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Effects of Ionizing Radiations on Aqueous

Solutions of Formic and Oxalic Acid

Contractor: Professor Joseph J. Weiss,
King's College,
University of Durham,
Newcastle upon Tyne, 1.

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ABSTRACT

It has been shown that in aqueous solutions CO_2 and bicarbonate react with negatively charged polarons $(\text{H}_2\text{O})^{\cdot -}$ formed by the irradiation of water by γ -rays, leading to the formation of $\cdot\text{CO}_2^-$, i.e. the carboxyl radical ion.

In the presence of organic solutes, the carboxyl radical ion may add on to other free radicals, e.g. those formed by the action of radiation-produced OH radicals on organic solutes, to give the corresponding carboxylic acids.

Using C-14 labelled carbon dioxide or bicarbonate, this process could provide a method for the production of carboxylic acids labelled in the carboxyl group.

In neutral solutions two reducing species, i.e. negative polarons and primarily formed H atoms, have been shown to be present in irradiated water; their reactions with various solutes have been studied.

All irradiations were carried out with Co^{60} γ -rays.

For irradiation of aqueous solutions in the presence and absence of different gases (O_2 , CO_2 , H_2O) standard irradiation techniques have been used.

Analysis of the gaseous irradiation products has been carried out by means of the mass-spectrometer. Other irradiation products have been determined spectrophotometrically or by radioactive tracer techniques.

INTRODUCTION

Although an appreciable amount of work has already been carried out with the object of establishing the nature of the primary reactive species produced by the action of ionizing radiation on water and on the mechanism of their reactions, a complete and satisfactory understanding has not, as yet, been achieved.

In the present work, special attention has been directed towards the irradiation of aqueous solutions of some relatively simple organic molecules such as formic acid, methanol, oxalic acid, etc., in the range pH 5 - 9. Particular attention has been given to the investigation of the nature and the yields of the different reducing species produced by the action of ionizing radiations on water.

From a chemical point of view, the distinction between the different primary species must be based on some specific reactions. In those cases where their reactions are similar, a differentiation may be obtained by means of two-solute systems. For instance, O_2 reacts rapidly with both the reducing species $(H_2O)^{\cdot -}$ and H-atoms and cannot therefore be used for their differentiation, and also the reaction product (H_2O_2) is the same. However, as Allan and Scholes¹⁾ have found, e.g. acetone can be used for this purpose; from experiments in this system, they have been able to show that in addition to polarons there is a primary formation of H-atoms in neutral solutions of $G \sim 0.5$.

Search for other satisfactory scavengers has drawn attention to the possible uses of CO_2 and N_2O . We have found that CO_2 and bicarbonate

react readily with negative polarons, but relatively very slowly with H-atoms and OH radicals. It has been suggested²⁾ that N_2O also reacts readily with the reducing species but not with OH radicals. The use of N_2O by itself does not appear to be very satisfactory. On the other hand, we have found that N_2O is very useful when used as a second solute; in many instances it may behave very similarly to CO_2 .

EXPERIMENTAL TECHNIQUES

All irradiations were carried out with Co^{60} γ -rays. Radiation doses were measured by the Fricke dosimeter, assuming a value of $G(Fe^{III}) = 15.5$ for Co^{60} γ -rays.

Solutions for irradiation were prepared under conditions of the utmost purity. Water was purified by triple distillation. Ordinary distilled water was distilled from an alkaline potassium permanganate solution into a dilute phosphoric acid solution (0.1 ml. of concentrated phosphoric acid in 2 l.), from which it was further distilled into a pyrex flask. The pH of the water was usually in the range 5.3 to 5.7.

Most of the chemicals used were "Analar" grade. Sodium formate was recrystallised three times and dried in a vacuum desiccator over sodium hydroxide pellets. The middle fraction of methanol distillate was used. Carbon dioxide was prepared from sodium carbonate and sulphuric acid and purified by fractional distillation in vacuo. Medical grade of "British Oxygen" nitrous oxide was used, and also purified by fractional distillation in vacuo.

Standard irradiation techniques were used for irradiation of aqueous solutions in the presence and absence of different gases (O_2 , CO_2 , H_2O). The irradiation vessels were made of pyrex.

Most of the analytical work was concerned with measurements on gaseous products. An apparatus for the collection and separation of semi-micro quantities of gases (.01 to 1 cc.) has been constructed. The total amount of gaseous products was determined by PVT measurements, followed by mass-spectrometric analysis.

Spectrophotometric analysis was used for the detection of some products, such as H_2O_2 , formaldehyde, glyoxylic acid, etc.

Carboxylic acids were determined by using C-14 tracer methods. The activities of the samples were measured by means of a Geiger-Müller counter. Labelled oxalic acid was determined by the addition of a certain amount of oxalic acid, to act as a carrier, and precipitation as calcium salt was carried out with a subsequent measurement of the activity of the samples. In some cases oxalic acid was determined gravimetrically as the calcium salt.

EXPERIMENTAL RESULTS

In all irradiations yield-dose plots were obtained with at least 4 points and the proportionality of yields to radiation dose checked. In some cases (e.g. H_2 yields in irradiated formate solutions) the yield-dose plots were non-linear, presumably due to secondary reactions. In such cases, initial G-values (number of molecules per 100 eV absorbed) were

taken into consideration.

Fig. 1 shows the concentration dependence of the hydrogen yield in deaerated neutral sodium formate solution.

The formation of glyoxylic acid at higher formate concentrations was not determined due to the interference by the formate.

Fig. 2 shows the hydrogen yield, $G(\text{H}_2)$, in deaerated 1 mM sodium formate solution as a function of the concentration of added sodium bicarbonate.

In the presence of added oxalate the hydrogen yield drops to $G = 1.05$.

Fig. 3 shows $G(\text{CO}_2^-)$, i.e. the yield of the carboxyl group in oxalic acid derived from the bicarbonate, as a function of the formate and bicarbonate concentration. C-14 labelled bicarbonate was used to differentiate between carboxyl groups in the radiation-produced oxalic acid from bicarbonate and from formate.

Fig. 4 shows the pH-dependence of $G(\text{H}_2)$ from 10 mM formic acid solution irradiated in vacuo and in the presence of 20 mM CO_2 . The yield of CO_2^- in oxalic acid (from C^{14}O_2) is also given. pH was adjusted with H_2SO_4 .

Fig. 5 shows yield-dose plots of radiation products in neutral aqueous solution of N_2O . The concentration of N_2O was 17 mM. The positive intercept of the N_2 line is due to very small amounts of N_2 from the irradiated glass.

