AAEC/E482

AAEC/E482

AUSTRALIAN ATOMIC ENERGY COMMISSION

RESEARCH ESTABLISHMENT

LUCAS HEIGHTS

THE RADIATION CHEMISTRY OF AQUEOUS SODIUM TEREPHTHALATE SOLUTIONS

by

R.W. MATTHEWS

April 1980

ISBN 0 642 59683 2

AUSTRALIAN ATOMIC ENERGY COMMISSION
RESEARCH ESTABLISHMENT
LUCAS HEIGHTS

THE RADIATION CHEMISTRY OF AQUEOUS SODIUM TEREPHTHALATE SOLUTIONS

by

R.W. MATTHEWS

ABSTRACT

The radiation chemistry of cobalt-60 gamma-irradiated aqueous sodium terephthalate solutions has been studied. In aerated 4×10^{-4} M sodium hydroxide solutions, the main products are hydroxyterephthalate (HTA) ($G = 0.99 \pm 0.01$), carbonate ($G = 1.31 \pm 0.08$), and peroxides ($G = 2.84 \pm 0.04$). The HTA and carbonate species are both formed as a result of hydroxyl radical attack and account for approximately 90 per cent of hydroxyl radical reactions. Oxygen needs to be present for efficient conversion of the terephthalate-OH radical adduct to HTA and oxygenation increases G(HTA) above the aerated solution value. G(HTA) is unaffected by changes in terephthalate concentration between 1×10^{-4} M and 1×10^{-2} M in sodium hydroxide solutions at pH 10. Decreasing the solution pH does however affect G(HTA). In phosphate buffered solutions at pH 6.85, G(HTA) is 0.93 ± 0.01 and lower

values are obtained with further decrease in solution pH. The lowering of the G(HTA) value is attributed to recombination reactions between the terephthalate-OH radical products and reducing radical products. Experimental evidence supporting the recombination postulate was obtained from the measurement of a parallel decrease in the peroxide yield and the observation of a dose rate effect on G(HTA). Competition kinetic studies with the added solutes carbonate and bicarbonate gave the rate ratios $k(OH + TA^{=}) : k(OH + CO_3^{=}) : k(OH + HCO_3^{-}) = 1 : 0.105 : 0.0036$.

National Library of Australia card number and ISBN 0 642 59683 2

The following descriptors have been selected from the INIS Thesaurus to describe the subject content of this report for information retrieval purposes. For further details please refer to IAEA-INIS-12 (INIS: Manual for Indexing) and IAEA-INIS-13 (INIS: Thesaurus) published in Vienna by the International Atomic Energy Agency.

RADIATION CHEMISTRY; SODIUM COMPOUNDS; AQUEOUS SOLUTIONS; PHTHALATES; GAMMA RADIATION; CHEMICAL DOSEMETERS

CONTENTS

CONTENTS (Continued)

1. INTRODUCTION

Solutions of sodium terephthalate were first proposed as a chemical dosimeter by Armstrong et al. [1963a]. Compared with other chemical dosimeters used for the measurements of low doses the terephthalate system performed well, particularly at doses below 1 Gy (100 rad) [Matthews et al. 1978]. Although the G value for the product, hydroxyterephthalate anion (HTA), is reported to be only 0.94, high sensitivity is achieved because of the brilliant fluorescence of this compound when excited by 315 nm light.

A desirable feature of any chemical dosimeter is that the main radiation-induced reactions occurring in the dosimeter be known. Such information is important because it enables a prediction of the nature and magnitude of possible impurity effects and the effect of such parameters as degree of aeration, solute concentration, dose rate, and quality of the radiation.

It is known that the terephthalate ion reacts rapidly with hydroxyl radicals [Anbar et al. 1966] and hydrated electrons [Gordon et al. 1964], and the pK_a values of the electron adduct are known [Neta and Fessenden 1973; Lilie and Fessenden 1973]. However, since Armstrong et al. published their original paper, nothing appears to have been reported on the yields of the stable products and the reactions giving these products, except that the HTA is formed as a result of hydroxyl radical attack [Matthews et al., in press].

It has been assumed that the reaction mechanism obtaining in irradiated aqueous benzoic acid [Armstrong et al. 1960] will also prevail in irradiated aqueous terephthalate solutions [Armstrong et al. 1963a] but there are important differences. For example, the post-irradiation reactions that detract from the value of the benzoate system as a dosimeter [Armstrong et al. 1963b; Matthews et al. 1978] appear to be absent from the terephthalate system. In addition, the sum of the 100 eV yields of hydroxybenzoic acid products in the benzoate system is about 1.4 [Loebl et al. 1951; Downes 1958; Armstrong et al. 1960; Loeff and Swallow 1964], which is significantly greater than the reported value of 0.94 for HTA from the terephthalate system [Armstrong et al. 1963a].

Additional information on the yields of stable products formed in irradiated aqueous terephthalate solutions and possible reaction mechanisms are reported here.

2. EXPERIMENTAL

2.1 Materials

Chemicals used were analytical reagent grade unless otherwise stated. Laboratory reagent terephthalic acid was recrystallised once from ethanol. Triply distilled water was used for the preparation of solutions unless otherwise stated. Gases used were industrial grade oxygen, high purity grade nitrogen, medical grade nitrous oxide, and a special analysis preparation of nitrous oxide/oxygen mixture. The pH of solutions was adjusted with sodium hydroxide, potassium acid phosphates, and sulphuric acid. The hydroxyterephthalic acid was prepared by the method of Kuhn et al. [1950, 1951] and recrystallised twice from water (activated charcoal). Potentiometric titration indicated a purity of 98.9 per cent.

2.2 Apparatus

Solutions were irradiated in four different vessels:

(a) Twenty millilitre glass vials, normally used as liquid scintillation counting containers, fitted with a plastic screw cap and a polyethylene liner.

(b) Fifteen millilitre Pyrex cylinders sealed with ground glass stoppers.

(c) Five centimetre pathlength cylindrical silica spectrophotometer cells fitted with ground glass stoppers.

(d) Thirty millilitre glass syringes fitted with cut-down plungers and ground glass caps.

Type (a) vessels were normally used for aerated solutions whereas types (b) and (c) were used for those irradiations in which the dissolved gas was other than air. The required gas was passed through the solution contained in an apparatus similar to that described by Boyle et al. [1959] which allowed a convenient transfer of the solution under controlled atmosphere to the irradiation cell. Fluorescence-induced photocurrents were measured with a Farrand spectrofluorometer. Absorbance measurements were taken using a Cary model 16 spectrophotometer fitted with a thermostatted cell compartment. Type (d) vessels were used in the experiments in which carbon dioxide was determined.

2.3 Irradiations

The dose rate was determined by ferrous sulphate dosimetry for each source and irradiation vessel taking $G(Fe^{3+})$ to be 15.6 [Fricke and Hart 1968], where G is the number of ions per 100 eV. Unless otherwise stated, the dose rate was approximately 0.4 Gy min^{-1} (40 rad min^{-1}). Some experiments were carried out at 8.3 Gy min^{-1} (830 rad min^{-1}). The molar extinction coefficient of the ferric species was taken as 2180 M^{-1} cm^{-1} at 304 nm and 25°C [Matthews 1973]. The energy absorbed in each solution was assumed to be directly proportional to the ratio of electron densities. Appropriate corrections were applied for the decay of the cobalt-60.

2.4 Analyses

(a) Hydroxyterephthalic acid

The HTA fluorescence measurements were taken at an analysing wavelength of 425 nm with an exciting wavelength of 315 nm. Before every measurement of current, the instrument was standardised against a 10^{-5} M salicylic acid solution prepared each day from a 10^{-3} M stock solution. The stock solution was freshly prepared every three days. In the standardisation, the exciting wavelength was set at 300 nm and the analysing wavelength at 410 nm. It was found that the efficiency of fluorescence of HTA did not vary significantly over the solution pH range 6 to 11, therefore, solution pH was adjusted to within this range before measurement. Acid solutions were adjusted to neutral pH by addition of sodium bicarbonate which does not quench the fluorescence. Solutions of sodium terephthalate have a small optical absorbance at 315 nm and therefore some apparent loss of fluorescence efficiency with increasing

terephthalate concentration is to be expected. To correct for this, aliquots of a known concentration of HTA were added to the various terephthalate solutions before and after irradiation. It was found that only in 10^{-2} M terephthalate solutions was a correction necessary and this was of the order of 5 per cent. The irradiation products, even at the highest doses, made no significant difference to the fluorescence efficiency.

(b) o-Hydroxybenzoic acid

The fluorescence characteristics of o-hydroxybenzoic acid (SAL) and HTA are similar, but the optimum λ_{ex} and λ_{an} for SAL are at wavelengths about 15 nm shorter than those for HTA. When the excitation monochromator was at 270 nm and the analysing monochromator at 375 nm, the fluorescence efficiency of SAL was 2.6 per cent of its maximum value whereas at these settings HTA had only 0.12 per cent of its maximum value. Therefore, fluorescence measurements were taken on some of the irradiated and unirradiated solutions at excitation and analysing wavelengths of 270 nm and 375 nm, respectively, to determine the upper limit of the SAL concentration.

