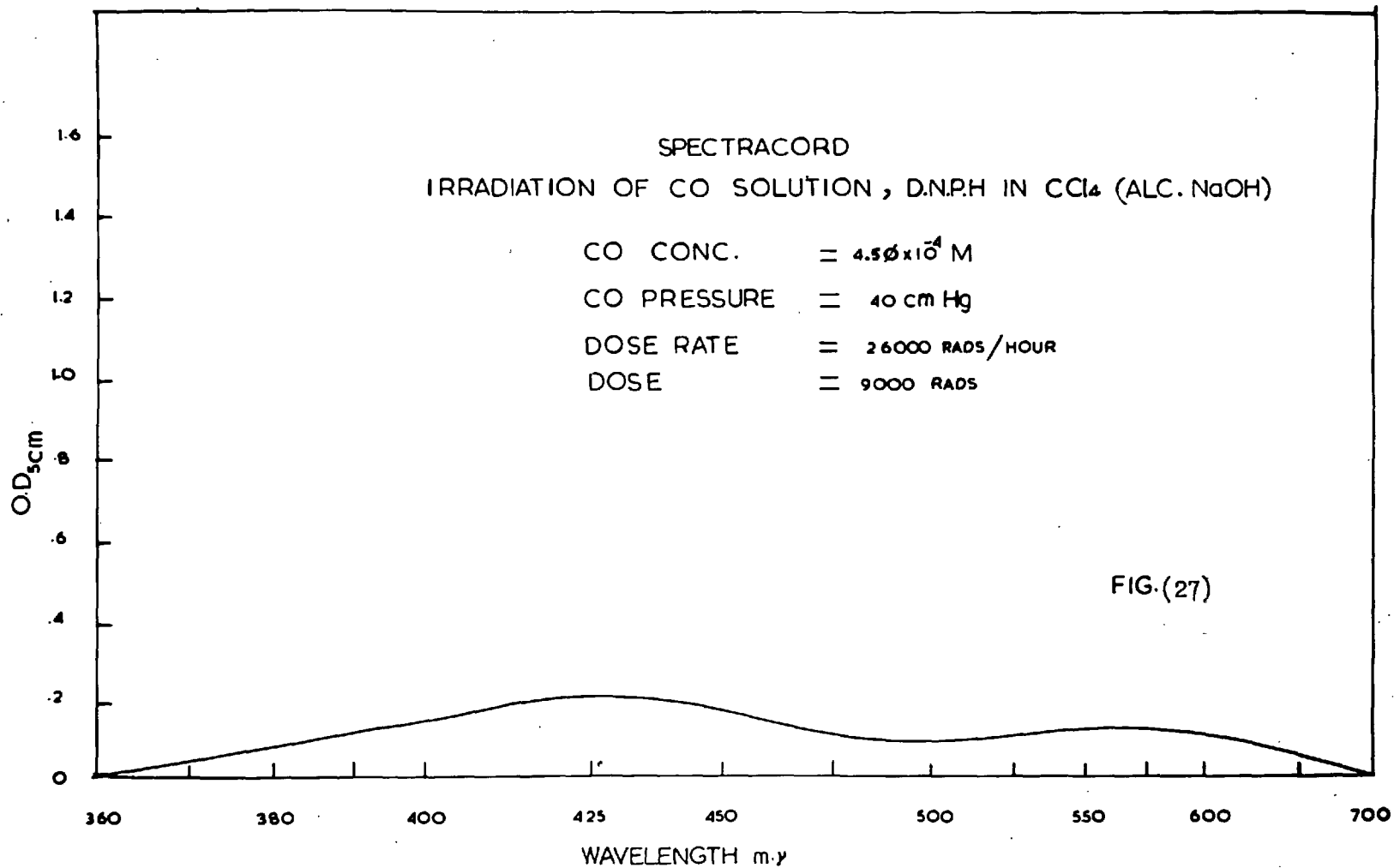
WAVELENGTH m.γ

It shows the absorption of formaldehyde hydrazone at 430 mμ and that of glyoxal at 570 mμ. Because the absorption maximum of the two compounds was at a different wave length, it was possible by taking measurements at 430 mμ and 570 mμ to determine both compounds quantitatively. Table (9) shows the experimental values of the absorption at these two wave lengths for the different irradiated solutions.

Table (9).

Irradiated CO solutions, D.N.P.H. in CCl$_4$ (alc. NaOH).

Dose (rads).	9000		18000		36000		54000	
Solution.	0.D5 cm.		0.D5 cm.		0.D5 cm.		0.D5 cm.	
	430mμ	570mμ	430mμ	570mμ	430mμ	570mμ	430mμ	570mμ
0.1N H$_2$SO$_4$	0.18	0.21	0.285	0.285	0.38	0.40	0.47	0.50
10^{-4}N H$_2$SO$_4$	0.18	0.17	0.19	0.17	0.18	0.17	0.17	0.17
Neutral	0.18	0.10	0.22	0.12	0.11	0.09	0.11	0.09
2x10^{-4}MFe^{++}	0.06	0.05	0.08	0.06	0.12	0.07	0.16	0.08
2x10^{-4}MFe^{+++}	0.09	0.06	0.13	0.08	0.20	0.09	0.25	0.11
0.1N NaOH	0.11	0.07	0.17	0.13	0.17	0.13	0.17	0.13

To calculate the concentration of both aldehydes : since glyoxal (or glycolaldehyde) D.N.P.H. does not absorb at 430 mμ (see Fig.(17)), the absorption at 430 mμ gives the concentration of formaldehyde directly (from the calibration curve Fig.(10)). As formaldehyde

D.N.P.H. absorbs at 570 m.μ with a value equal to 0.33 of its absorption at 430 mμ (see Fig.(5)), then glyoxal D.N.P.H. absorption can be readily obtained at 570 mμ and hence its concentration from the calibration curve Fig.(18). For example in 0.1N sulphuric at 9000 rads, the absorption at 570 mμ due to glyoxal $= 0.21 - \dfrac{0.18}{3} = 0.15$. The concentration of formaldehyde as a function of dose for various irradiated solutions is shown in Fig.(28) and that for glyoxal in Fig.(26). Once the concentration of the two aldehydes is known, their G-value can be calculated. Formaldehyde formation is $G = 0.5$ for acid and neutral solutions, and less in the presence of ferrous or ferric ions or 0.1 N sodium hydroxide. The initial yield for glyoxal formation is $G = 0.3$ in 0.1N sulphuric acid solution and decreases as the acidity decreases till it is almost zero in neutral and alkaline solutions. It is also very small in ferrous and ferric solutions. Fricke, Hart and Smith found the initial yield of formaldehyde at pH 3.5 to be 0.3μ M per 1000 r(2). This corresponds to $G = 0.27$ (54), in reasonable agreement with our result, considering the analytical methods available at the time.

The irradiated 0.1N sulphuric acid solutions of carbon monoxide were tested for organic acids. Specific colour tests had to be used since paper chromatography could not be applied owing to the low concentrations of the products (see Experimental).These tests showed that if glyoxalic, oxalic or glycolic acids were formed, the