Fig. 6 shows the dependence of the gaseous yields in neutral aqueous solutions of methanol and N_2O on the concentration of methanol. The yield-dose plots for hydrogen peroxide are non-linear but deviate less from linearity with increasing methanol concentration.

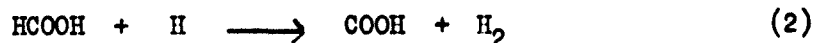
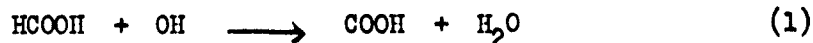
Fig. 7 shows the dependence of the gaseous yields in neutral solution of sodium formate and N_2O on the concentration of formate.

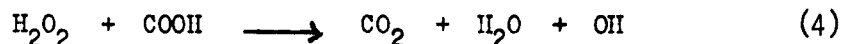
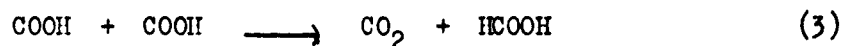
Irradiation of aqueous solution of deuterated sodium formate in the presence of N_2O gives rise to hydrogen (H_2) and deuterium hydride (HD). The yield of hydrogen, $G(H_2) = 0.4$, is independent of formate concentration over the range $10^{-3} - 10^{-1}$ M.

As there is no suitable analytical method for micro-quantities of oxalic acid, we have irradiated aqueous solutions of sodium formate in the presence of sodium bicarbonate and N_2O using very high doses ($2 - 7 \times 10^{19}$ eV/ml). The yield of oxalic acid has been determined gravimetrically as the calcium salt. Under these conditions, the yield of oxalic acid depends on the concentration of formate and only slightly on the dose; initial values could not be determined and G-values for a dose of 2×10^{19} eV/ml are given. These oxalic acid yields were found to be: $G = 3.03$ in 5×10^{-1} M HCOONa with 5×10^1 M $NaHCO_3$, and $G = 3.2$ in 10^{-1} M HCOONa and latn. N_2O , and $G = 3.4$ in 5×10^{-1} M HCOONa and 1 atm. N_2O .

DISCUSSION

In acid solution, where formic acid exists in the unionized form, the following sequence of reactions is envisaged:





H-atoms are formed via the process:

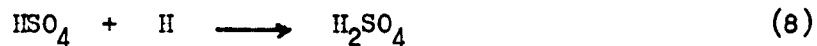
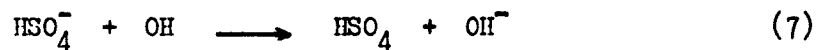


The lower yield of H_2 ($G = 3.2$) could be explained assuming that reaction (6):



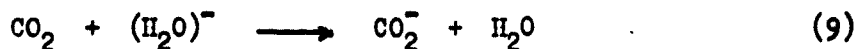
plays a more important role than reaction (4). The initial yields probably represent the full yield, as is indicated by the results of Czapski, Rabani and Stein³).

Hydrogen yields are dependent to some extent on the relative concentrations of formic and sulphuric acids (Fig. 4). This could be explained by:



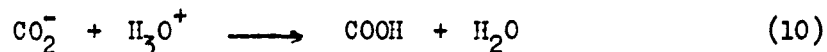
The influence of sulphuric acid has been observed by many workers.

In the presence of CO_2 (Fig. 4), $G(\text{H}_2)$ is markedly lower and depends on pH and relative concentrations of formic acid and CO_2 . It is important to note that at higher pH the $G(\text{H}_2)$ drops to 0.95, the value also obtained in the presence of bicarbonate. The drop in hydrogen yield is due to reaction (9):



which competes with reaction (5).

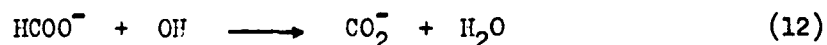
The carboxyl radical, CO_2^- , may undergo the reaction:



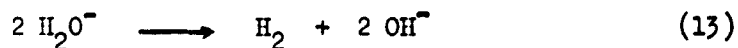
or recombine, giving oxalic acid, viz.



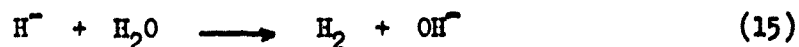
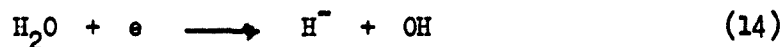
In neutral solution, formic acid is present in the ionized form, and the following reaction takes place:



Reaction (10) then is negligible and only reaction (11) takes place. The formation of oxalic acid has been observed by a few authors⁴⁾. The fate of $(\text{H}_2\text{O})^-$ has not been satisfactorily explained. Garrison et al.⁵⁾ suggested as a general reaction:



which cannot be accepted on the basis of our results. We have found that in the case of deuterated formate, the hydrogen yield is composed of H_2 as well as HD. $G(\text{H}_2)$ was found to be very nearly equal to the molecular hydrogen yield, though slightly higher, possibly due to isotopic impurity of the deuterated formate. On the same grounds, the sequence⁵⁾

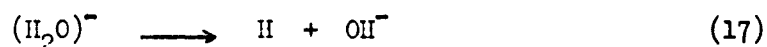


cannot be accepted.

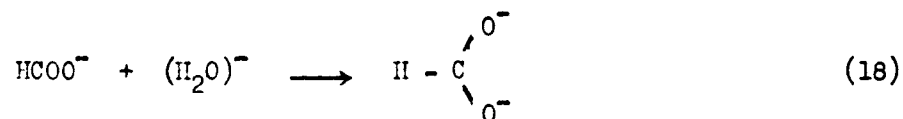
The fact that the total hydrogen yield is in excess of the molecular yield (see Fig. 1) could be explained in the following way:

$$G(\text{H}_2) = G_{\text{H}_2} + G_{\text{H}_a} + G_{\text{H}} \quad (16)$$

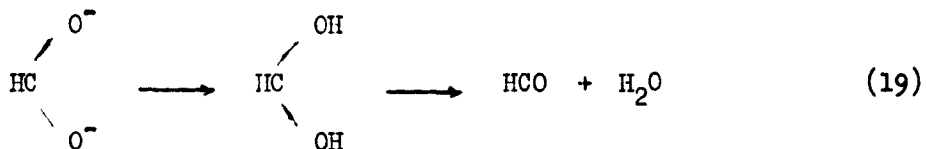
where $G(\text{H}_2)$ represents the total hydrogen yield; G_{H_2} , the molecular hydrogen yield; G_{H_a} , the yield of hydrogen atoms formed directly⁶); and G_{H} , the yield of hydrogen atoms formed by reaction (5) or possibly by a small contribution from



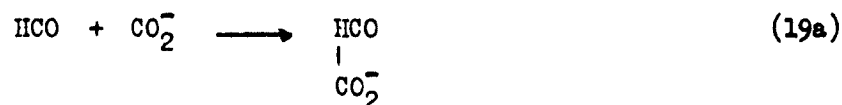
One has further to assume that the reaction:



takes part to some extent though it must be very slow. The free radical formed in this way represents the hydrated carbonyl radical and the step

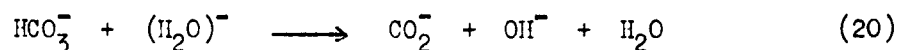


which leads to the formation of glyoxylic acid according to:

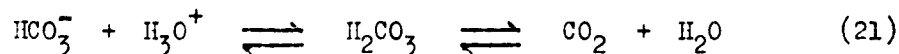


The decrease of $G(\text{H}_2)$ (Fig. 1) could be explained by competition between reactions (5), (17) and (18).