(c) m-Hydroxybenzoic acid

The meta isomer of hydroxybenzoic acid (m-HBA) can be distinguished in mixtures with SAL and HTA by making use of the marked dependence of the fluorescence of m-HBA on the pH of the solution. Neither SAL nor HTA fluorescences are affected by changes in solution pH between 6.85 and 12.0 whereas m-HBA fluoresces strongly at pH 11 with λ_{ex} at 315 nm, but not at all at pH 6.85. The upper limit of m-HBA concentration can therefore be obtained from the change in fluorescence of the irradiated solution with λ_{ex} at 315 nm when the pH is changed from 11 to 6.85.

(d) p-Hydroxybenzoic acid

The para isomer of hydroxybenzoic acid (p-HBA) can be estimated in the presence of other hydroxybenzoic acids and HTA from the fluorescence of a solution at pH 12 using an exciting wavelength of 290 nm and an analysing wavelength of 330 nm.

(e) Carbon dioxide

The carbonate concentration of solutions was determined using a Van Slyke gas analyser. The standard method for determining carbon dioxide in blood [Peters and Van Slyke 1932] was used with the following modifications. The volume of solution for analysis was increased to 25 mL because the carbonate concentration in these solutions was much lower than in blood. Apart from increasing the amount of carbon dioxide to an amount that was measurable on the manometer, this modification introduced two problems:

(i) the much greater volume of dissolved air displaced the mercury level in the manometer off scale; and

(ii) the carbon dioxide was more difficult to remove from this large volume of solution because of the greatly decreased gas space to liquid ratio.

The first problem was solved by first extracting the air from the alkaline solution. The second problem was more difficult to overcome. The procedure finally adopted was to repeat the extraction of carbon dioxide from the acidified solution until a constant pressure was obtained on the manometer. This usually entailed 7 or 8 extractions and was extremely tedious. A single analysis generally took around 45 minutes. To avoid complicating radiation-induced decarboxylation reactions of the primary products, it was desirable to keep the total absorbed dose as low as possible. However, a 25 mL sample containing 10 μmol L^{-1} of carbonate only gave a manometric pressure difference of about 10 mm of mercury and reproducibility cannot be better than $\pm$ 1 mm. Accurate analysis at these low concentrations by this method is therefore difficult and time-consuming.

(f) Peroxides

The Ghormley iodide method [Hochanadel 1952] was used. A portion of the irradiated solution (10 mL for aerated, 14.7 mL for other gases) was added to 20 mL of the mixed reagent and diluted to 50 mL for the measurement. It was noticed that the absorbance decreased with time, therefore, measurements were made immediately after mixing. A small increase in absorbance at 350 nm was also observed in irradiated solutions treated in identical manner except that the iodide component of the reagent was omitted. Appropriate blanks were

therefore determined for all solutions.

(g) Other radiolytic products

Paper chromatography was used to look for the hydroxybenzoic acids and other radiolytic products. Solutions of 10^{-4} M and 10^{-3} M terephthalic acid in 4×10^{-4} M and 2.4×10^{-3} M sodium hydroxide were each given irradiations of 100 Gy (10 krad). Aliquots of 10 mL were evaporated to dryness on a steam bath and the residue dissolved in 300 mL of water. Approximately 30 µL of the concentrated extracts was spotted onto the paper together with control spots of o-, m- and p-hydroxybenzoic acids and HTA. The chromatograms were developed by the ascending method using standard techniques with two solvent systems:

(i) n-Butanol saturated with 5 M ammonium hydroxide [Downes 1958].

(ii) Benzene acetic acid water (2:2:1 by volume) [Bray et al. 1950].

3. RESULTS

3.1 Identity of Fluorescence Species at λ_{ex} 318 nm and λ_{an} 425 nm

The excitation and analysing wavelengths giving the maximum signal from irradiated solutions were the same as those required for the maximum signal from a solution of authentic HTA.

The fluorescence of an irradiated terephthalate solution was measured at various pHs; the results are plotted in Figure 1. Between pH 6 and 11 the fluorescence intensity is constant but a sharp decrease occurs at lower pH. The line drawn through the points is that calculated for a compound having a pK_a value of 2.55, a non-fluorescent molecular form and a fluorescent ionic form. The first ionisation constant of HTA is 2.60 [Heilbron and Bunburry 1953].

Solvent (i) used in the paper chromatography experiments gave an excellent separation of o-, m- and p-hydroxybenzoic acids but the R_f value for HTA was only 0.05 and did not allow resolution from the para isomer. However, a good separation of HTA was achieved in solvent (ii), with R_f values of 0.96,

0.34, 0.34 and 0.25 for the o, m and p isomers and HTA respectively. The irradiated solutions showed spots with an R_f value of 0.25 corresponding to the HTA in the control but no evidence of o-, m- or p-hydroxybenzoic acids. The irradiated 10^{-4} M terephthalate showed at least two additional unidentified overlapping spots with R_f values of about 0.007 and 0.04. Since these were absent from the irradiated 10^{-3} M terephthalate, they are possibly secondary radiolytic decomposition products resulting from hydroxyl radical attack on the HTA.

It is thus confirmed that HTA is a major product from the radiolysis of terephthalate solutions and it seems unlikely that significant interference could arise from any other fluorescent product. However, to obtain an estimate of the maximum possible contribution to the fluorescence registered in the HTA analysis arising from the o-, m- and p-hydroxybenzoic acids, solutions were analysed for these isomers.

Since the fluorescence intensity of the irradiated solution is unaffected by change in pH between 6 and 11, it is evident that the solution contains very little of the meta isomer. The concentration of meta isomer which would have registered a detectable change in fluorescence under the experimental conditions is 0.7 micromolar. For the irradiation dose used this concentration would have been present if G(m-HBA) = 0.07. It can therefore be stated that G(m-HBA) is less than 0.1.

Fluorescence measurements were taken with λ_{ex} and λ_{an} values of 270 nm and 375 nm, respectively, on 10^{-3} M terephthalate solution in 2.4×10^{-3} M NaOH irradiated to 100 Gy (10 krad) and unirradiated. The results showed that G(SAL) is less than 0.03.

The para isomer is much less fluorescent than the ortho and meta isomers and therefore the fluorescence measurements are likely to include significant contributions from traces of other fluorescent materials. Measurements were taken with λ_{ex} and λ_{an} values of 290 nm and 330 nm, respectively, on irradiated and unirradiated solutions adjusted to pH 12 before measurement. The results showed that G(p-HBA) is less than 0.27.

Fluorescence measurements with λ_{ex} and λ_{an} values of 318 nm and 425 nm respectively on solutions containing known concentrations of o-, m- and p-hydroxybenzoic acids showed that at the above G values the contribution of

these to the fluorescence intensity would be negligible. It is therefore concluded that at the wavelengths used, the difference in fluorescence intensity between irradiated and unirradiated terephthalate solutions is caused by HTA alone.

3.2 Fluorescence Intensity versus Absorbed Dose

The majority of experiments in which the fluorescence of the irradiated solution was followed were done using a dose rate of about 0.4 Gy min^{-1} (40 rad min^{-1}). In general, 1 x 10^{-4} M terephthalate solutions received seven irradiations ranging from about 0.40 to 4.0 Gy (40 to 400 rad). The fluorescence intensity versus absorbed dose plots showed no deviation from linearity unless otherwise stated. Slopes and standard errors were determined by the method of least squares. At higher concentrations, terephthalic acid precipitates from acid solutions, and therefore neutral or alkaline solutions must be used for these concentrations. When higher concentrations are used, the fluoresence of the unirradiated solution increases and, in some cases, it was necessary to use higher doses to maintain a satisfactory signal-to-blank ratio.

3.3 Effect of Terephthalate Concentration

G(HTA) was determined as a function of terephthalate concentration in dilute sodium hydroxide solution at pH approx. 10 and in 0.01 M phosphate buffer solution at pH 6.85. The results are given in Table 1. The G(HTA) values found in the dilute sodium hydroxide solutions are in reasonable agreement with those found by Armstrong et al. [1963].

3.4 Effect of pH on G(HTA)

It is apparent from the results in Table 1 that G(HTA) is significantly lower in the phosphate buffered solutions than in the sodium hydroxide solutions. It has already been established that this is not an effect of pH on the fluorescence intensity of HTA and therefore the decrease is attributable to a real decrease in G(HTA) with decrease in pH. The HTA yield was therefore determined in solutions at other pHs and the results are given in Table 2. The fluorescence intensities from the acid solutions were corrected for the lower fluorescence intensities of HTA at these pH values.