FORMALDEHYDE FORMATION VERSUS DOSE
DOSE RATE 26000 RADS/HOUR

FIGURE (28)
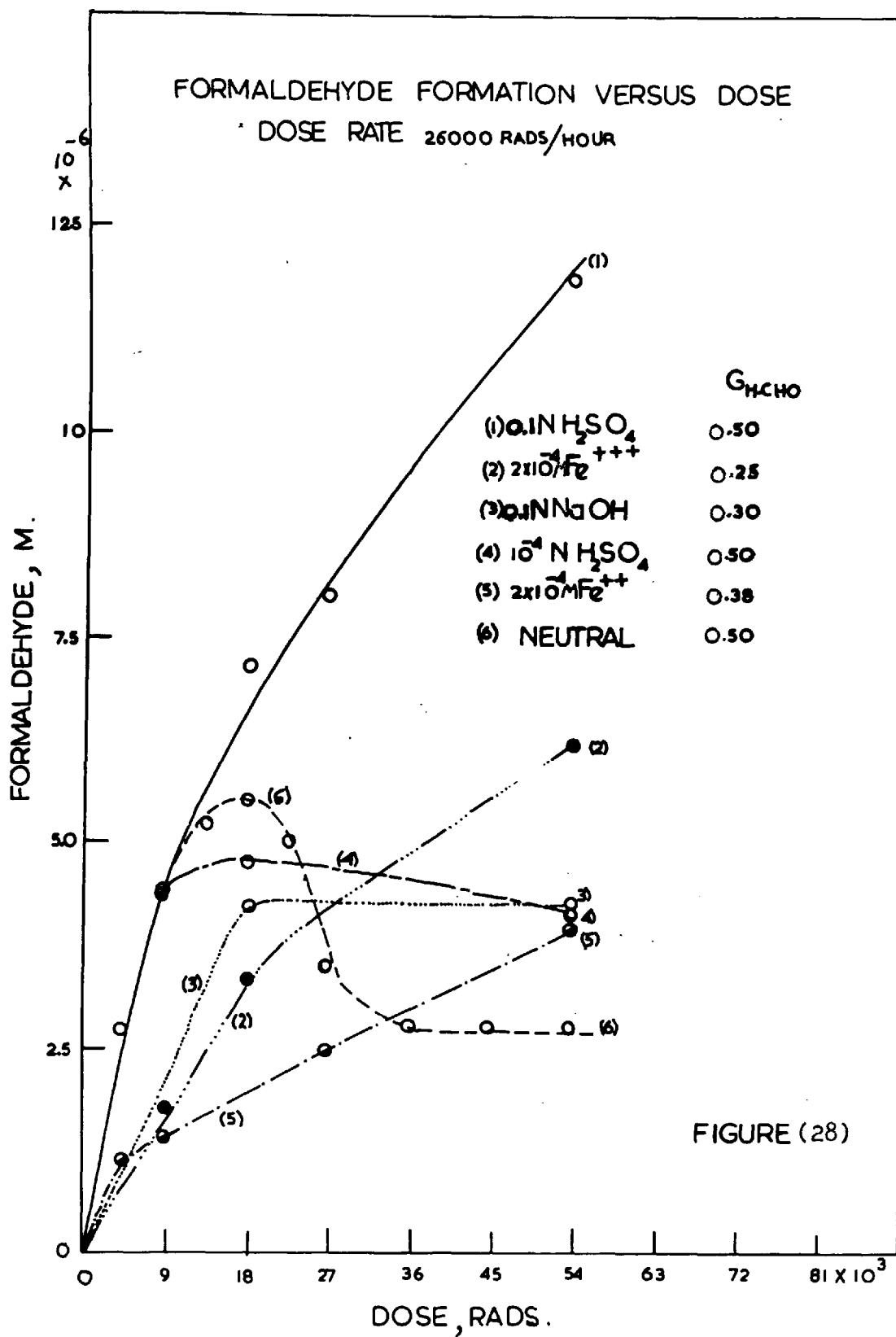
G-value must be less than 0.1. However, formic acid was found in some of the irradiated solutions. Formic acid was determined only in 0.1N sulphuric acid, in $2x10^{-3}M$ ferrous ion solution, and in 0.1N sodium hydroxide. It was found that a blank of carbon monoxide in 0.1 N sodium hydroxide did not produce formic acid at room temperature in the absence of radiation. Table (10) shows the experimental values obtained for the determination of formic acid through reduction to formaldehyde (see Experimental).

Table (10).

Formic acid yields in irradiated CO solutions.
in (M).

Dose (rads).	0.1 N H_2SO_4.	$2x10^{-3}M$ Fe^{++}.	0.1N NaOH.
6000	-	-	2.6×10^{-4}
9000	3.7×10^{-6}(3.8)	3.8×10^{-6}(3.6)	3.3×10^{-4}
12000	-	-	2.5×10^{-4}
15000	-	-	2×10^{-4}

The corresponding G-values for formic acid formation are : 0.1N H_2SO_4 = 0.4, $2 \times 10^{-3}M$ Fe^{++} solution = 0.4 and 0.1N sodium hydroxide = 44. Fig.(29) shows the formation of formic acid against dose in 0.1N sodium hydroxide solution. The yield reaches a maximum at about 9000 rads then it decreases. At 9000 rads the formic acid produced is 3.3×10^{-4}, i.e. about 75% of the carbon monoxide in

FORMIC ACID FORMATION VERSUS DOSE
DOSE RATE 28000 RADS/HOUR
0.1 N Na OH
CO CONC. $= 4.50 \times 10^{-4}$ M

$G_{HCOOH} = 44$

FIGURE (29)
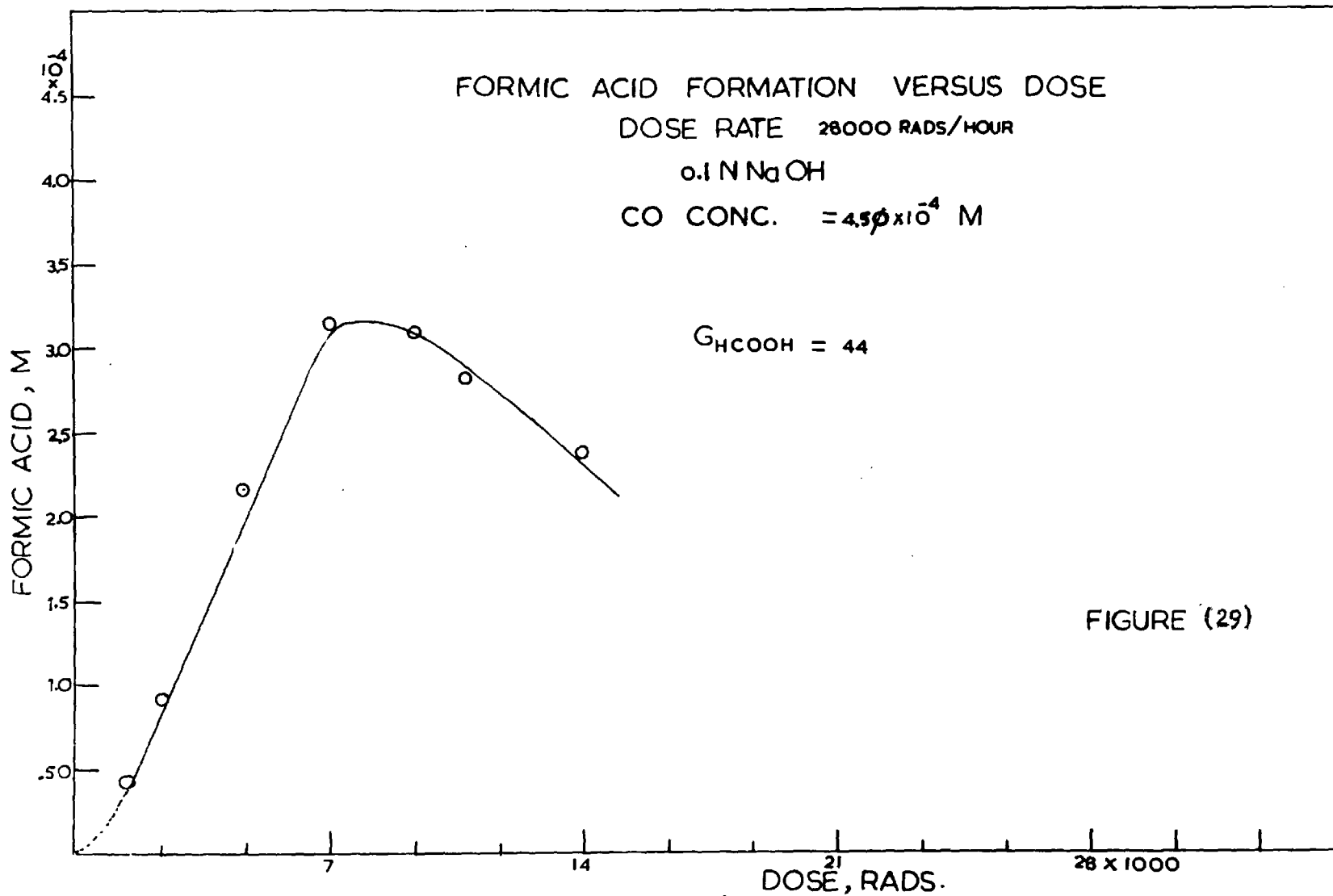
the solution has been consumed to give formic acid. Fricke, Hart and Smith give indirect evidence that formic acid is formed in high yield in alkaline solution on irradiation (2), in qualitative agreement with our result.

Ethylene glycol is a possible secondary irradiation product but could not be detected with certainty in the 0.1N sulphuric acid solutions due to interference from other irradiation products (see Experimental). However, from the material balance, glycol may be formed with $G \simeq 0.35$ in 0.1N sulphuric acid (see below).

In the experiments with ferrous ions present initially, ferric ions did not appear on irradiation, but in the experiments with added ferric ions, the yield of ferrous was $G = 6.4$ independent of ferric concentration in the range studied, as shown in Table (11).