In the presence of bicarbonate, $G(H_2)$ decreases in formate solution (Fig. 2). The decrease is probably due to



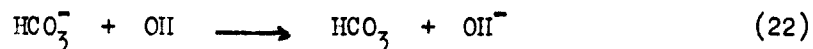
One may argue that the bicarbonate ion does not react with negative polarons and that reaction (20) should be replaced by the reaction with CO_2 which is in equilibrium with the bicarbonate ion according to:



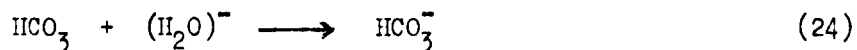
G_{H_a} is more or less constant due to the very low reactivity of H_a either with bicarbonate ion or CO_2 and the high reactivity of H_a with formate ion; the relatively long plateau in Fig. 2 is evidence for this.

The carboxyl radical arising from reaction (20) could be differentiated from the one coming from formate (according to reaction 12) by the use of $NaHC^{14}O_3$. The contribution of the bicarbonate towards oxalic acid formation is then represented by the C-14 labelled radioactive oxalic acid. The dependence of $G(C^{14}O_2^-)$ on the concentrations of formate and bicarbonate is shown in Fig. 3. The increased yield for higher concentrations of formate and bicarbonate could be explained on the basis of the increased scavenging of the primary species (negative polarons) which would otherwise undergo recombination.

In bicarbonate solutions, the formation of oxalic acid does not take place. Molecular hydrogen is fully protected and the molecular hydrogen peroxide has the value of $G = 0.45$. These results would indicate the following mechanism:

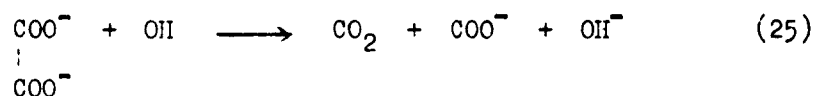


The reaction

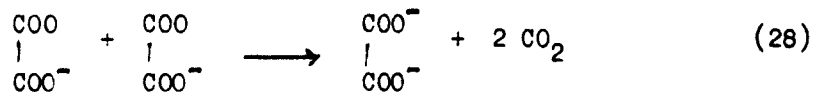
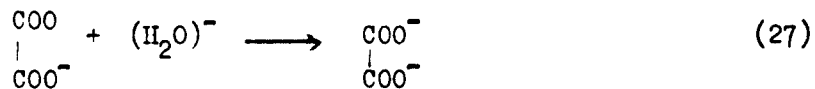
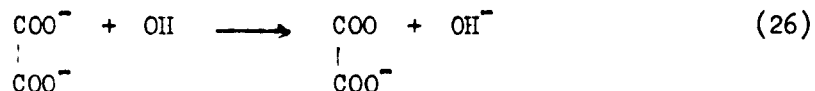


may possibly take place besides or instead of reaction (23).

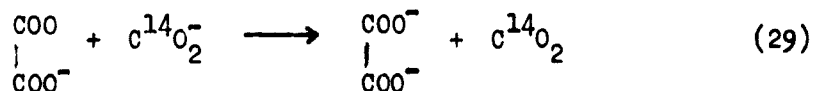
In the system ($\text{C}^{14}\text{O}_2 + \text{oxalate}$), formation of labelled oxalic acid could not be detected and therefore the reaction⁷⁾:



has to be ruled out. A probable mechanism appears to be:

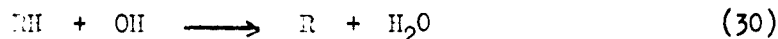


In the presence of C^{14}O_2 , reaction (27) is replaced by:



In formate solutions, in the presence of oxalate, G_H disappears via reaction (27), resulting in an apparent decrease in $G(H_2)$.

In general, carboxylation takes place when free organic radicals are present:



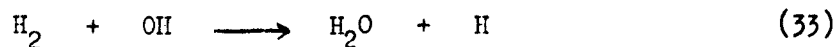
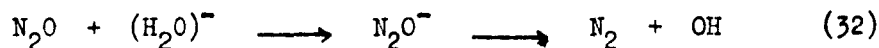
followed by:



Reaction (31) is much faster than reaction (11). Therefore, formation of oxalic acid does not take place in the presence of free organic radicals. Various substrates have been successfully carboxylated⁸⁾.

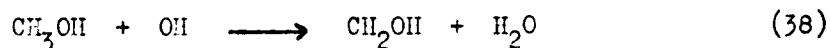
In the case of a solute which can accept polarons, the relative concentrations of solute and CO_2 , or bicarbonate, have to be adjusted according to the relative rate constants for the polaron reactions.

It has been suggested²⁾ that N_2O can react with the reducing species, converting them into OH radicals. In a neutral solution of nitrous oxide (cf. Fig. 5) the following reactions are envisaged:



The low stationary yields of H_2 and H_2O_2 which we have found are in agreement with this mechanism, whereas Dainton and Peterson's results, which indicate protection of both hydrogen and hydrogen peroxide, cannot be explained because reaction (37) is much slower than reactions (33) and (35). $G(H_2) = 3.1$ indicates the yield of negative polarons. On the basis of these results, one has to assume a very high reactivity of H_2O with negative polarons.

In the methanol + N_2O solutions (Fig. 6), the yield of H_2 remains virtually the same. The oxygen formed (reactions 35 and 36) disappears because the reaction



predominates.