3.5 Dissolved Gas

The yield of HTA is markedly affected by the oxygen concentration as is shown by the results in Figure 2. Oxygenation of a 10^{-4} M terephthalate solution increases G(HTA) above the value obtained from aerated solutions by about 8 per cent. A much greater change is observed on de-aeration of the solution by bubbling with nitrogen; the yield of HTA falls sharply. The slope of the line passing through the somewhat scattered results from the de-aerated solution gave a G(HTA) value of 0.06 ± 0.03. The somewhat greater initial value was probably caused by incomplete removal of the last trace of oxygen.

Saturating a 10^{-4} M solution of terephthalate with a gas mixture of 80 per cent nitrous oxide and 20 per cent oxygen doubles the G(HTA) value obtained for aerated solution in the absence of nitrous oxide. In one experiment in which pure nitrous oxide was used, a practically identical yield was obtained, provided that the cells contained air, when filled with the nitrous oxide saturated solution. The results of this experiment are represented in Figure 3 by hollow circles. However, when oxygen was rigorously excluded from the nitrous oxide saturated solution and the cells, the results shown by the solid circles were obtained. The majority of these lie below the values from the aerated solution having no nitrous oxide. Scatter was again marked when oxygen was absent, as was the case with the nitrogen bubbled solution (Figure 2). The least squares analysis of this set of data gave a G(HTA) value of 0.29 ± 0.08.

3.6 Dose Rate

The results of Armstrong et al. [1963] show that G(HTA) is independent of dose rate for ^{60}Co gamma rays within the range 0.005 to 0.19 Gy min^{-1} (0.5 to 18.8 rad min^{-1}). The effect of higher dose rates was studied in the present investigation. It was found that when the dose rate was increased to about 7 Gy min^{-1} (700 rad min^{-1}), G(HTA) was significantly depressed. G(HTA) was found to be 0.91 ± 0.01 for 10^{-3} M terephthalate solutions at pH 10 and 0.79 ± 0.01 for 10^{-3} M terephthalate solution in 0.01 M phosphate buffer at pH 6.85. This represents a decrease of 7 per cent for the pH 10 solution and 14 per cent for the pH 6.85 solution below the respective values observed from 10^{-3} M solutions at these pH values, and a dose rate of 0.4 Gy min^{-1} (40 rad min^{-1}) (Table 1).

3.7 Added Solutes, Carbonate and Bicarbonate

The effect of sodium carbonate concentration on the yield of HTA, measured by the fluorescence current of irradiated aerated 1 x 10^{-4} M terephthalate solutions is shown in Figure 4. The pH of solutions ranged from 10.25 for no added sodium carbonate to 10.7 for 4 x 10^{-3} M added carbonate. Sodium carbonate had no effect on the fluorescence efficiency of HTA.

The effect of sodium bicarbonate on the yield of HTA from aerated 1 x 10^{-4} M terephthalate solutions is shown in Figure 5. The pH of solutions was adjusted to between 8.5 and 8.6 with potassium dihydrogen phosphate solution before irradiation. The addition of 0.05 M sodium bicarbonate to a solution of HTA showed no quenching effect.

3.8 Carbon Dioxide Analyses

The results of the analyses for carbon dioxide from a standard sodium carbonate solution are shown in Figure 6. The straight line drawn through the points is the theoretical yield. Figure 7 shows the yield of carbon dioxide obtained from irradiated aliquots of a solution of 1 x 10^{-3} M terephthalate in 2.4 x 10^{-3} M sodium hydroxide. The majority of analyses were completed within a few hours of the irradiations but some were allowed to stand for a number of hours before analysis. The results given in Figure 7 show that no significant post-irradiation effect occurred in the time period used. The straight line drawn through the points was obtained by the method of least squares and corresponds to a $G(CO_2)$ value of 1.31 ± 0.08. Results for an oxygenated solution are also shown in Figure 7 and indicate no significant difference from the aerated solution results. The addition of 0.1 M ethanol to the aerated solution depressed $G(CO_2)$ markedly.

3.9 Peroxide Analyses

The results shown in Figure 8 were obtained with the Ghormley iodide reagent added to 1 x 10^{-4} M terephthalate solutions irradiated at various pH values. The absorbance at 350 nm decreased with time, therefore, measurements were taken immediately after mixing with the reagents. The data deviate noticeably from linearity at the higher doses but adhere well to a straight line up to doses of about 30 Gy (3000 rad). The calibration plot made with standard hydrogen peroxide solutions gave good linearity and a molar

extinction coefficient equivalent for hydrogen peroxide of 23 390 $\underline{M}^{-1}$ cm^{-1}. No significant fading of the colour was observed with the standard hydrogen peroxide solutions.

Figure 9 shows the absorbance observed at 350 nm when the peroxide reagent was added to 1 x 10^{-4} $\underline{M}$ terephthalate in 0.01 $\underline{M}$ phosphate buffer solutions in the presence of various dissolved gases. The solutions containing oxygen gave results which are almost linear for doses up to about 60 Gy (6000 rad). However, with the de-aerated solution results, the onset of curvature occurs at very low doses. Rapid fading occurred in these solutions. The G(peroxides) values corresponding to the straight lines shown in Figures 8 and 9 are given in Table 3.

4. DISCUSSION

4.1 Hydroxylation by the Superoxide Radical Anion

The results obtained with added carbonate and bicarbonate, both of which react with hydroxyl radicals, and the results obtained with nitrous oxide, support the view that the HTA is formed as a result of hydroxyl radical attack on the terephthalate species [Armstrong et al. 1963; Matthews et al 1979]. It is also clear, however, that oxygen plays a significant part in the formation of the HTA. In de-aerated solutions, G(HTA) is only 0.06 ± 0.03 (Figure 1). This result seems to preclude the possibility of reaction 1 being significant in the formation of HTA:

$$2\ \cdot OH\ C_6H_4(COO)_2^{=} \longrightarrow C_6H_3OH(COO)_2^{=} + C_6H_4(COO)_2^{=} + H_2O \qquad (1)$$

Even in solutions saturated with nitrous oxide, in which the hydroxyl radical yield is approximately doubled, G(HTA) is less than in aerated solutions unless oxygen is present (Figure 3).

Since oxygen is clearly involved, it is necessary to deal with the possibility that HTA is formed by a superoxide radical attack on terephthalate species. Some support for this possibility comes from the significant increase in G(HTA) above the aerated solution value obtained by saturating the solution with oxygen (Figure 2). The suppression of G(HTA) by the OH radical scavengers, carbonate and bicarbonate, is not definitive evidence for OH

radical involvement in the formation of HTA since both of these solutes are known to react with the superoxide radical [Adams et al. 1966; Hayon and McGarvey 1967; Behar et al. 1970; Schmidt 1972]. However, the results obtained with the nitrous oxide/oxygen saturated gas mixture do provide good evidence for OH radical as the species initiating the reactions leading to the formation of the HTA.

The solubilities of nitrous oxide and oxygen in water at 23°C have been calculated to be 2.42×10^{-2} M [Hodgman et al. 1958] and 1.30×10^{-3} M [Hodgman et al. 1960] respectively. Therefore, in an aqueous solution saturated with a 4:1 nitrous oxide/oxygen gas mixture, the concentrations of nitrous oxide and oxygen are approximately 1.9×10^{-2} M and 2.6×10^{-4} M respectively. The specific reaction rate constants for the reactions of hydrated electrons with nitrous oxide [Gordon et al. 1963; Keene 1964; Hart and Fielden 1965; Asmus and Fendler 1968; Hickel and Schmidt 1970] and oxygen [Gordon et al. 1963; Keene 1964; Hart and Fielden 1965] are, respectively, approximately 8×10^{9} L M^{-1} s^{-1} and 2×10^{10} L M^{-1} s^{-1}, and with terephthalate anion [Gordon et al. 1964], 7×10^{9} L M^{-1} s^{-1}. The fraction of hydrated electrons reacting with nitrous oxide in a 1×10^{-4} M terephthalate solution saturated with a 4:1 nitrous oxide/oxygen gas mixture is, therefore, approximately 96 per cent, hence the yield of hydroxyl radicals should be approximately doubled in this solution. The increase in G(HTA) from 0.99 to 1.98 is, therefore, quite consistent with a reaction mechanism involving OH radical. On the other hand, since the superoxide radical yield decreases from approximately 88 per cent of the electron yield in an aerated 1×10^{-4} M terephthalate solution to approximately 4 per cent of the electron yield when the solution is saturated with a 4:1 nitrous oxide/oxygen mixture, some decrease in G(HTA) would be observed if the superoxide radical contributed significantly to the formation of HTA.