<div align="center">

Table (11).

Fe^{+++} solution (M).	$G (Fe^{++})$.
1×10^{-4}	6.4
1.5×10^{-4}	6.44
2×10^{-4}	6.30
1×10^{-3}	6.4

</div>

Table (12) summarises the G-values of the various products in the irradiated solutions.

Table (12).

G-values in irradiated carbon.monoxide solutions.

	GH_2 (26000 rads).	GCO_2 (9000 rads).	GH_2O_2	GHCHO (9000 rads).	GCHO.CHO (9000 rads).	GHCOOH (9000 rads).	GFe^{++} (5000 rads).	GFe^{+++} (5000 rads).
$0.1N\,H_2SO_4$	0.95	2.6	0	0.5	0.3	0.4	-	-
$10^{-4}N\,H_2SO_4$	0.445	2.65	0	0.5	0.24	-	-	-
Neutral	0.44	2.75	0	0.5	0.075	-	-	-
$2\times10^{-4}M\,Fe^{++}$	1.1	2.6	0	0.38	0.06	-	0	0
$0.1N\,H_2SO_4$ $2\times10^{-3}M\,Fe^{++}$	-	1.3	-	-	-	0.4	0	0
$2\times10^{-4}M\,Fe^{+++}$	0.86	3.5	0	0.25	0.065	-	6.3	0
$0.1N\,H_2SO_4$ $1\times10^{-3}M\,Fe^{+++}$	-	3.55	-	-	-	-	6.4	0
$0.1N\,H_2SO_4$ 0.1N NaOH	1.2	-	0	0.3	0.07	44	-	-

Chapter IV.   Discussion.

(A). <u>Mixtures of carbon monoxide and acetylene in neutral solution.</u>

The addition of 5×10^{-4}M carbon monoxide to the 10^{-2}M

solution of acetylene appreciably reduced the yield of aldehydes.

This is an indication that carbon monoxide takes part in the free

radical reactions induced by radiation and that it probably competes

with acetylene for H atoms and OH radicals. No mechanism can be

given for the free radical reactions as no detailed analysis was

made for the products. However, the following reactions seem likely:

$$H + HC \equiv CH \longrightarrow CH_2 = CH \qquad \underline{\qquad} (1)$$

$$H + CO \longrightarrow CHO \qquad \underline{\qquad} (2)$$

$$OH + HC \equiv CH \longrightarrow OH.HC = CH \qquad \underline{\qquad} (3)$$

$$OH + CO \longrightarrow COOH \qquad \underline{\qquad} (4)$$
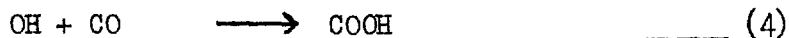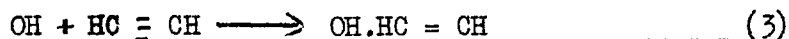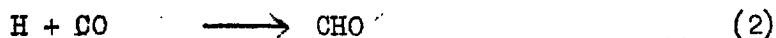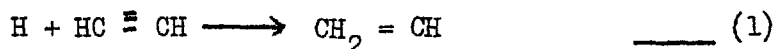
The free radicals resulting from reactions (1) to (4) may then react

further to produce various products. Further work on this system

would be of interest in view of the wide variety of products which

could conceivably be formed.

(B). <u>Aqueous solutions of carbon monoxide.</u>

(1) <u>0.1N sulphuric acid</u> :

In 0.1N sulphuric acid, the following mechanism would account

for the results obtained (at 9000 rads).

$$4.45\ H_2O \xrightarrow{\hspace{1cm}} 3.65\ H + 2.85\ OH + 0.4\ H_2 + 0.8H_2O_2 \underline{\hspace{1cm}}(0)$$

$$\underset{3.30\quad 3.30}{H + CO} \xrightarrow{\hspace{1cm}} \underset{3.30}{CHO} \underline{\hspace{1cm}}(1)$$

$$\underset{3.10\quad 3.10}{OH + CO} \xrightarrow{\hspace{1cm}} \underset{3.10}{COOH} \underline{\hspace{1cm}}(2)$$

$$\underset{1.45\quad 1.45}{CHO + CHO} \xrightarrow{\hspace{1cm}} \underset{1.45\quad\ 1.45}{CO + HCHO} \underline{\hspace{1cm}}(3)$$

$$\underset{0.3\quad 0.3}{CHO + CHO} \xrightarrow{\hspace{1cm}} \underset{0.3}{CHO.CHO} \underline{\hspace{1cm}}(4)$$

$$\underset{0.45\quad 0.45}{COOH + COOH} \xrightarrow{\hspace{1cm}} \underset{0.45\quad\ \ 0.45}{CO_2 + HCOOH} \underline{\hspace{1cm}}(5)$$

$$\underset{0.7\quad\ \ 0.7}{CHO + COOH} \xrightarrow{\hspace{1cm}} \underset{0.7\quad\ 0.7}{CO_2 + HCHO} \underline{\hspace{1cm}}(6)$$

$$\underset{0.35\quad 0.35}{H + HCHO} \xrightarrow{\hspace{1cm}} \underset{0.35\quad\ 0.35}{H_2 + CHO} \underline{\hspace{1cm}}(7)$$

$$\underset{0.55\quad\ \ 0.55}{OH + HCHO} \xrightarrow{\hspace{1cm}} \underset{0.55\quad\ 0.55}{H_2O + CHO} \underline{\hspace{1cm}}(8)$$

$$\underset{0.7\quad\ \ 0.7}{COOH + HCHO} \xrightarrow{\hspace{1cm}} \underset{0.7\quad\ 0.7}{CO_2 + CH_2OH} \underline{\hspace{1cm}}(9)$$

$$\underset{0.35\quad\ \ 0.35}{CH_2OH + CH_2OH} \xrightarrow{\hspace{1cm}} \underset{0.35}{CH_2OH.CH_2OH} \underline{\hspace{1cm}}(10)$$

$$\underset{0.8\quad\ \ 0.8}{COOH + H_2O_2} \xrightarrow{\hspace{1cm}} \underset{0.8\quad 0.8\quad\ 0.8}{CO_2 + H_2O + OH} \underline{\hspace{1cm}}(11)$$

The significance of the numbers in the equations will be explained below.

Reaction (0) is the generally accepted mechanism for the decomposition of water by γ-rays, where the species H and OH may exist in any of several possible forms. The numbers in this equation are the G-values given by Johnson and Weiss (78). Reactions (1),(3) and (4) were first introduced by Frankenburger in 1930 to explain

the formation of formaldehyde and glyoxal during the ultraviolet irradiation of carbon monoxide and hydrogen in the gas phase in the presence of mercury vapour (10). Evidence that reaction (2) can readily happen in aqueous solutions at room temperature has been put forward by Dainton and Hardwick (92). They suggested that the COOH radicals formed in reaction (2) may rearrange to form CO_2 + H or may stay as such. Either of these mechanisms would explain their quantitative results. In the present work GCO_2 = 2.6 in good agreement with the mechanism shown above, in which COOH does not rearrange. If COOH is slowly transformed to CO_2 + H, the GCO_2, GHCHO, GCHO.CHO and GHCOOH would have been much higher than the experimental values.
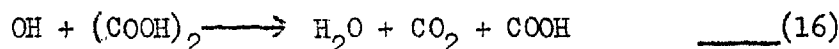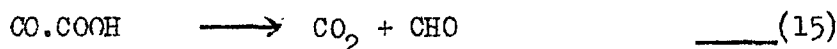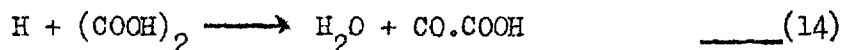
Also, if this rearrangement occurs, a chain reaction would have happened in the irradiation of deaerated dilute formic acid solutions according to :

$$H + HCOOH \longrightarrow H_2 + COOH \qquad \underline{\quad\quad}(12)$$

$$COOH \longrightarrow CO_2 + H \qquad \underline{\quad\quad}(13)$$
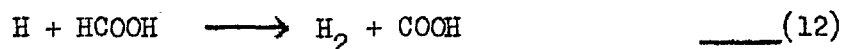
No chain reaction was found by Hart in the irradiation of this system. (58). For these reasons, it is most likely that the carboxyl radical does not rearrange in aqueous solutions under the conditions employed.