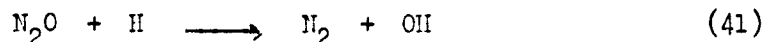
Reactions (33) and (35) also disappear and the molecular hydrogen and hydrogen peroxide yields are fully protected. According to reaction (16), the hydrogen yield is represented by

$$G(H_2) = G_{H_2} + G_{H_a} \quad (39)$$

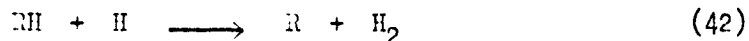
G_{H_a} is dependent to some extent on the concentration of the OH scavenger, probably due to the recombination



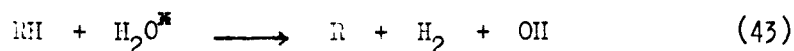
Similarity between CO_2 and N_2O is evident. Negative polarons react very fast with N_2O and reactions (5) and (17) cannot compete efficiently in neutral solution. The reaction



is a slow one and cannot efficiently compete with the reaction

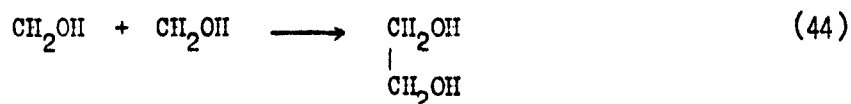


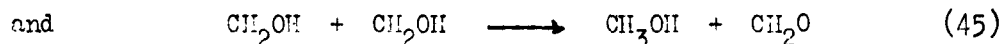
The nature of H_a is not quite clear; it shows some characteristics of an H-atom, but at the same time it could possibly represent an excited water molecule, H_2O^* , reacting in the same manner as an H-atom (as has been indicated by Dainton⁶), viz.



H_a does not appear in the kinetic considerations of Czapski and Allen⁹) and on the basis of their results they rule out the existence of independently produced H-atoms. Hayon¹⁰), in an attempt to reconcile his previous results (Hayon and Allen¹¹), assumes quenching of the excited water molecule by oxygen, and according to him, H_a can appear in oxygen-free solution only. This hypothesis is in direct contradiction with the results of Hummel and Allen¹²), who find in aqueous solution of ethanol saturated with air or oxygen, $G(\text{H}_2) > G_{\text{H}_2}$. The apparent non-existence of H_a in the inorganic systems must have some other explanation, e.g. reaction (40) or a similar reaction.

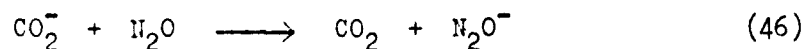
As has been shown, the reaction mechanism in methanol solution is very simplified, in the presence of N_2O . All the polarons ($G = 3.1$) react with N_2O , viz. (32). The reaction (38) is followed by:





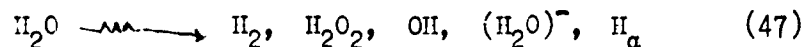
G-values of 3.2 and 0.4 for ethylene glycol and formaldehyde respectively have been found¹³⁾, which supports the proposed mechanism.

In formate-N₂O systems, the G(H₂) is slightly higher than in H₂O and methanol-N₂O systems. Initial yields of oxalic acid could not be measured. The G(oxalate) = 3.4 in 5 x 10⁻¹ M formate + N₂O (atm.), though not fully 'initial', indicates an increase in radical yield (G_T = 6.8). A chain reaction



could possibly take place, but it should not be dependent on the concentration of formate. The measurement of the initial G-value for the formation of oxalic acid could give a definite answer.

On the basis of our results, the radiolysis of water and aqueous solutions by γ-rays should be represented, viz.



where H₂ and H₂O₂ represent molecular hydrogen and molecular hydrogen peroxide; OH, the free hydroxyl radical; and (H₂O)⁻ and H_a, the reducing species.

FUTURE WORK

Having established further the existence of two primary reducing species, viz. the negative polarons $(\text{H}_2\text{O})^-$ and H-atoms, in irradiated (deaerated) neutral aqueous solutions, our intention is to study the relative rates of the reactions of these species with different organic solutes.

It is also hoped, using the systems we have studied, to get more accurate assessments of the actual yields of the reducing species produced in the primary radiolysis of water and aqueous systems.

Annex to Final Technical Report

Contract No. DA-91-591-EUC-1977

Mr. Mionir Simic was employed as Research Associate under this contract. There have been no further administrative actions or changes in research policies. No important property was acquired at contract expense.

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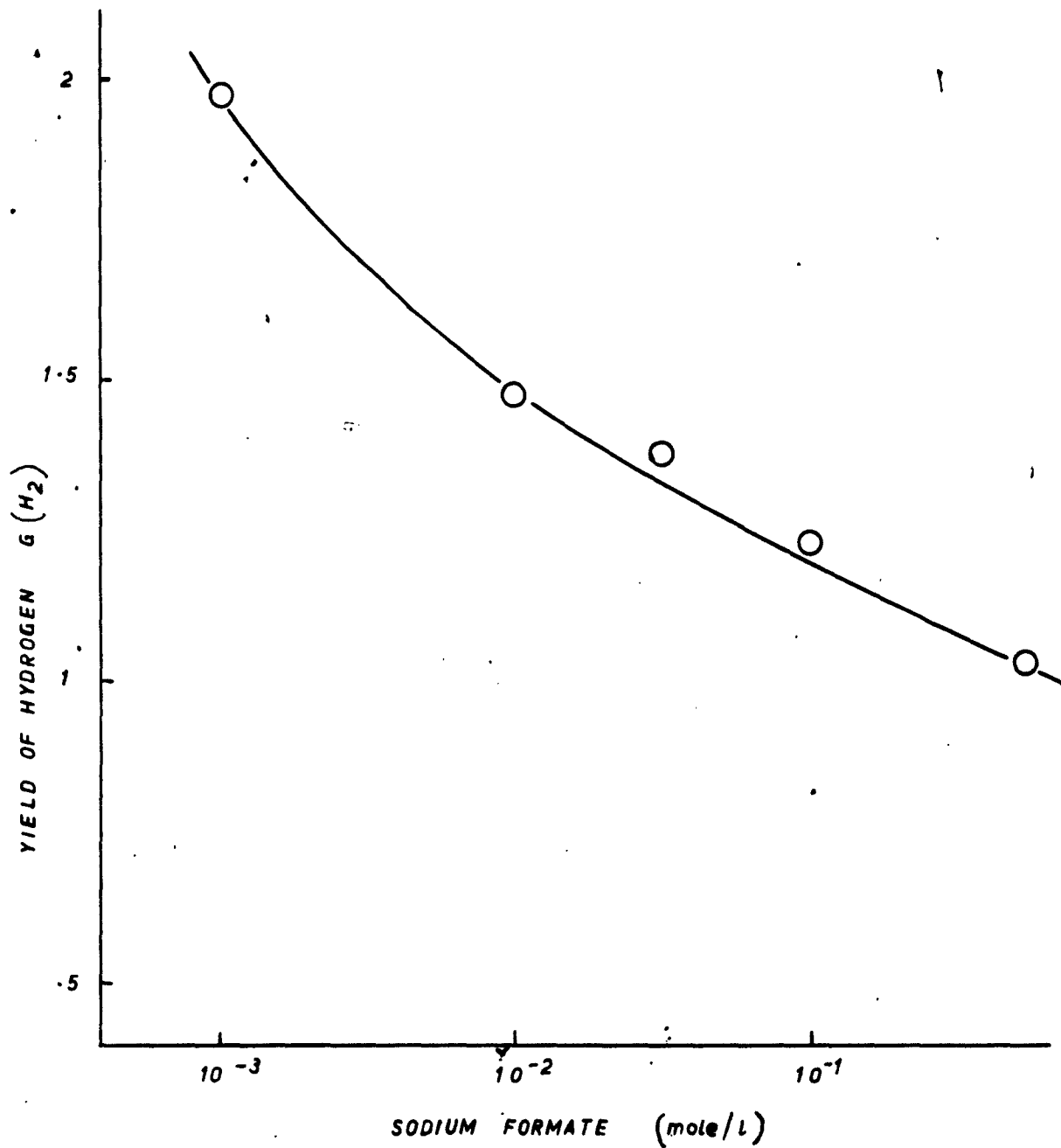