Other evidence against the superoxide radical contributing to the hydroxylation comes from the independence of G(HTA) on terephthalate concentration from 10^{-4} to 10^{-2} M in dilute sodium hydroxide solutions (Table 1). In this concentration range, the fraction of hydrated electrons reacting with oxygen to give superoxide radicals decreases markedly with increasing terephthalate concentration. Since there is no decrease in G(HTA) with increasing terephthalate concentration, it is concluded that the superoxide radical is not responsible for the formation of HTA.

4.2 The Role of Oxygen

There is good evidence from pulse radiolysis studies that oxygen reacts with the hydroxycyclohexadienyl radical formed in irradiated aqueous benzene solutions [Dorfman et al. 1962]. It is assumed that an analogous reaction (2) occurs in irradiated, aerated terephthalate solutions:

$$.OH\ C_6H_4(COO)_2^{=} + O_2 \longrightarrow .O_2OH\ C_6H_4(COO)_2^{=} \qquad (2)$$

The peroxy adduct radical may decompose unimolecularly to HTA (reaction 3) or undergo bimolecular dismutation to HTA by reaction 4:

$$.O_2OH\ C_6H_4(COO)_2^{=} \longrightarrow C_6H_3OH(COO)_2^{=} + H^+ + .O_2^- \qquad (3)$$

$$2\ .O_2OH\ C_6H_4(COO)_2^{=} \longrightarrow 2\ C_6H_3OH(COO)_2^{=} + H_2O_2 + O_2 \qquad (4)$$

An alternative possibility is that the peroxy adduct radical reacts in a bimolecular disproportionation reaction 5:

$$2\ .O_2OH\ C_6H_4(COO)_2^{=} \longrightarrow C_6H_3OH(COO)_2^{=} + C_6H_4(COO)_2^{=} + H_2O + 2\ O_2 \qquad (5)$$

The results of the CO_2 analysis (Figure 7) show that CO_2 is also formed as a result of OH radical attack, hence if reaction 5 is the source of the HTA, the total OH radical yield would be equal to

$$G(CO_2) + 2G(HTA) = 1.3 + 2.0$$

This is about one unit greater than the accepted value of G_{OH} at pH 10 allows. Therefore reaction 5 is dismissed as a significant reaction pathway for the formation of HTA.

4.3 Recombination Reactions

Reactions may occur between radiolytic products from the oxidising radical and radiolytic products from reducing radical species. Reactions of this type which reform terephthalate anions and water are called recombination reactions. The hydrated electron forms an electron adduct with terephthalate [Lilie and Fessenden 1973; Neta and Fessenden 1973] which has a pK_a value of 10.1 [Lilie and Fessenden 1973]. The reaction products from the adduct are

not known but the present results for de-aerated terephthalate solutions (Figure 2) suggest that considerable recombination takes place between the electron adduct and the hydroxycyclohexadienyl adduct. It appears that oxygen inhibits the recombination. The lower yield of HTA in aerated phosphate buffer and solutions of lower pH (Table 2) may also be related to more extensive recombination between protonated forms of the reducing radical products and the oxidising radical products.

The decrease in G(HTA) observed with increasing dose rate to aerated solutions, both at pH 10 and 6.85, supports the recombination reaction postulate. The greater effect is observed at the lower pH; this is in agreement with the suggestion that recombination is more extensive at this pH.

4.4 The Effect of Carbonate and Bicarbonate

The low values of G(HTA) obtained in aerated 10 micromolar terephthalate solutions (Table 1) were thought to be caused by impurities competing with terephthalate for the OH radicals. In the alkaline solutions, carbonate ion was considered as a likely impurity and prompted the competition kinetic study with carbonate ions (Figure 4).

The carbonate concentration was calculated assuming the second ionisation constant to be 10.25 [Vogel 1957]. The reported rate constant for hydroxyl radicals with bicarbonate ions [Keene et al. 1965; Weeks and Rabani 1966] is more than an order of magnitude slower than the reaction rate with carbonate ions, therefore, to a first approximation, its reaction at the pH of these solutions can be ignored. It was also assumed that the carbonate concentration of the freshly-prepared terephthalate in sodium hydroxide solution is insignificant in relation to the added carbonate.

If the yield of HTA in the presence of carbonate ions is controlled by a simple competition between terephthalate and carbonate ions for hydroxyl radicals, expression (I) should describe this yield:

$$S = S^0/(1 + k_6[CO_3^{=}]/k_7[TA^{=}]) \qquad (I)$$

where S = the fluorescence-induced photocurrent (arbitrary units) /min, S^0 = S at zero carbonate concentration, and k_6, k_7 = the rate constants for the reaction between OH radicals and carbonate ions, and the reaction between OH

radicals and terephthalate ions ($TA^{=}$) respectively; the square brackets denote concentrations. The slope, S, obtained by the method of least squares from the data in Figure 4, is plotted against the ratio of concentrations in Figure 10. The line drawn through the data was calculated by the method of least squares, assuming expression (I). It is seen that the data adhere reasonably well to the expression. The kinetic parameter k_6/k_7 evaluated in this analysis was 0.106 ± 0.011, which was in fair agreement with the ratio calculated from published values [Thomas 1965; Matthews and Sangster 1965; Adams et al. 1965; Anbar et al. 1966; Weeks and Rabani 1966] of k_6 and k_7 obtained by other methods.

The results in Figure 5 can be treated in the same way as those involving carbonate ion at various concentrations. The slopes of the lines, determined by the method of least squares are plotted against the ratio of concentration of bicarbonate ion to terephthalate ion in Figure 11. It was assumed that at this pH the added bicarbonate was entirely in the bicarbonate ion form in the solution.

Assuming that a simple competition obtains between bicarbonate ions and terephthalate ions for OH radicals, the expression relating the rate of formation of HTA to the ratio of solutes should be given by expression (II):

$$S = S^0/(1 + k_8[HCO_3^-]/k_7[TA^{=}]) \qquad (II)$$

where S^0 = S at zero bicarbonate concentration, and k_8 = the rate constant for the reaction between OH radicals and bicarbonate ions. The line drawn through the data was calculated by the method of least squares assuming expression (II), which describes the data well. The ratio of rate constants, k_8/k_7 evaluated in the analysis is $(5.67 \pm 0.86) \times 10^{-3}$.

The ionisation constants for carbonic acid are given [Vogel 1957] as 6.37 and 10.25. Ignoring corrections for activity coefficients, it can be shown that in the solutions used at pH 8.56, the species are present as approximately 98 per cent in the bicarbonate form and 2 per cent in the carbonate form. The evaluated ratio of rate constants therefore applies to a mixture of carbonates in this proportion, not to pure bicarbonate as written in expression (II). It is of interest to calculate the ratio for pure bicarbonate. In the competition kinetic experiments involving predominantly carbonate as the $CO_3^{=}$ form, a ratio of rate constants of 0.106 was obtained for

k_6/k_7. When the contribution from the $OH + CO_3^=$ reaction to the observed k_8/k_7 parameter is allowed for, the rate ratio $k(OH + HCO_3^-)/k(OH + TA^=)$ becomes 3.62×10^{-3}.

The same result can be reached by writing an expression which includes both forms of carbonate:

$$S = S^0/(1 + k_8[HCO_3^-]/k_7[TA^=] + k_6[CO_3^=]/k_7[TA^=]) \qquad (III)$$

and repeating the analysis of the pH 8.56 data, assuming expression (II) and the corrected bicarbonate and carbonate concentrations, and a numerical value of 0.106 for the ratio k_6/k_7 in the analysis. When this is done, exactly the same variance of fit and S^0 value is obtained as with expression (II) but the kinetic parameter k_8/k_7 becomes $(3.6 \pm 0.9) \times 10^{-3}$. The small amount of undissociated carbonate exists principally as a solution of carbon dioxide in water [Pusch 1916] and this is reported to be fairly unreactive to OH radicals [Keene et al. 1965, p.161]. Therefore, from the ratio $(3.6 \pm 0.9) \times 10^{-3}$ it should be possible to derive a reasonable estimate of $k(OH + HCO_3^-)$. Assuming a value [Farhataziz and Ross 1977] of 3.2×10^9 L $\underline{M}^{-1}$ s^{-1} for $k(OH + TA^=)$, a value of 1.15×10^7 L $\underline{M}^{-1}$ s^{-1} is obtained for $k(OH + HCO_3^-)$. Literature values [Keene et al. 1965; Weeks and Rabani 1966; Buxton et al. 1969; Buxton 1969; Waltz et al. 1973] range from 1×10^7 to 8×10^7 L $\underline{M}^{-1}$ s^{-1}. A reading of the methods used for these determinations reveals that the lower values of 1.0×10^7 and 1.5×10^7 were obtained from measurements at pH 7.6 [Keene et al. 1965, p.99] where carbonate interference would have been negligible or else the carbonate interference was allowed for [Weeks and Rabani 1966], but the pH was not specified in those determinations which yielded the higher values [Buxton 1969; Buxton et al. 1969; Waltz et al. 1973]. It seems possible that the higher values may not have been corrected for the contribution from the $CO_3^=$ component.