By a similar argument it can be shown that the radical COOH.CO, if it exists, does not decompose to CO_2 + CHO as suggested

by Draganić to explain the formation of formaldehyde and glyoxal
in the irradiation of oxalic acid aqueous solutions (134). In
this system Draganić suggested the following mechanism :

$$H + (COOH)_2 \longrightarrow H_2O + CO.COOH \qquad \underline{\qquad}(14)$$

$$CO.COOH \longrightarrow CO_2 + CHO \qquad \underline{\qquad}(15)$$

$$OH + (COOH)_2 \longrightarrow H_2O + CO_2 + COOH \qquad \underline{\qquad}(16)$$

The radical CHO may then react to form formaldehyde and glyoxal.
The G-value of the products were : $G(CO_2) = 7.8$, $G(H_2) = 0.46$,
$G(HCHO) = 0.08$, $G(CHO.CHO) = 0.004$ and $G-(COOH)_2 = 4.9$. The oxalic
acid concentration was above 2×10^{-2} M. The COOH.CO radical
would easily be formed in the irradiation of aqueous solutions of
carbon monoxide, and if it decomposes as suggested by Draganić, then
the yield of all the products would have been much higher than that
obtained.

Allen (135) points out that the Draganić mechanism for the
irradiation of oxalic acid ignores the finding of Fricke, Hart and
Smith (2) that $G(H_2)$ increases at lower oxalic acid concentrations
(at 10^{-4}M, $G(H_2) = 1.5$ and at 10^{-1}M, $G(H_2) = 0.5$). Allen suggests
that H adds to oxalic acid to form a complex which then reacts with
a second oxalic acid molecule. Hence Allen supports the view that
reactions (14) and (15) do not occur.

Reactions (5) and (11) are long accepted reactions for the
irradiation of deaerated formic acid solutions (58),(59) and (60).

Hydrogen peroxide could not be detected in this work, similarly
to
~~in~~ the case of formic acid, because of the chain reaction of
reactions (2) and (11). Reaction (6) is a possible hydrogen
abstraction reaction which has been postulated before (68).
Reaction (7) has previously been suggested for the irradiation of
dilute aqueous formaldehyde solutions(54). It is postulated here
to account for the production of hydrogen. Its occurrence in the
carbon monoxide solutions is justified because, as will be shown
later, hydrogen atoms react with formaldehyde about thirteen times
as fast as with carbon monoxide, so that once formaldehyde is
produced, reaction (7) will compete with reaction (1) as the con-
centration of carbon monoxide is rather low. Reaction (8) has been
suggested before by Pollard and Wyatt (136) and Norrish (13β) to
occur in the gas oxidation of formaldehyde. Reaction (9) was
suggested by Hart and Smithies to explain results in the γ-irradiation
of formaldehyde $(10^{-3}M)$ and formic acid solution (5M) (67), where
formaldehyde disappeared with a high yield without affecting the
yields of gaseous products. Like reactions (7) and (8), it would
be expected to occur in the carbon monoxide system once formaldehyde
builds up. The CH_2OH radical formed in reaction (9) would then
dimerize to form ethylene glycol (reaction (10)). The possibility
that CH_2OH radicals would form methyl alcohol and formaldehyde by
disproportionation is negligible as shown from the γ-irradiation of
aqueous methyl alcohol solutions/ (75). Weiss and co-workers found

indications that a glycol is formed in the γ-irradiation of carbon dioxide in aqueous solutions (80). In carbon dioxide solutions, both COOH radicals and formaldehyde are produced, thus satisfying the conditions for reaction (9).

We have attempted to investigate the material balance of the 0.1N sulphuric acid system at a dose of 9000 rads. At this dose the concentration of most products, except hydrogen, was high enough for quantitative determination but, although curve (3) of Fig.1 is drawn as a straight line, according to the mechanism discussed some of the hydrogen is a secondary product so that the hydrogen yield at 9000 rads would be less than the yield at higher doses. From Fig.1 the hydrogen yield at 27000 rads is $G(H_2) = 0.95$. Knowing that $GH_2^W = 0.4$, then the yield of hydrogen at 27000 rads due to reaction (7) $= 0.95 - 0.4 = 0.55$. The concentration of formaldehyde has increased non-linearly from zero at the beginning of the irradiation to $8.1 \times 10^{-6} M$ at 27000 rads (see Fig.28) and the carbon monoxide concentration has decreased from $4.5 \times 10^{-4} M$ to $3.2 \times 10^{-4} M$ (assuming G-CO $= 4.95$, which must be **approximately** true on any reasonable material balance). To estimate the ratio of the rate constants for reactions (7) and (1) we take the mean value of the formaldehyde concentration for the dose region up to 27000 rads to be $5 \times 10^{-6} M$ (see Appendix (2) for calculation of this value) and the corresponding carbon monoxide concentration to be $3.8 \times 10^{-4} M$.

The average G-value for hydrogen atoms which react with formaldehyde $g(7)$ is then given by

$$g(7) = g(1) \; \frac{k(7) \times 5 \times 10^{-6}}{k(1) \times 3.8 \times 10^{-4}} \qquad\qquad (17)$$

where $g(1)$ is the G-value for hydrogen atoms which react with carbon monoxide. Since $g(7) = 0.55$ and $g(1) + g(7) = GH^{W} = 3.65$, we find $\frac{k(7)}{k(1)} = 13.5 \pm 3$. This value is not very different from the value of 5.3 estimated from the ratio $\frac{kH + HCHO}{kH + H^{+} + Fe^{++}} = \frac{90 \times 10^{5}}{6.7 \times 10^{5}} = 13.4$ at pH = 1 obtained by Riesz and Hart using data in the gas phase (Table (13)), and the the ratio $\frac{kH + CO}{kH + H^{+} + Fe^{++}} = 2.5$

<u>Table (13)</u>.

<u>Approximate rate constants for R + H at 25°C.</u> (139).

	$k \times 10^{-5} l.mol^{-1}.sec^{-1}$.	pH
Fe^{+++}	48	2.1
Fe^{++}	6.7	2.1
O_2	10^4	—
HCOOH	19	3 and 1
CH_3OH	29	1
HCHO	90	1

obtained in the present work (see below). It may be noted from Table (13) that the rate constant for the reaction of H atoms with for-maldehyde is higher than that with other compounds which may be produced in the irradiated carbon monoxide solution such as formic
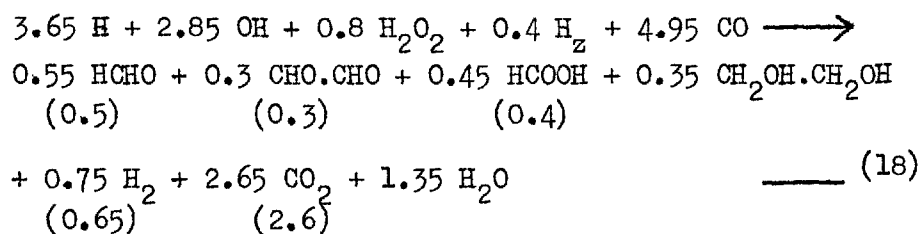
acid, which justifies the assumption that hydrogen is produced only through reaction (7). The ratio $\dfrac{k(7)}{k(1)}$ can now be used to calculate the hydrogen yield due to reaction (7) at 9000 rads, knowing that the arithmetic mean value of $[HCH\bar{O}]$ up to 9000 rads is $2.3 \times 10^{-6}M$ and of $[C\bar{O}]$ is $4.3 \times 10^{-4}M$. This G-value comes to 0.25 so that the measured $G(H_2)$ at 9000 rads should be 0.65. The stoichiometry of reactions (1) to (11) can now be worked out by trial and error, knowing the G-values of the products at 9000 rads, and that any radical which is produced must be consumed as shown in Table (14).

<u>Table (14).</u>

Radical	Produced or consumed per 100 e.v. at 9000 rads.
H	3.65
OH	3.65
CHO	4.20
COOH	3.10
CH_2OH	0.70

For example, according to the mechanism, H atoms produced are equal to 3.65 per 100 e.v. and this should equal to the sum of hydrogen atoms consumed and so, assuming H atoms reacting according to (7) $= 0.35$, then that reacting according to reaction (1) $= 3.65 - .35 = 3.30$. It may be noted that OH radical is produced according to reaction (11) with $G = 0.8$ which is equal to $GH_2O_2{}^W$, and so the total OH radical produced per 100 e.v. $= 2.85 + 0.8 = 3.65$ and this should be consumed according to reactions (2) and (8). The other figures below the equations are calculated in the same way.