Fig 1. Irradiation (Co⁶⁰ γ-rays) of deaerated aqueous solutions of sodium formate. Dependence of the hydrogen yield on the concentration of formate.

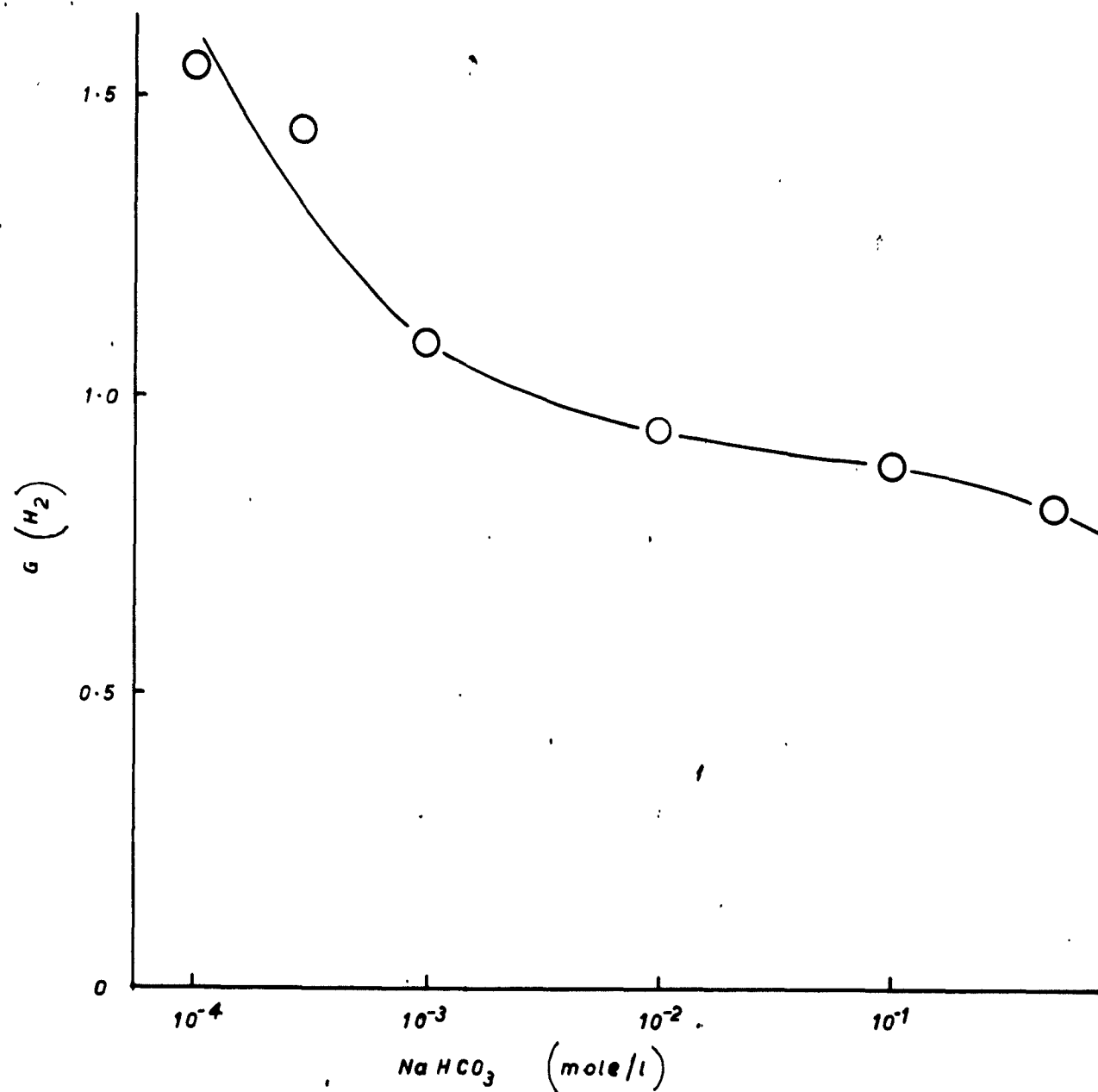


Fig. 2 Irradiation (Co^{60} γ -rays) of deaerated aqueous solutions of 1 mM sodium formate in the presence of sodium bicarbonate. Dependence of the hydrogen yield on the concentration of bicarbonate.