The ratio of rate constants, $k(OH + CO_3^=) / k(OH + TA^=)$, measured as 0.106 ± 0.011, was not corrected for any contribution from the bicarbonate species. At pH 10.6 the carbonate exists as approximately 69 per cent as the $CO_3^=$ species and 31 per cent as the HCO_3^- species. Least squares analysis of the data in Figure 10 was repeated assuming that expression (III) described the data, allowing for the two forms of carbonate and supplying a value of 3.6×10^{-3} for k_8/k_7. The value for k_6/k_7 obtained in this analysis was 0.105 ±

0.011 which is not significantly different from the value obtained when the contribution from bicarbonate is neglected. If the value of 3.2×10^9 is assumed for k_7 [Farhataziz and Ross 1977], the estimated value for $k(OH + CO_3^=)$ is 3.4×10^8 L $\underline{M}^{-1}$ s^{-1}, which is in fair agreement with published values of this rate constant [Matthews and Sangster 1965; Thomas 1965; Adams et al. 1965; Weeks and Rabani 1966].

4.5 Carbon Dioxide Yield

The results indicate that hydroxyl radicals are responsible for the decarboxylation as has been found for benzoate solutions [Matthews and Sangster 1965]. Within the fairly large limits of experimental error, the change in oxygen concentration from 2.7×10^{-4} $\underline{M}$ to 1.3×10^{-3} $\underline{M}$ had no significant effect (Figure 7). The fraction of hydrated electrons reacting with the terephthalate is significantly affected by oxygenation. Therefore neither hydrated electrons nor the product of reaction between hydrated electrons and oxygen, i.e. superoxide radical anions, appear to be significant contributors to the decarboxylation. The fact that 0.1 $\underline{M}$ ethanol almost completely suppresses the CO_2 yield supports the hydroxyl radical postulate since ethanol is a known scavenger for OH radicals [Farhataziz and Ross 1977].

A significant difference from the benzoate decarboxylation is the apparent absence of any post-irradiation increase in the CO_2 yield. The absence of any observable post-irradiation increase in the HTA yield also contrasts with the marked post-irradiation increase of salicylate from irradiated benzoate solutions [Matthews et al. 1978]. The post-irradiation increase in CO_2 yield may be related to OH radical attack on benzoate at the ring carbon para to the carboxy group. This attack may be more difficult in terephthalate since the para position is already substituted with another carboxy group. Alternatively, the additional carboxy group may disturb the electron distribution so that the transient precursor, which slowly releases carbon dioxide, is either not formed or else is rapidly decomposed.

The $G(CO_2)$ value from irradiated terephthalate is approximately twice the $G(CO_2)$ value for the prompt yield of carbon dioxide from irradiated benzoate solution [Matthews and Sangster 1965]. Since there are twice as many carboxylate groups in terephthalate, the prompt yield of carbon dioxide may be initiated by OH radical attack on the carboxylate groups.

The fate of the decarboxylated moiety remains unknown. Although the p-benzoate species could be formed with a G value of up to 0.27, it is most probably significantly lower than this and, in any case, $G(CO_2)$ was found to be 1.3. The majority of CO_2 eliminated from the molecule is therefore not simply replaced by an OH group.

4.6 The Peroxide Yield

It can be assumed that the iodide method used for the analysis will register all peroxides formed irrespective of their chemical form. The reactions 3 and 4 proposed to form HTA also give a hydrogen peroxide yield equal to 0.5 G(HTA) since

$$.O_2^- + .O_2^- \xrightarrow{2H^+} H_2O_2 + O_2 \qquad (6)$$

If the reaction forming carbon dioxide also yields hydrogen peroxide equal to 0.5 $G(CO_2)$, the H_2O_2 yield from hydroxyl radical reactions will be approximately 0.5 G_{OH}, since $G(HTA) + G(CO_2) \simeq G_{OH}$.

The product of the reactions of hydrated electrons and hydrogen atoms with terephthalate may also give hydrogen peroxide from reactions having stoichiometries equivalent to reaction 7.

$$C_6H_4(COO)_2^{=}....e^-_{aq} + O_2 \longrightarrow C_6H_4(COO)_2^{=} + .O_2^- \qquad (7)$$

The contribution of hydrated electron and hydrogen atom reactions of this stoichiometry towards the peroxide yield would therefore be 0.5 $(G^-_{e_{aq}} + G_H)$.

The total yield of peroxides based on the above reaction stoichiometries is given by expression (IV):

$$G(\text{peroxides}) = G_{H_2O_2} + 0.5(G_{OH} + G_{e^-_{aq}} + G_H) \qquad (IV)$$

where $G_{H_2O_2}$ = the interspur yield of hydrogen peroxide.

Substitution of the generally accepted primary radiolytic yields [Draganic and Draganic 1971] in the expression gives a G(peroxides) value of about 3.6. The experimentally found G(peroxides) values (Table 3) are all

significantly less than 3.6.

It is therefore clear that not all the radical species participate in reactions of the above stoichiometries. Recombination reactions between oxidised and reduced radical forms of terephthalate have already been invoked to account for differences in the HTA yield with oxygen concentration, pH, and dose rate. The stoichiometry of these recombination reactions is assumed to be given by reaction 8:

$$C_6H_4(COO)_2^{=}OH\ O_{2\cdot} + C_6H_4(COO)_2^{=}\ O_2e^-_{aq} \longrightarrow 2\ C_6H_4(COO)_2^{=} + OH^- + 2\ O_2 \quad (8)$$

for solutions containing oxygen, and the reaction 9:

$$C_6H_4(COO)_2^{=}\ OH\cdot + C_6H_4(COO)_2^{=}\ \ldots\ldots e^-_{aq} \longrightarrow 2\ C_6H_4(COO)_2^{=} + OH^- \quad (9)$$

for de-aerated solutions. Peroxides are not formed in either reaction and the assumed precursors of peroxides are destroyed.

If the depression in G(HTA) is a reflection of the extent of recombination, the results indicate that the most extensive recombination occurs in de-aerated solutions. The low value of G(peroxides) found for de-aerated solutions (Figure 9) provides corroboration. The deviation of the results from linearity in the de-aerated solutions may be due to a reaction between reducing species and the triiodide ion.

With one exception, the G(peroxides) values parallel the increase in G(HTA), indicating that at least a portion of the OH radicals giving HTA also give peroxides. The exception is the terephthalate solution saturated with 4:1 nitrous oxide/oxygen mixture. In this solution the value of G(HTA) is 1.98 but the G(peroxides) value is only 2.32. Since the extent of the reaction of hydrated electrons with terephthalate species is greatly decreased in this solution, the result suggests that, in the absence of recombination, a high proportion of the terephthalate-hydrated electron adduct is converted to peroxides.

It is observed that in aerated 4×10^{-4} M NaOH solution containing 1×10^{-4} M terephthalate, G(peroxides) = 2.84 ± 0.04 which is in good agreement with $G_{H_2O_2} + {}^1/_2(G_{e_{aq}} + G_H + G_{HTA})$ (≈ 2.8). This observation may indicate that:

(a) all of the hydrated electrons and hydrogen atoms react to give half an equivalent of peroxides;

(b) the portion of hydroxyl radicals giving HTA also gives half an equivalent of peroxides; and

(c) the portion of hydroxyl radicals giving CO_2 gives no peroxides.

The G(peroxides) value calculated on this basis for the 4:1 nitrous oxide/oxygen saturated solution, in which approximately 96 per cent of the hydrated electrons react with nitrous oxide, is 2.3; this is in agreement with the found value of 2.32 ± 0.05. The depression of found G(peroxides) values below 2.8 in the other solutions is attributed to recombination reactions.

5. CONCLUSIONS

It has been confirmed that HTA is the main fluorescent product formed when aerated sodium terephthalate solutions are irradiated. G(HTA) was found to be 0.99 ± 0.01 in aerated 4×10^{-4} M sodium hydroxide solutions of terephthalate. The yield of HTA is little affected by change in the terephthalate concentration within the range 10^{-4} to 10^{-2} M but it decreases with decreasing pH. The oxygen concentration has a marked effect on G(HTA); low yields are formed if oxygen is excluded. Addition of nitrous oxide to the solution doubles the yield when oxygen is present. Increasing the dose rate from 0.4 to 7 Gy min^{-1} decreases G(HTA) by about 10 per cent. Carbonate and bicarbonate ions both depress the yield in aerated solutions. The extent of the decrease is in excellent agreement with a simple competition between terephthalate ion and carbonate or bicarbonate ion for the hydroxyl radical. The specific rate ratio $k(OH + TA^{=}):k(OH + CO_3^{=}):k(OH + HCO_3^{-})$ was found to be 1:0.105:0.0036. Analyses for o-, m-, and p-hydroxybenzoic acids showed that the G values for these compounds were less than 0.03, 0.1 and 0.27 respectively. Other major products formed in aerated solution are carbon dioxide and peroxides. In 4×10^{-4} M sodium hydroxide solution $G(CO_2) = 1.31 \pm 0.08$ and G(peroxides) = 2.84 ± 0.04. The results are consistent with recombination reactions occurring to a significant extent under some experimental conditions and these cause a concomitant decrease in the yields of both HTA and peroxides.