The following overall material balance, based on reactions (0) to (11) may now be given :

$$3.65 \text{ H} + 2.85 \text{ OH} + 0.8 \text{ H}_2\text{O}_2 + 0.4 \text{ H}_2 + 4.95 \text{ CO} \longrightarrow$$

$$0.55 \text{ HCHO} + 0.3 \text{ CHO.CHO} + 0.45 \text{ HCOOH} + 0.35 \text{ CH}_2\text{OH.CH}_2\text{OH}$$
$$(0.5) \qquad\qquad (0.3) \qquad\qquad (0.4)$$

$$+ 0.75 \text{ H}_2 + 2.65 \text{ CO}_2 + 1.35 \text{ H}_2\text{O} \qquad\qquad \underline{\hspace{1cm}} (18)$$
$$(0.65) \qquad\quad (2.6)$$

where the G-values measured at 9000 rads (or in the case of hydrogen calculated for 9000 rads) are shown in parenthesis. The agreement between the equation and the experiments is quite good. It should be noted that in principle several ratios of rate constants could be calculated from equation (0) - (11) and (18). However, more detailed work is required before the values could be regarded as reliable.
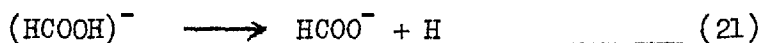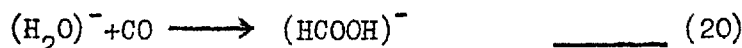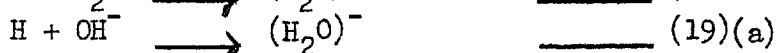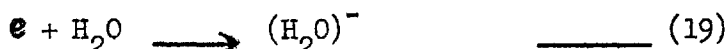
(2) 10^{-4} N sulphuric acid and neutral solutions :

No detailed examination was done to determine all the products in the irradiated 10^{-4}N sulphuric acid and neutral solutions, and hence no mechanism can be given for these solutions. However, some of the results obtained are of interest. For example, $G(\text{H}_2)$ is reduced to almost the molecular yield, a fact consistent with the suggestion that the solvated electrons are the predominant reducing species in these solutions, since in such a case, the hydrogen abstraction reaction (reaction (7)) might be expected not to occur, so reducing $G(\text{H}_2)$ to the value of the molecular yield.
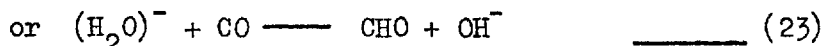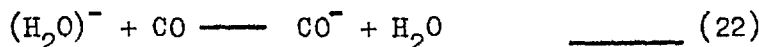
(3) <u>0.1N sodium hydroxide</u> :

In 0.1N sodium hydroxide solutions, formic acid is the main

product under irradiation and is formed with G = 44, probably

through a chain reaction. The following mechanism would explain

this result :

$$e + H_2O \longrightarrow (H_2O)^- \qquad \underline{\hspace{2cm}} (19)$$
$$H + OH^- \longrightarrow (H_2O)^- \qquad \underline{\hspace{2cm}} (19)(a)$$
$$(H_2O)^- + CO \longrightarrow (HCOOH)^- \qquad \underline{\hspace{2cm}} (20)$$
$$(HCOOH)^- \longrightarrow HCOO^- + H \qquad \underline{\hspace{2cm}} (21)$$

where $(H_2O)^-$ represents that form of the H atom which is present

in alkaline solutions. Reaction (20) is similar to the reactions:

$$(H_2O)^- + CO \longrightarrow CO^- + H_2O \qquad \underline{\hspace{2cm}} (22)$$
$$or \quad (H_2O)^- + CO \longrightarrow CHO + OH^- \qquad \underline{\hspace{2cm}} (23)$$

put forward by Weiss and co-workers (139). In the present state of

knowledge, it is impossible to distinguish between the various

possible forms of the CHO radical :

$$(HCOOH)^- \underset{}{\overset{H_2O}{\rightleftharpoons}} CO^- \underset{}{\overset{\cdot H^+}{\rightleftharpoons}} CHO \underset{}{\overset{H_2O}{\rightleftharpoons}} CH(OH)_2$$

where $(HCOOH)^-$ and $CH(OH)_2$ are the solvated forms of CO^- and

CHO respectively.

These different forms of the CHO radical are similar to those which

exist for H atoms, OH radicals and COOH radicals. We suggest that

the existence of different. ionized forms is general for radicals

in aqueous solutions, and that these forms might be expected to have

different modes of behaviour. In alkaline solutions, the form$(HCOOH)^-$

might be more stable than CHO and CO$^-$. Reaction (21) is suggested
by the electron impact studies of Melton and Ropp (70). Reactions 19,
(19)(a),(20), (21) will form formic acid by a chain reaction. As an
alternative to reaction (21) followed by reaction (19)(a) we may suggest:

$$(HCOOH)^- + H_2O \rightleftharpoons HCOOH + (H_2O)^- \underline{\hspace{1cm}} (25)$$
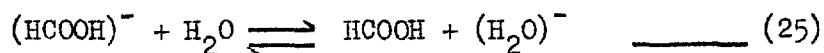
followed by (20). Reaction (25) in reverse had been suggested by
Hart (65) to occur in concentrated solutions of formic acid, but in
dilute solutions it seems reasonable to suppose that the reaction
might go from left to right. To account for the aldehyde formed in
alkaline solutions, we suggest that the CHO radical which exists in
equilibrium with (HCOOH)$^-$ will react according to (3) & (4), thus at the same
time breaking the chain.

It should be noted that carbon monoxide can react with con-
centrated sodium hydroxide solutions at about 100°C., at a pressure
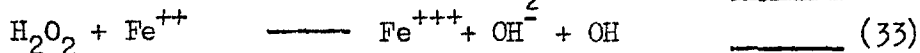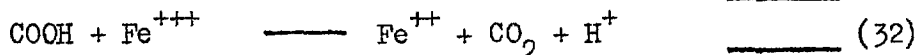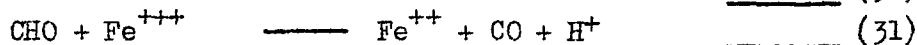of 40 atmospheres (140). This reaction can be represented by :

$$CO_{(g)} + OH^-_{(aq)} \longrightarrow HCOO^-_{(aq)} \underline{\hspace{1cm}} (26)$$
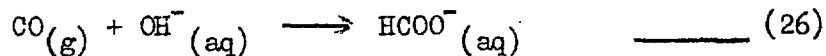
$$\Delta F^{\circ} \quad -32.8 \quad -37.6 \quad\quad -80 \quad k.cal/mol. \quad (143).$$

Reaction (26) has a decrease of free energy $\Delta F^{\circ} = -80 - (-32.8 - 37.6)$
$= -9.6$ k.cal/mol. at 25°C., showing that the reaction is thermo-
dynamically feasible. However, in the absence of the radiation, the
rate must be low at room temperature since no formic acid was formed
in a blank of carbon monoxide in 0.1N sodium hydroxide solution at

400 mm. pressure. The production of hydrogen in alkaline solutions may be a secondary hydrogen abstraction from the formic acid which is produced in large quantities in a short irradiation time(Fig.(29). The value of $G(H_2)$ = 1.2 is very close to that obtained by Hardwick $(G(H_2)$ = 1.18) in the radiolysis of sodium formate solutions (71) which supports this suggestion for hydrogen production.

(4) Ferrous solutions (0.1N sulphuric acid) :

In these solutions no oxidation to ferric occurs, whereas in ferrous solutions in the absence of carbon monoxide and air, the initial GFe^{+++} = 7.8 (86). This could be explained by the formation of the reducing CHO and COOH radicals in the irradiated carbon monoxide solutions which would reduce any ferric produced. The results, and especially the formation of formic acid, appear to be inconsistent with decomposition of the COOH radical into CO_2 + H. The following mechanism accounts for the results obtained at low doses where secondary reactions do not occur :

$$H + CO \longrightarrow CHO \qquad (1)$$

$$OH + CO \longrightarrow COOH \qquad (2)$$

$$OH + Fe^{++} \longrightarrow Fe^{+++} + OH^- \qquad (27)$$

$$H + H^+ + Fe^{++} \longrightarrow Fe^{+++} + H_2 \qquad (28)$$

$$CHO + H^+ + Fe^{++} \longrightarrow Fe^{+++} + HCHO \qquad (29)$$

$$COOH + H^+ + Fe^{++} \longrightarrow Fe^{+++} + HCOOH \qquad (30)$$

$$CHO + Fe^{+++} \longrightarrow Fe^{++} + CO + H^+ \qquad (31)$$

$$COOH + Fe^{+++} \longrightarrow Fe^{++} + CO_2 + H^+ \qquad (32)$$

$$H_2O_2 + Fe^{++} \longrightarrow Fe^{+++} + OH^- + OH \qquad (33)$$
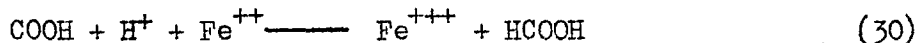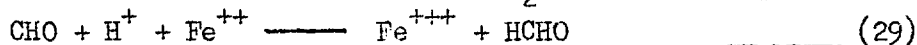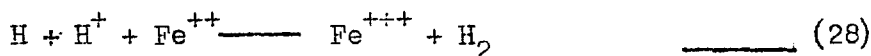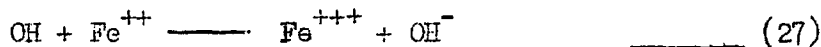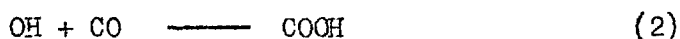
From this mechanism, the ratio of some rate constants can be obtained:

(a) $\dfrac{k(OH + CO)}{k(OH + Fe^{++})}$ can be calculated according to the following equation

$$\frac{g_{(2)}}{g_{(27)}} = \frac{k_{(2)}\ [CO]}{k_{(27)}\ [Fe^{++}]} \qquad\qquad \underline{\hspace{1cm}} \quad (34)$$

where $g_{(2)}$ and $g_{(27)}$ are the G-values for OH radicals reacting according to reaction (2) and (27) respectively, $k_{(2)}$ and $k_{(27)}$ being their rate constants. $[CO]$ and $[Fe^{++}]$ are the concentrations of carbon monoxide and ferrous ions in the solution. From the mechanism shown above, we obtain the following equations :

$$g_{(2)} = G(CO_2) + G\,(HCOOH) \qquad\qquad \underline{\hspace{1cm}} \quad (35)$$

$$g_{(2)} + g_{(27)} = GOH^{W} + GH_2O_2^{\ W} \qquad\qquad \underline{\hspace{1cm}} \quad (36)$$

where GOH^{W} and $GH_2O_2^{\ W}$ = the yields from water radiolysis.

Substituting the values of $g_{(2)}$ and $g_{(27)}$ in equation (34) :

$$\therefore\ \frac{G(CO_2) + G(HCOOH)}{GOH^{W} + GH_2O_2^{\ W} - (G(CO_2)+G(HCOOH))} = \frac{k_{(2)}}{k_{(27)}}\ \frac{[CO]}{[Fe^{++}]} \quad \underline{\hspace{1cm}} \quad (37).$$

taking $GOH^{W} = 2.85$ and $GH_2O_2^{\ W} = 0.8$, $[CO] = 4.5 \times 10^{-4}M$ and $[Fe^{++}] = 2\times10^{-3}$ M and substituting for $G(CO_2) = 1.3$ and $G(HCOOH) = 0.4$ (see Table (12)), then :

$$\frac{k_{(2)}}{k_{(27)}} = \frac{k(OH + CO)}{k(OH + Fe^{++})} = 3.9 \pm 0.5 \text{ at } 23^{\circ}C.$$

This value agrees with he value 3.79 obtained by Hardwick (93) for the same ratio using OH radicals from Fenton's reagent in 0.1N

perchloric acid. The value 2.14 obtained by Dainton and Hardwick (92) in 0.8 N sulphuric acid is slightly different and this variation raises the question whether the rate constants are pH-dependent, maybe owing to the existence of OH radicals as H_2O^+ in acid solutions, or to reactions of OH radicals with the acid used in the solutions. Sworski has found evidence that OH reacts with sulphuric acid in aqueous solutions (142). The effect of this reaction will be enhanced under conditions of low carbon monoxide and ferrous ions concentrations and high acid concentrations but, in the present work, where the concentration of CO = 4.5×10^{-4}M, Fe^{++} = 2×10^{-3}M, and sulphuric acid = 0.1N, if the latter reaction happens, the fraction of OH radicals reacting with sulphuric acid will be only 7% of the total OH radicals present (141) thus contributing only a small error to the rate constant ratio of 3.9.

(b) $\dfrac{k(H + CO)}{k(H + H^+ + Fe^{++})}$ can be calculated similarly :

$$\frac{g_{(1)}}{g_{(28)}} = \frac{k_{(1)} [CO]}{k_{(28)} [Fe^{++}]} \quad \underline{\hspace{2cm}} (38)$$

and

$$\frac{GH^W - (G(H_2) - GH_2^W)}{G(H_2) - GH_2^W} = \frac{k_{(1)} [CO]}{k_{(28)} [Fe^{++}]} \quad \underline{\hspace{2cm}} (39)$$

where $g_{(1)}$ and $g_{(28)}$ are the G-values for H atoms reacting according to (1) and (28) respectively, GH^W and GH_2^W are the yields from the radiolysis of water and $G(H_2)$ is the measured yield of hydrogen produced. It may be noted that hydrogen production in the ferrous

solution is an initial yield and not a secondary one as in the case of 0.1N sulphuric acid. Substituting the values $GH^W = 3.65$, $GH_2^W = 0.4$, $CO = 4.5 \times 10^{-4}$ M, $Fe^{++} = 2 \times 10^{-4}$ M and $G(H_2) = 1.1$, the ratio $\dfrac{k_{(1)}}{k_{(28)}} = \dfrac{k(H + CO)}{k(H + H^+ + Fe^{++})} = 1.85$. However this value should be corrected for two factors :

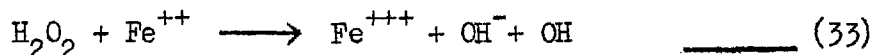(a) at 26,000 rads, where the hydrogen yield was measured, the carbon monoxide concentration is less than 4.5×10^{-4} M, which will increase the number of hydrogen atoms reacting according to (25).

(b) at 26,000 rads, the production of hydrogen from formaldehyde according to (7) cannot be neglected.

Allowing for these two factors using data in this paper and similar calculations as before (see Appendix (3)), increases the ratio of $\dfrac{k(H + CO)}{k(H + H^+ + Fe^{++})}$ to 2.5 ± 0.3.

(5) Ferric solutions (0.1N sulphuric acid).

In these solutions, ferrous ions are produced with $G = 6.4$ in the range of ferric ion concentrations examined ($2 \times 10^{-4} - 1 \times 10^{-3}$M Fe^{+++}) : in ferric solutions in the absence of carbon monoxide and of air, no reduction happens (91). The following mechanism is in accord with the results obtained in these solutions under conditions

where secondary reactions do not interfere :

$$H + CO \longrightarrow CHO \qquad \underline{\quad\quad} (1)$$

$$OH + CO \longrightarrow COOH \qquad \underline{\quad\quad} (2)$$

$$H + Fe^{+++} \longrightarrow Fe^{++} + H^+ \qquad \underline{\quad\quad} (40)$$

$$CHO + Fe^{+++} \longrightarrow Fe^{++} + CO + H^+ \qquad \underline{\quad\quad} (31)$$

$$COOH + Fe^{+++} \longrightarrow Fe^{++} + CO_2 + H^+ \qquad \underline{\quad\quad} (32)$$

$$H_2O_2 + Fe^{++} \longrightarrow Fe^{+++} + OH^- + OH \qquad \underline{\quad\quad} (33)$$
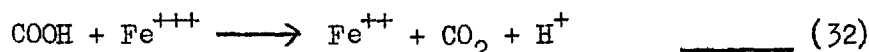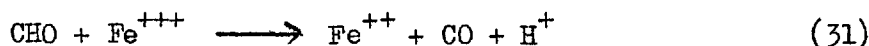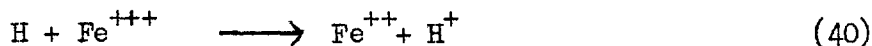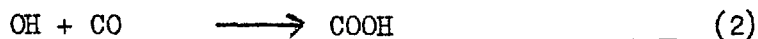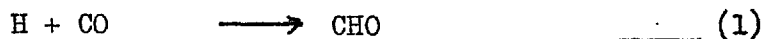
From the above reactions it can be seen that the yield of ferrous

ions should be given by :

$$G(Fe^{++}) = GH^W + (GOH^W + GH_2O_2{}^W) - GH_2O_2{}^W \quad \underline{\quad\quad} (41)$$

$$= GH^W + GOH^W$$

$$= 6.5$$

The experimental value of 6.4 is in excellent agreement with the

theoretical value, and so $G(Fe^{++})$ gives the sum of the radical yields

for water radiolysis.

$G(CO_2)$ should be given by :

$$G(CO_2) = G(COOH) = GOH^W + GH_2O_2{}^W = 3.65$$

The values for $G(CO_2)$ found in Table (12) are independent of ferric

ion concentrations in the range studied as predicted from the above

mechanism and are in good agreement with the theoretical value of

3.65.