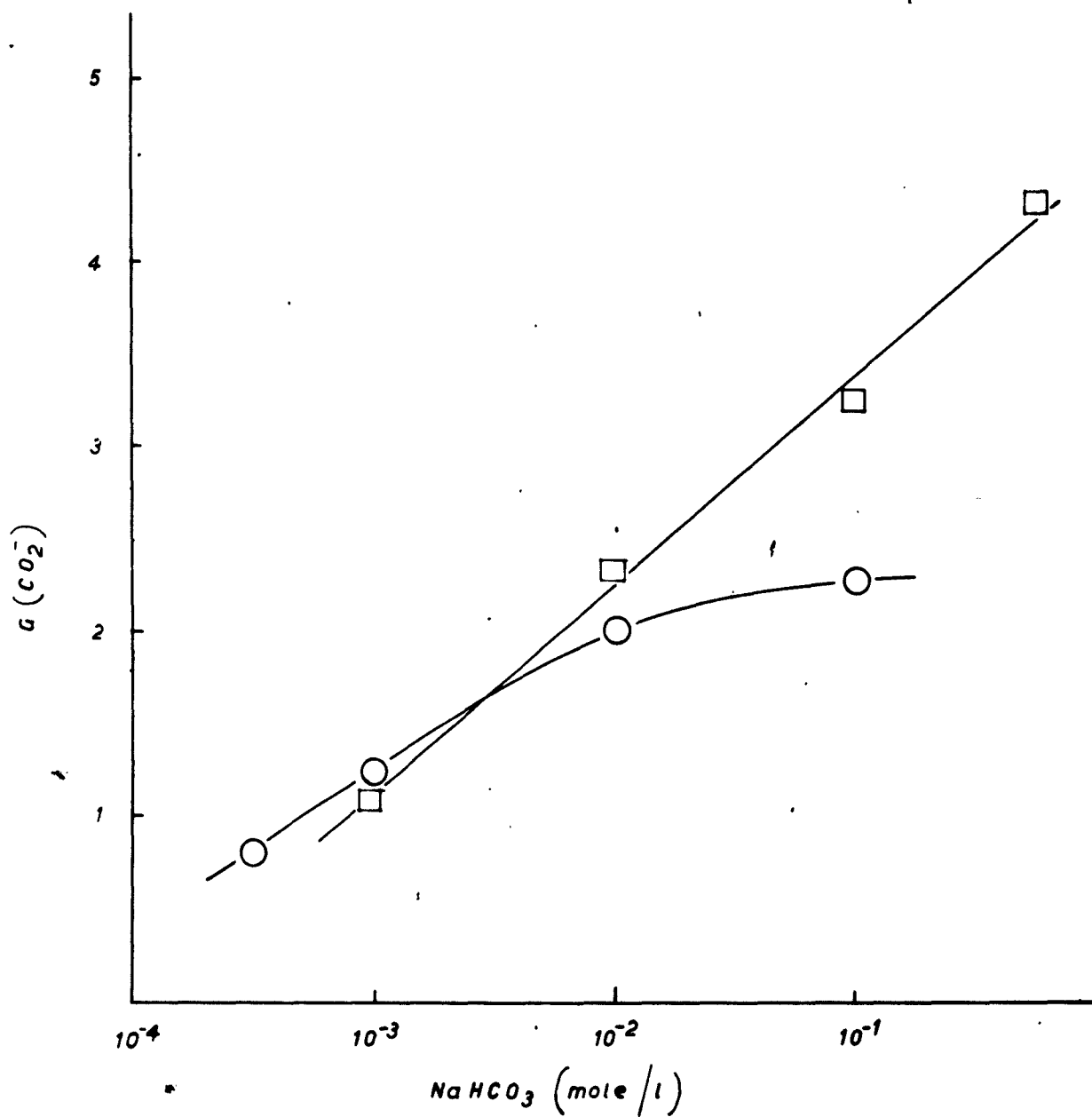


Fig. 3 Irradiation (Co^{60} γ -rays) of deaerated aqueous solutions of sodium formate in the presence of sodium bicarbonate. Dependence of the yield of C-14 labelled carboxyl group in oxalic acid on the concentration of C-14 labelled bicarbonate. \circ 10^{-3} M formate; \square 10^{-1} M formate.

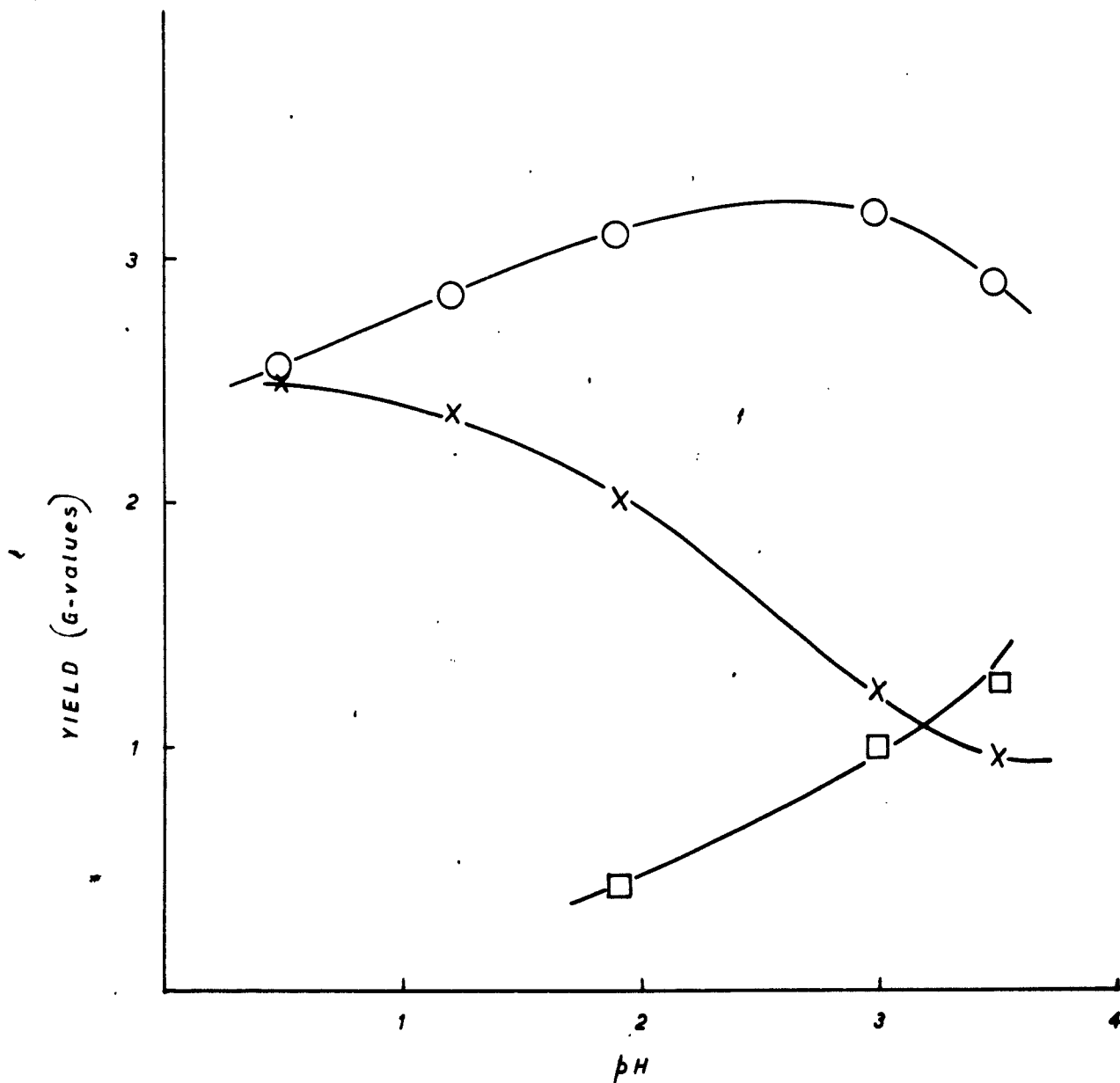


Fig 4 Irradiation (Co^{60} γ -rays) of aqueous solutions of 10^{-2} M formic acid. pH-dependence of the yield of O hydrogen in vacuum; X hydrogen in the presence of 2×10^{-2} M CO_2 ; □ C-14 labelled carboxyl group in oxalic acid from C^{14}O_2 .