6. ACKNOWLEDGEMENT

I wish to thank Dr J.G. Wilson of this laboratory for providing the hydroxyterephthalic acid.

7. REFERENCES

Adams, G.E., Boag,J.W. and Michael, B.D. [1965] - Trans. Faraday Soc., 61:1417.

Adams, G.E., Boag, J.W. and Michael, B.D. [1966] - Proc. Roy. Soc., A289:321.

Anbar, M., Meyerstein, D. and Neta, P. [1966] - J. Phys. Chem., 70:2660.

Armstrong, W.A., Black, B.A. and Grant, D.W. [1960] - J. Phys. Chem., 64:1415.

Armstrong, W.A., Facey, R.A., Grant, D.W. and Humphreys, W.G. [1963a] - Canad. J. Chem., 41:1575.

Armstrong, W.A., Facey, R.A., Grant, D.W. and Humphreys, W.G. [1963b] - Radiat. Res., 19:120.

Asmus, K.D. and Fendler, J.H. [1968] - J. Phys. Chem., 72:4285.

Behar, D., Czapski, G. and Duchouny, I. [1970] - J. Phys. Chem., 74:2206.

Boyle, J.W., Weiner, S. and Hochanadel, C.J. [1959] - J. Phys. Chem., 63:892.

Bray, H.G., Thorpe, W.V. and White, K. [1950] - Biochem, J., 46:271.

Buxton, G.V. [1969] - Trans. Faraday Soc., 65:2150.

Buxton, G.V., Dainton, F.S. and Kalecinski, J. [1969] - Int. J. Radiat. Phys. Chem., 1:87.

Dorfman, L.M., Taub, I.A. and Buhler, R.E. [1962] - J. Chem. Phys., 36:3051.

Downes, A.M. [1958] - Aust. J. Chem., 11:154.

Draganic, I.G. and Draganic, Z.D. [1971] - The Radiation Chemistry of Water, Academic Press, New York and London, p.140.

Farhataziz, and Ross, A.B. [1977] - Selected Specific Rates of Reactions of Transients from Water in Aqueous Solution. III - Hydroxyl Radical and Perhydroxyl Radical and Their Radical Ions. NSRDS-NBS59, National Bureau of Standards, Washington.

Fricke, H. and Hart, E.J. [1968] - Radiation Dosimetry, Vol.II (ed. Attix, F.H. and Roesch W.C.) Academic Press, New York, p.167.

Gordon, S., Hart, E.J., Matheson, M.S., Rabani, J., Thomas, J.K. [1963] - Discuss. Faraday Soc., 36:193.

Gordon, S., Hart, E.J. and Thomas, J.K. [1964] - J. Phys. Chem., 68:1262.

Hart, E.J. and Fielden, E.M. [1965] - Advan. Chem. Ser., 50:253.

Hayon, E. and McGarvey, J.J. [1967] - J. Phys. Chem., 71:1472.

Heilbron, I. and Bunburry, H.M. [1953] - Dictionary of Organic Compounds, Vol.2, Eyre and Spottiswoode, London, p.828.

Hickel, B. and Schmidt, K.H. [1970] - J. Phys. Chem., 74:2470.

Hochanadel, C.J. [1952] - J. Phys. Chem., 56:587.

Hodgman, C.D., Weast, R.C. and Selby, S.M. [1958] - Handbook of Physics and Chemistry, Chemical Rubber Publishing Co. Cleveland, Ohio, 39th edition, p.1609.

Hodgman, C.D., Weast, R.C. and Selby, S.M. [1960] - Ibid, 42nd edition, p.1706.

Keene, J.P. [1964] - Radiat. Res., 22:1.

Keene, J.P., Raeff, Y. and Swallow, A.J. [1965] - In 'Pulse Radiolysis' (ed. Baxendale, J.H., Ebert, M., Keene, J.P. and Swallow, A.J.) Academic Press, p.161.

Kuhn, R., Zilliken, F., Trischman, H. and Hoppe-Seylers, Z. [1951] - Physiol. Chem., 286:264.

Kuhn, R., Zilliken, F. and Trischman, H. [1950] - Chem. Ber., 83:304.

Lilie, J. and Fessenden, R.W. [1973] - J. Phys. Chem., 77:674.

Loebl, H., Stein, G. and Weiss, J. [1951] - J. Chem. Soc., 405.

Loeff, I. and Swallow, A.J. [1964] - J. Phys. Chem., 68:2470.

Matthews, R.W. and Sangster, D.F. [1965] - J. Phys. Chem., 69:1938.

Matthews, R.W. [1973] - Radiat. Res., 55:242.

Matthews, R.W., Barker, N.T. and Sangster, D.F. [1978] - Int. J. Appl. Radiat. Isotopes, 29:1.

Matthews, R.W., Barker, N.T. and Sangster, D.F. [1979] - Int. J. Appl. Radiat. Isotopes (in press).

Neta, P. and Fessenden, R.W. [1973] - J. Phys. Chem., 77:620.

Peters, J.P. and Van Slyke, D.D. [1932] - Quantitative Clinical Chemistry, Vol.II. The Williams and Wilkins Co., Baltimore, p.284.

Pusch, L. [1916] - Elektrochem. Z. 22:206.

Schmidt, K.H. [1972] - Int. J. Radiat. Phys. Chem., 4:439.

Thomas, J.K. [1965] - Trans. Faraday Soc., 61:702.

Vogel, A.I. [1957] - Quantitative Inorganic Analysis, second ed., p.7, Longmans, Green and Co.

Waltz, W.L., Akhtar, S.S. and Eager, R.L. [1973] - Canad. J. Chem., 51:2525.

Weeks, J.L. and Rabani, J. [1966] - J. Phys. Chem., 70:2100.

TABLE 1
EFFECT OF TEREPHTHALATE ION CONCENTRATION ON G(HTA), AERATED SOLUTIONS

$[TA^{=}]$ ($\underline{M}x10^{4}$)	G(HTA) (NaOH)	[NaOH] ($\underline{M} \times 10^{4}$)	G(HTA) (0.01 $\underline{M}$ phos.)
0.1	0.74*	2	0.69 ± 0.01
1.0	0.99 ± 0.01	4	0.93 ± 0.01
10.0	0.98 ± 0.01	24	0.92 ± 0.01
100.0	0.97 ± 0.02	204	

*There was evidence of some deviation from linearity in this solution. Therefore, since the mathematical relationship describing the curvature was not known, a least squares fit was not possible. The numerical value of 0.74 is the estimated initial yield.

TABLE 2
EFFECT OF pH ON G(HTA) FROM AERATED 1×10^{-4} $\underline{M}$ TEREPHTHALATE SOLUTIONS

pH	Solution	G(HTA)
11.0	Sodium hydroxide	0.99 ± 0.01
10.4		0.99 ± 0.01
9.6		0.99 ± 0.01
6.85	10^{-3} $\underline{M}$ mixed phosphates	0.93 ± 0.01
6.85	10^{-2} $\underline{M}$ mixed phosphates	0.93 ± 0.01
5.0	Sulphuric acid	0.83 ± 0.02
2.0		0.88 ± 0.02
1.4		0.68 ± 0.06

TABLE 3
G(PEROXIDES) IN IRRADIATED 1 x 10^{-4} M
TEREPHTHALATE SOLUTIONS

Solution	pH	G(peroxides)
4 x 10^{-3} M H_2SO_4, aerated	2.2	2.26 ± 0.05
10^{-2} M phosphate, aerated	6.85	2.68 ± 0.06
4 x 10^{-4} M NaOH, aerated	10.4	2.84 ± 0.04
10^{-2} M phosphate, de-aerated	6.85	0.7
10^{-2} M phosphate	6.85	2.32 ± 0.05
4:1 N_2O : O_2		
10^{-2} M phosphate, oxygenated	6.85	3.13 ± 0.06