CHAPTER (V) Conclusions.

(A) Industrial implications of carbon monoxide irradiation.

(1) irradiation in alkaline solutions.

In the γ-irradiation of alkaline carbon monoxide solutions G (HCOOH) = 44. An approximate estimate for the cost of irradiation to produce one lb. of sodium formate can be calculated as follows:

$$1 \text{ watt} = 6.25 \times 10^{18} \text{ e.v/sec.}$$

Therefore, 1 watt hour = $6.25 \times 10^{18} \times 3600 = 2.25 \times 10^{22}$ e.v

Since G = number of molecules produced per 100 e.v of energy imput.

$\therefore$ number of molecules formed per 1 watt hour absorbed

$$= \frac{2.25 \times 10^{22} \times G}{100} = 2.25 \times 10^{20} G$$

1 gm mol $= 6.02 \times 10^{23}$ molecules.

$\therefore$ Number of gm. mol. formed per 1 watt hour absorbed

$$= \frac{2.25 \times 10^{20} G}{6.02 \times 10^{23}}$$

and number of lbs. per 1 watt hour $= \dfrac{2.25 \times 10^{20} G}{6.02 \times 10^{23}} \times \dfrac{M.\ W.}{453}$

where M.W. = molecular weight in g

$\therefore$ $\dfrac{\text{watt hour}}{\text{lb.}} = \dfrac{6.02 \times 10^{23} \times 453}{2.25 \times 10^{20} \times G \times (M.W.)} = \dfrac{1.22 \times 10^{6}}{G \times M.W.}$

and $\dfrac{\text{kwh}}{\text{lb}} = \dfrac{1.22 \times 10^{3}}{G \times M.\ W.}$

Substituting G = 44 and M.W. for sodium formate = 68 then the energy necessary to produce sodium formate = 0.4 kwh/lb.

Table (15) shows an estimated cost in dollars per kilowatthour for different radiation sources (144).

TABLE (15)

Cost of radiation sources including

return on investment (dollars/kwh)

Cobalt 60		Radiation machines	
3kw	30 kw	3 kw	30 kw
8.70	2.95	7.75	1.70

Knowing that each lb. of sodium formate requires 0.4 kwh then the cost per lb. from different radiation sources can be calculated, Table (16).

TABLE (16)

Cost of irradiation to produce sodium formate (dollars/lb.)

Cobalt 60		Radiation machines	
3 kw	30 kw	3 kw	30 kw
3.48	1.18	3.1	0.68

Table (17) shows the selling prices for sodium formate and some other chemicals (145).

TABLE (17)

Compound	selling price (dollar/lb.)
Sodium formate	0.08
Formic acid (90%)	0.16
Ethylene glycol.	0.16
Formaldehyde (50%)	0.05
glyoxal (30%)	0.19

It is clear that the cost of radiation needed to produce sodium formate is many times the selling price. Also it must be borne in mind that the radiation cost is only a part of the total production cost. However, the use of fission fragments in a nuclear reactor may lower considerably the cost of irradiation, and if we assume that the H atom and oH radical in the gas phase react with carbon monoxide to produce CHO and COOH radicals, then it is possible that some products such as formic acid, formaldehyde, glyoxal and ethylene glycol would be formed.

(2) Fission fragment irradiation in the gas phase.

An approximate cost of irradiation of carbon monoxide and water vapur using fission fragments to produce formic acid can be calculated as follows: (146)

$$\text{Cost of irradiation /ton (in £)} = \frac{12000 \text{ x } 0.23}{G \text{ x}(x)\text{x (M.W.)}}$$

Where G = yield /100 e.v   assume = 2

  x = efficiency factor for energy utilization and equals 0.2 - 0.3 in a system of highly enriched fuel particles fluidized by the chemical reactant gases.

M.W.   = molecular weight = 46 for formic acid

∴ Cost/ton= $\frac{12000 \text{ x } 0.23}{2 \text{ x } 0.3 \text{ x } 46}$ = 100 £/ton.

The selling price of formic acid in £ = (T$_{able}$ (17))

$$= \frac{0.16}{0.9} \times 2000 \times \frac{1}{2.8} = 125 \text{ £/ton.}$$

The rate of production of formic acid in a chemical reactor is given by (146):

rate of production = $6.6 \times 10^{-3} \times Q \times (M.W) \times G \times (x)$ tons/day

where Q = reactor power in megawatt assume = 50

M.W., G and x as before

∴ rate of production = $6.6 \times 10^{-3} \times 50 \times 46 \times 2 \times 0.3$

$$= 9.1 \text{ tons/day}$$

$$= 9.1 \times 300 = 2730 \text{ tons/year.}$$

With similar calculations, the irradiation costs and production rates could be estimated for other possible irradiation products such as formaldehyde, glyoxal and ethylene glycol. T$_{able}$ (18) shows the results of such an estimation.

TABLE (18)

Chemical production in the irradiation of carbon monoxide and water vapour (fission fragments).

	G (min.)	Cost of irradiation (£/ton)	Selling price (£/ton)	Rate of Production (tons/year)
formic acid	2	100	125	2730
formaldehyde (100%)	4	75	70	3550
glyoxal (100%)	0.5	316	452	860
ethylene glycol	2	75	115	3660

The annual production and sales of these compounds in the
U.S. are shown in Table (19). (147). This table shows

TABLE (19)

	production (1959 tons/year	sales(1959) tons/year
formic acid (90%)	9850	9000
formaldehyde (37%)	875,000	430,000
glyoxal	---	---
ethylene glycol	600,000	300,000

that there is a good demand for these chemicals (no data was
given for glyoxal).

It may be noted that the actual production cost plus profit
in the fission fragment irradiation may be as much as four
times that of the irradiation cost and thus the G value
required for economic production of any of these chemicals
may be as much as four times G (min). (148). These G values
for economic production may be reached in the gas phase as
GH^W and GOH^W are higher than in the liquid phase, with the
result that CHO, COOH and the different products are expected
to be produced with a higher yield. If two (or more) of the
four chemicals are simultaneously produced, then their production
may be economical with G - values near to that G (min).

This cost estimation shows that the use of fission
fragments in a reactor to irradiate carbon monoxide and water
vapour may be of some industrial importance, but of course

further work is needed to determine the actual yield of these products under reactor conditions, and to overcome the technical problems which will be met in designing such a reactor.

B.   The atmosphere of the planet Venus.

The planet Venus is completely covered by yellowish white clouds which are believed to be 30 km. high. The atmosphere above the clouds has been found to consist mostly of carbon dioxide, with some carbon monoxide and water vapour. No free oxygen could be detected spectroscopically (149). The nature of these clouds has been the subject of different speculations. Wildt, in 1937, suggested that these clouds may consist of polymers of formaldehyde, but no formaldehyde, which would be in equilibrium with its polymer, could be detected. Kuiper (150) and Harteck and Dondes (151) suggested that carbon suboxide (C_3O_2) is responsible for these clouds, but malonic acid could be formed quite easily from the suboxide and water vapour according to:

$$C_3O_2 + 2H_2O \longrightarrow CH_2 \cdot (COOH)_2$$

As free water was positively detected, then the existence of the carbon suboxide is improbable. In 1955, Hoyle put forward the interesting suggestion that the clouds are nothing but droplets of hydrocarbon oil, and that the oceans of Venus are oceans of oil (152). In the same year, Menzel

and Whipple suggested that the clouds are supercooled water droplets and that the surface of Venus is completely covered with water (153). Spectroscopic studies could not help in distinguishing between the oil hypothesis and the water hypothesis because of the interference from the Earth's atmosphere. So it may be concluded that no definite picture could be drawn of the clouds on the planet. However, it seems possible that water vapour, which exists in the atmosphere above the clouds, would dissociate under the ultra violet radiation from the sun to give H and OH radicals (the average distance of Venus from the Sun is 0.72 of the distance of the Earth from the Sun so that the radiation intensity on Venus is about twice that on Earth). The photodissociation of water vapour starts near 2400 A^o but the cross section associated with the process remains extremely small until almost 1800 A^o, where it rises rapidly (154). Carbon dioxide can only absorb at wavelengths less than 1690° A. (154). So the photodissociation of water vapour in the atmosphere of Venus can proceed without intereference from CO_2. In the absence of molecular oxygen, we may expect that H and OH radicals would react with carbon monoxide and carbon dioxide according to:

$$H + CO \longrightarrow CHO \quad —— (1)$$
$$H + CO_2 \longrightarrow COOH \quad —— (2)$$
$$OH + CO \longrightarrow COOH \quad —— (3)$$
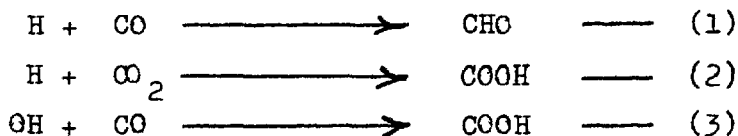
Reaction (1) may occur to certain extent in competition with reaction (2), as there is some indication, from the radiolysis of aqueous solutions of CO_2 (P. 47) that H reacts much faster with CO than with CO_2. The COOH and CHO radicals formed may further react according to some of the reactions shown in the present study to form one or more of the products.