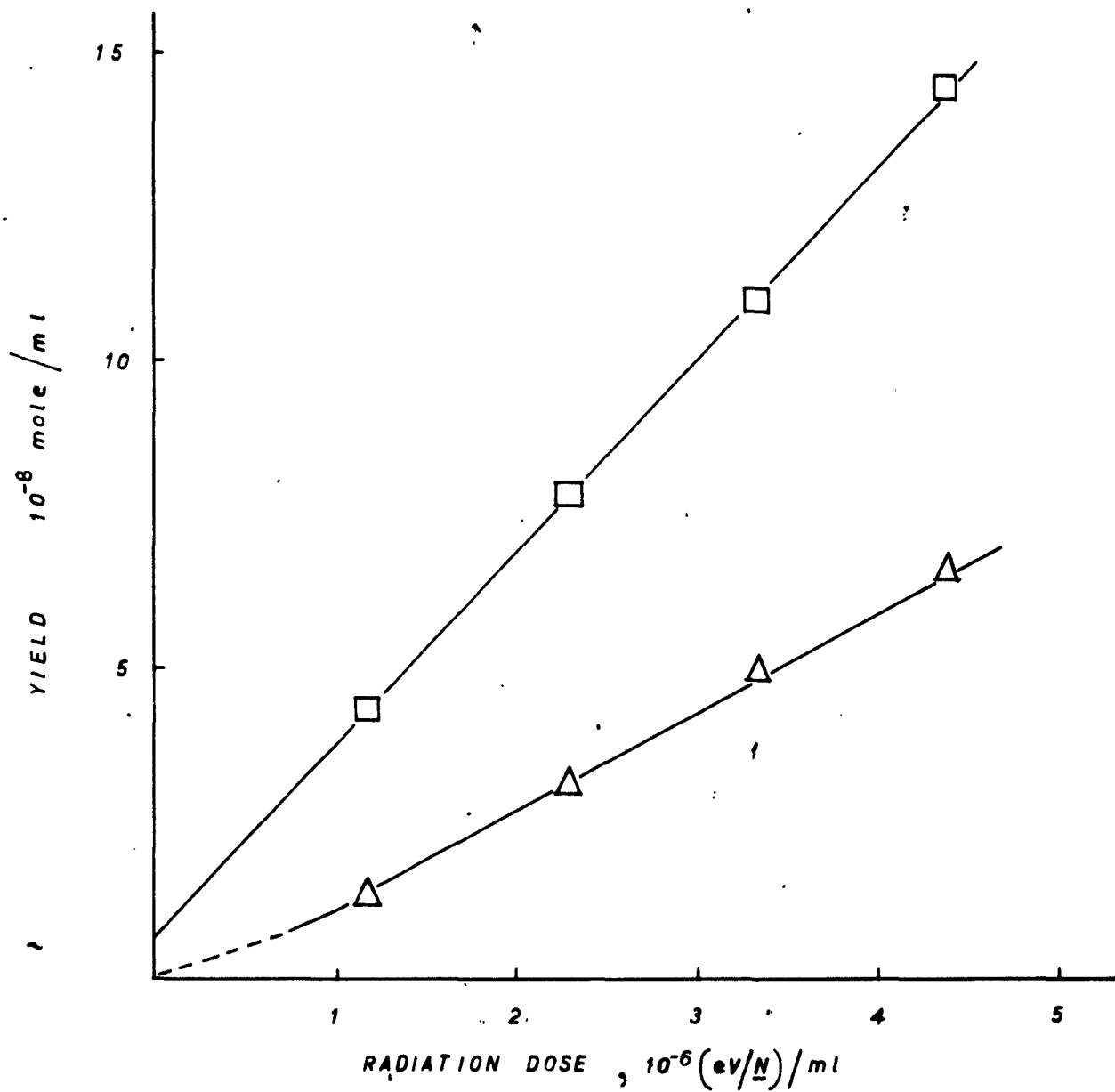


Fig. 5. Irradiation (Co^{60} , γ -rays) of aqueous solutions of 17 mM N_2O .
Yield vs. dose plot of \square nitrogen; Δ oxygen.