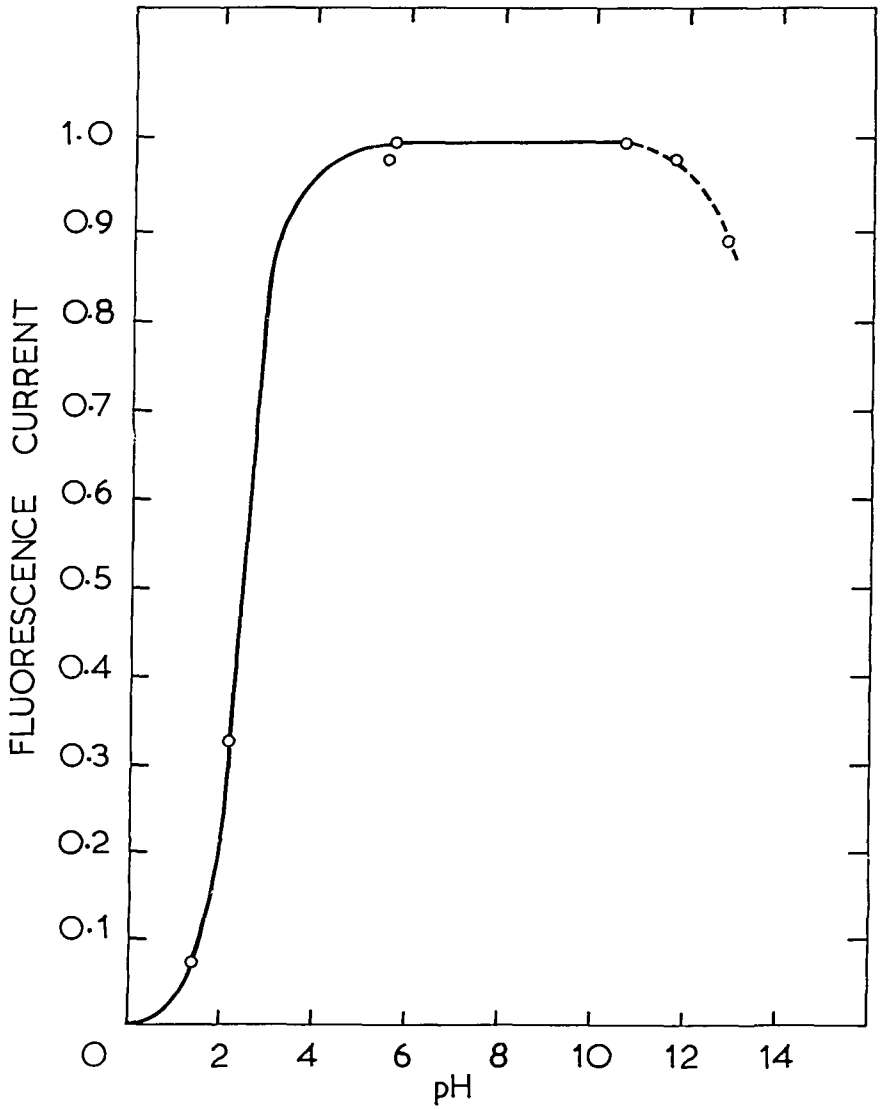

FIGURE 1. FLUORESCENCE-INDUCED PHOTOCURRENT OF IRRADIATED SODIUM TEREPHTHALATE SOLUTION vs. pH

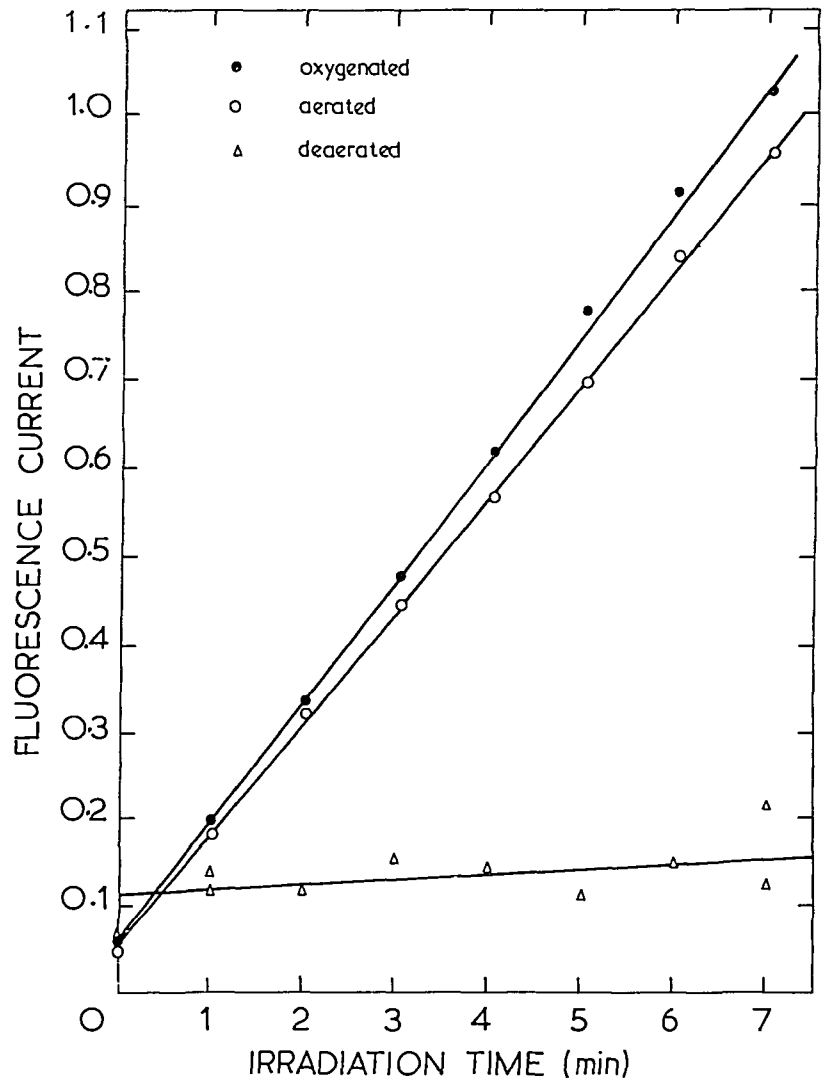

FIGURE 2. FLUORESCENCE-INDUCED PHOTOCURRENT vs. IRRADIATION TIME FOR 1×10^{-4} M SODIUM TEREPHTHALATE AT ~pH 10 CONTAINING VARIOUS CONCENTRATIONS OF O_2

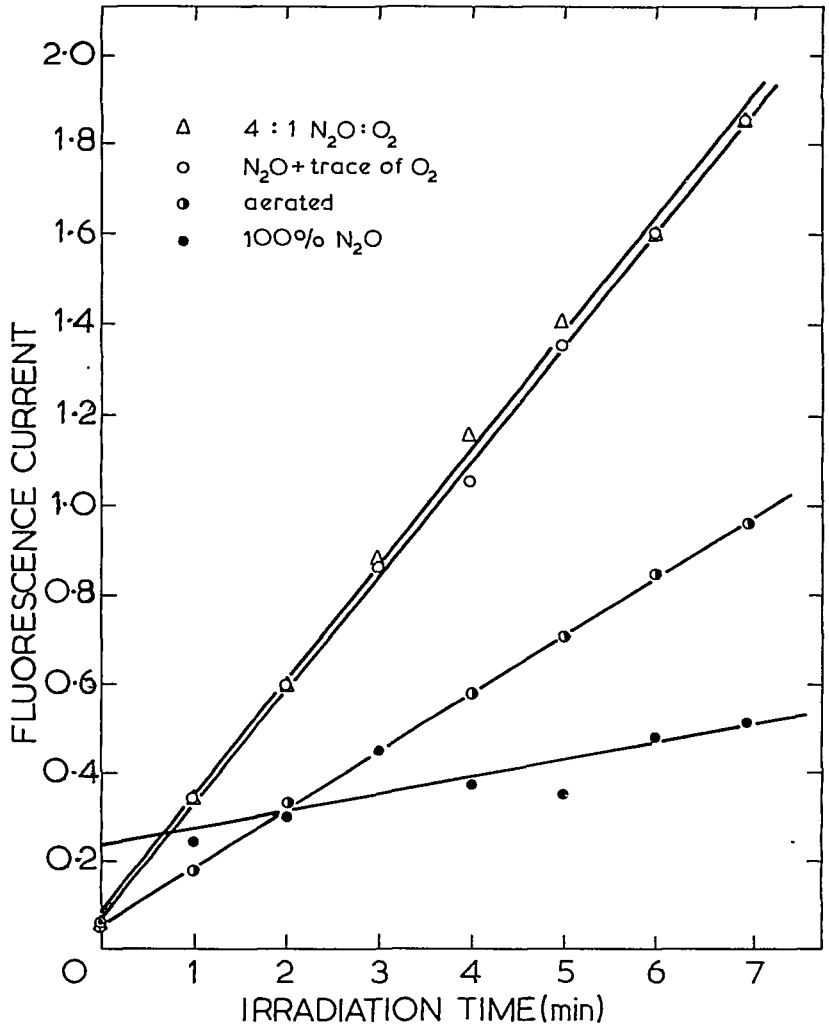

FIGURE 3. FLUORESCENCE-INDUCED PHOTOCURRENT vs. IRRADIATION TIME FOR 1×10^{-4} M SODIUM TEREPHTHALATE AT ~pH 10 CONTAINING N_2O IN VARIOUS PROPORTIONS WITH O_2