No doubt, more data is needed, such as the actual concentrations of the different gases and the rate constants of possible reactions, in order to have a better understanding about the possible chemicals formed in the atmosphere of Venus which possibly may contribute to the formation of the mysterious clouds.

APPENDIX (1)

To show that the amount of hydrogen in solution is negligible with respect to the amount of hydrogen in the gas phase:

For example in 0.1 N sulphuric acid, at 26000 rads :

volume of H_2 in the gas phase = 0.06 c.c at 23°c, 1 atm.

(Table (7))   = 2×10^{-6} mole

volume of gas space $=$ 200 c.c at ½ atm.

$=$ 100 c.c at 1 atm.

$\therefore$ partial pressure of H_2 in the gas phase = $\dfrac{0.06 \times 1 \text{ atm}}{100}$

$= 6 \times 10^{-4}$ atm.

The solubility of H_2 in water at room temp. and 1 atm. of $H_2 \simeq 10^{-3}$ M

$\therefore$ solubility at 6×10^{-4} atm. of $H_2 = 6 \times 10^{-4} \times 10^{-3}$ M

$= 6 \times 10^{-7}$ M

and the amount of H_2 in 100 c.c of water $= 6 \times 10^{-7} \times \dfrac{100}{1000}$ mole
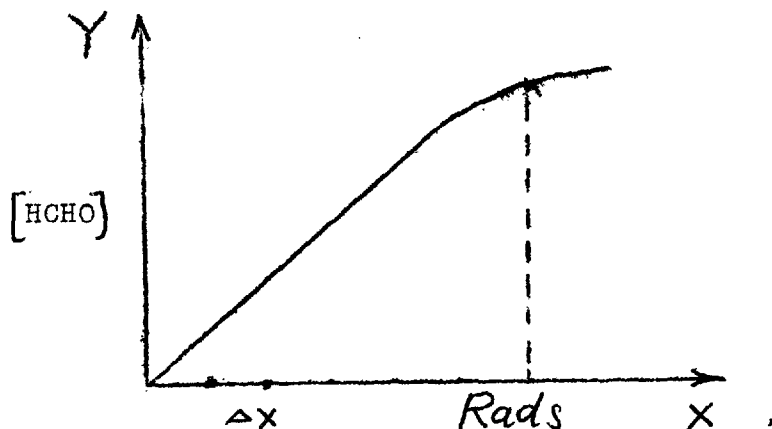
$= 6 \times 10^{-8}$ mole.

and $\therefore$ $\dfrac{\text{amount of } H_2 \text{ in the gas phase}}{\text{amount of } H_2 \text{ in solution}} = \dfrac{2 \times 10^{-6}}{6 \times 10^{-8}}$

$= 35$ times

or about less than 3% of the total hydrogen is in the solution.

APPENDIX (2)

Caluclation of the mean value of $[HCHO]$ between 0 and 27000 rads in the irradiation of 0.1 N H_2SO_4:

Mean value of $Y = \dfrac{\sum Y_{average} \cdot \Delta X}{\sum \Delta X}$

where Yav. is the value of Y at the middle of the increment

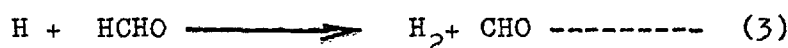Taking $\Delta X = 4500$ rads and $\sum \Delta X = 27000$ rads.

$[HCHO]$ av. can be found from (Fig. (28 curve (1)) then the following table can be obtained.

Rads	ΔX (rads)	$[HCHO]$ av.	$[HCHO]$ av $\cdot \Delta X$
4500	4500	1×10^{-6}	4.5×10^{-3}
9000	4500	3.5×10^{-6}	15.75×10^{-3}
13500	4500	5×10^{-6}	22.50×10^{-3}
18000	4500	6×10^{-6}	27.0×10^{-3}
22500	4500	7×10^{-6}	31.5×10^{-3}
27000	4500	7.75×10^{-6}	34.8×10^{-3}
			136×10^{-3}

$\therefore$ Mean value of $[HCHO] = \dfrac{\sum [HCHO] \text{ av.} \Delta X}{\sum \Delta X}$

$= \dfrac{136 \times 10^{-3}}{27 \times 10^{3}} = 5 \times 10^{-6}$ M

APPENDIX (3)

Correction of the hydrogen yield at 26000 rads in the irradiation of 2×10^{-4} N Fe^{++}:

$$H + CO \longrightarrow CHO \text{------------} (1)$$

$$H + H^{.+} + Fe^{++} \longrightarrow H_2 + Fe^{+++} \text{--------} (2)$$

$$H + HCHO \longrightarrow H_2 + CHO \text{--------} (3)$$

at 26000 rads:

From (Fig (28) curve (5)) H. CHO at 26000 rads = 2.5×10^{-6} M

and mean value of HCHO between 0 and 26000 rads = 1.5×10^{-6} M

G (- CO) = 3.7 (from mechanism in 2×10^{-4} M Fe^{++})

CO consumed till 26000 rads = $26 \times 3.7 \times 10^{-6} = 9 \times 10^{-5}$ M

CO at 26000 = $4.5 \times 10^{-4} - 9 \times 10^{-5} = 3.6 \times 10^{-4}$

CO mean value between o and 26000 rads = $\dfrac{4.5 + 3.6}{2} \times 10^{-4}$

$$= 4 \times 10^{-4} \text{M}$$

$Fe^{++} = 2 \times 10^{-4}$ M (unchanged)

The value of $GH_2 = 1.1$ obtained at 26000 rads has to be corrected for two factors :

(1) Increase of HCHO concentration.

using the value $\dfrac{kH + CO}{kH + H^{+} + Fe^{++}} = 1.85$

$\therefore$ 2×10^{-4} M Fe^{++} is equivalent (with respect to H atom)

$= \dfrac{2 \times 10^{-4}}{1.85} = 1.08 \times 10^{-4}$ M CO

$\therefore$ Total CO at 26000 rads = $4 \times 10^{-4} + 1.08 \times 10^{-4} = 5.08 \times 10^{-4}$ M

$\therefore$ $\dfrac{g~(3)}{g~(1)} = \dfrac{k~(3)~HCHO~~av.}{k~(1)~CO~~av.}$

taking $\dfrac{k\ H\ +\ HCHO}{k\ H\ +\ CO}$ = 13 (see P.125)

$\therefore$ g (3) = $13 \times \dfrac{1.25 \times 10^{-6}}{5.08 \times 10^{-4}}$ = 0.0.32 g (1)

$\qquad\qquad$ = $\dfrac{0.032}{1.032} \times 3.65$ = 0.11

(2) Decrease in CO concentration :

$$\dfrac{g(1)}{g(2)} = \dfrac{k1}{k2} \times \dfrac{4 \times 10^{-4}}{2 \times 10^{-4}} = 1.85 \times \dfrac{4}{2} = 3.7$$

$\therefore$ H atom reacting according to (2) to form H_2 =

$\qquad$ = (3.65 - 0.11) $\times \dfrac{1}{4.7}$ = 0.75

Total H_2 due to reaction (2) and (3) = 0.11 + 0.75 = 0.86

Measured H_2 = 1.10 - 0.4 = 0.7

Increase of H_2 = 0.86 - 0.7 = 0.16

increase in 0.7 value due to two corrections = $\dfrac{0.7 \times 0.16}{0.86}$

H_2 due to reaction (2) only = 0.7 - 0.14 = 0.56

$$\therefore \quad \dfrac{g\ (1)}{g\ (2)} = \dfrac{k1\ (CO)}{k2\ Fe^{++}}$$

$$\dfrac{3.09}{0.56} = \dfrac{k1}{k2} \times \dfrac{4.5 \times 10^{-4}}{2 \times 10^{-4}}$$

$$\therefore \dfrac{k1}{k2} = 2.5 \pm 0.3$$

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