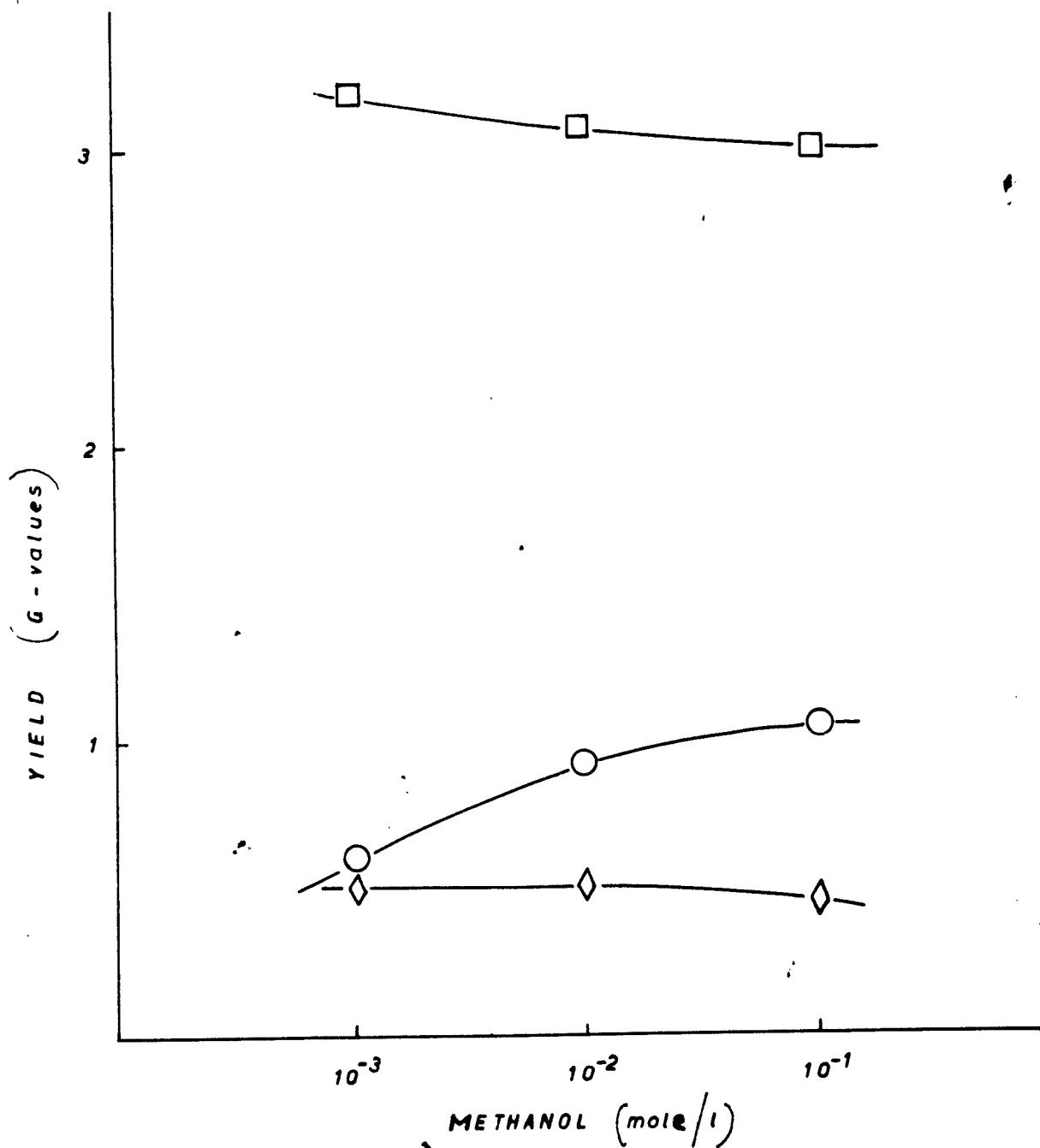


Fig. 6 Irradiation (Co^{60} γ -rays) of aqueous solutions of methanol in the presence of 17 mM N_2O . Dependence of the yield of \square nitrogen; \circ hydrogen; \diamond hydrogen peroxide, on the concentration of methanol.

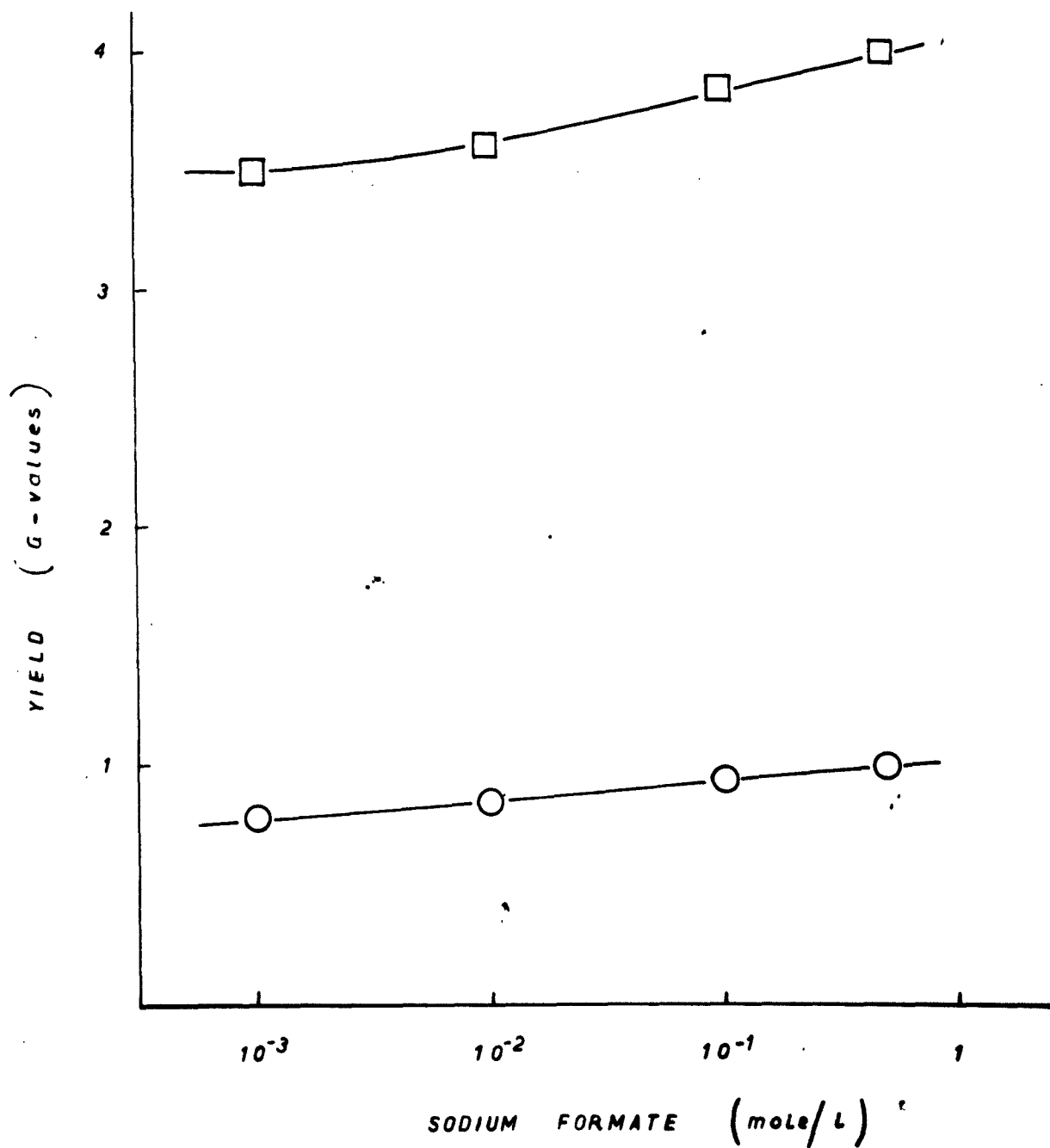


Fig. 7. Irradiation (Co^{60} γ -rays) of aqueous solutions of sodium formate in the presence of 17 mM N_2O . Dependence of the yield of \square nitrogen, and \circ hydrogen on the concentration of formate.