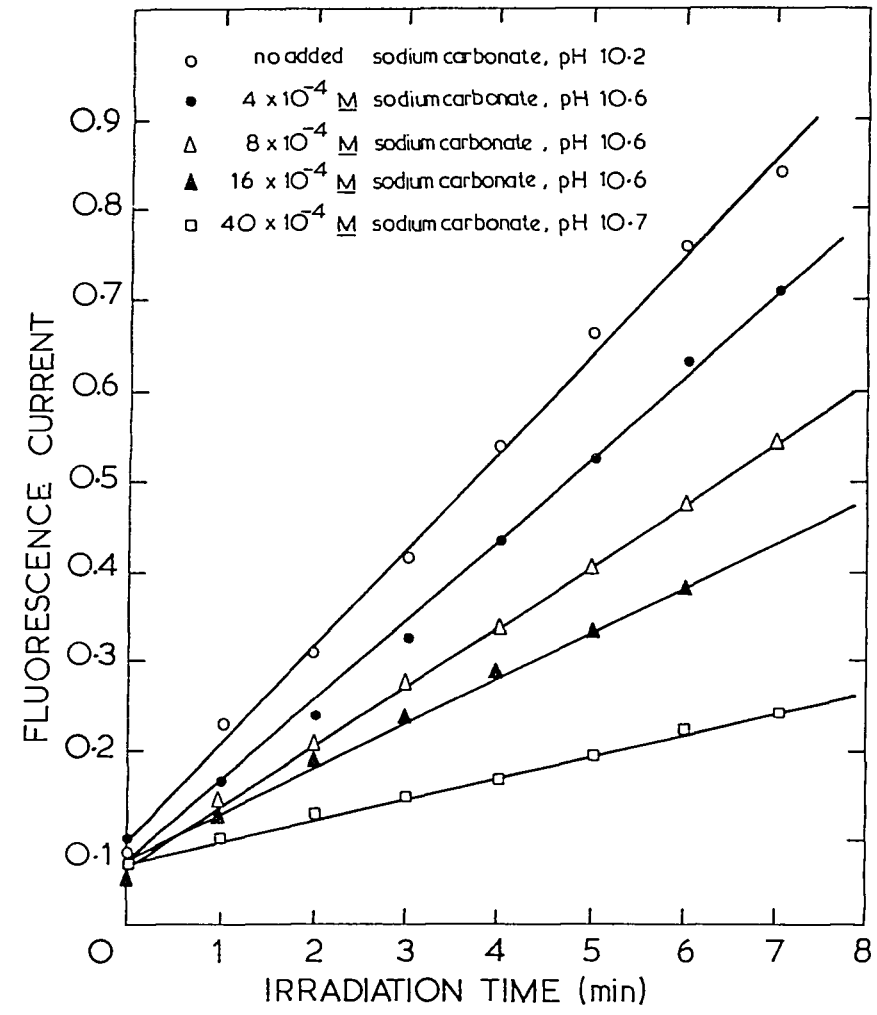

FIGURE 4. EFFECT OF CARBONATE ION CONCENTRATION ON G(HTA). FLUORESCENCE-INDUCED PHOTOCURRENT vs. IRRADIATION TIME. AERATED 1×10^{-4} M SODIUM TEREPHTHALATE SOLUTIONS

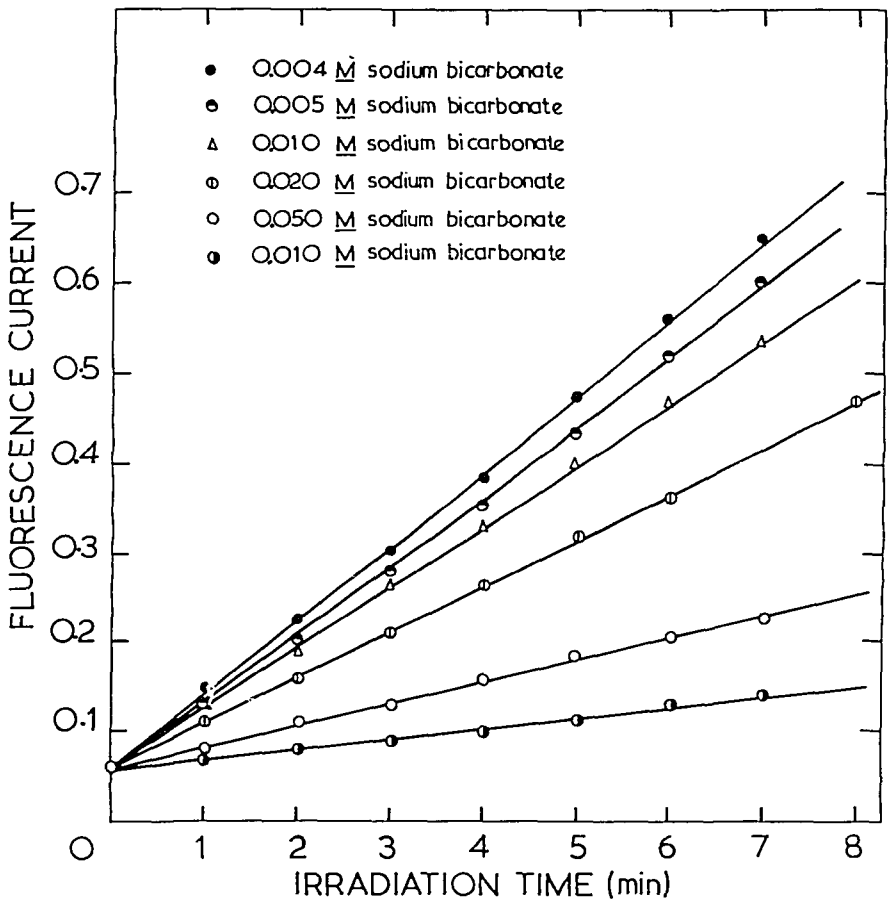

FIGURE 5. EFFECT OF BICARBONATE ION CONCENTRATION ON G(HTA). FLUORESCENCE-INDUCED PHOTOCURRENT vs. IRRADIATION TIME. AERATED 1×10^{-4} M SODIUM TEREPHTHALATE SOLUTIONS, pH 8.56

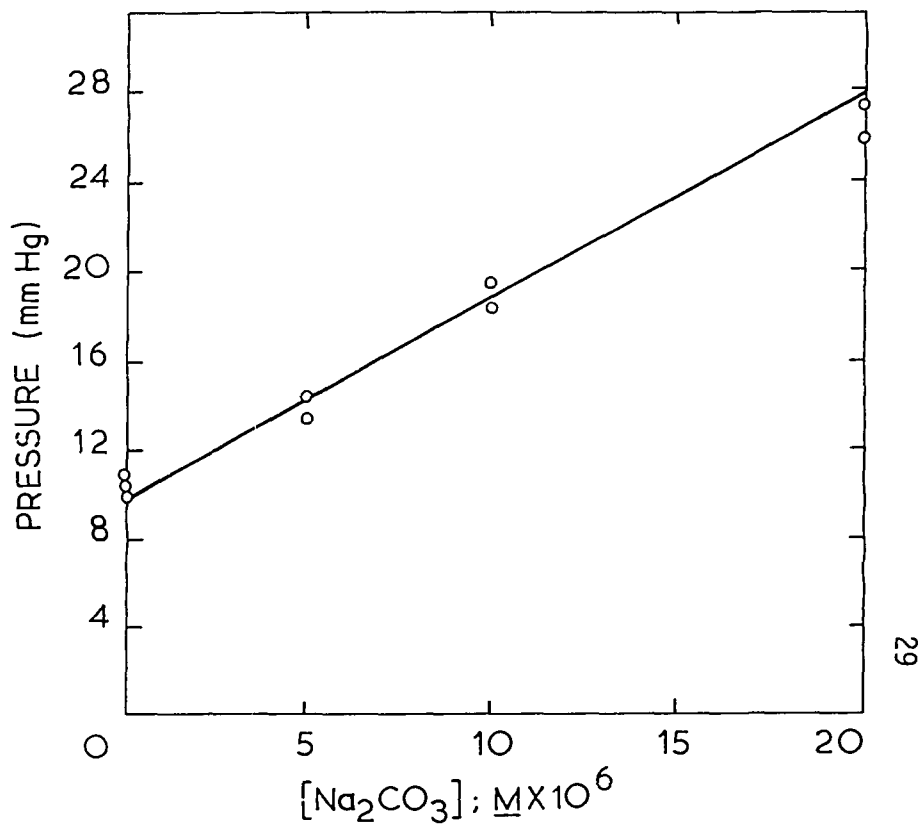

FIGURE 6. TEST OF ANALYTICAL METHOD FOR CARBON DIOXIDE

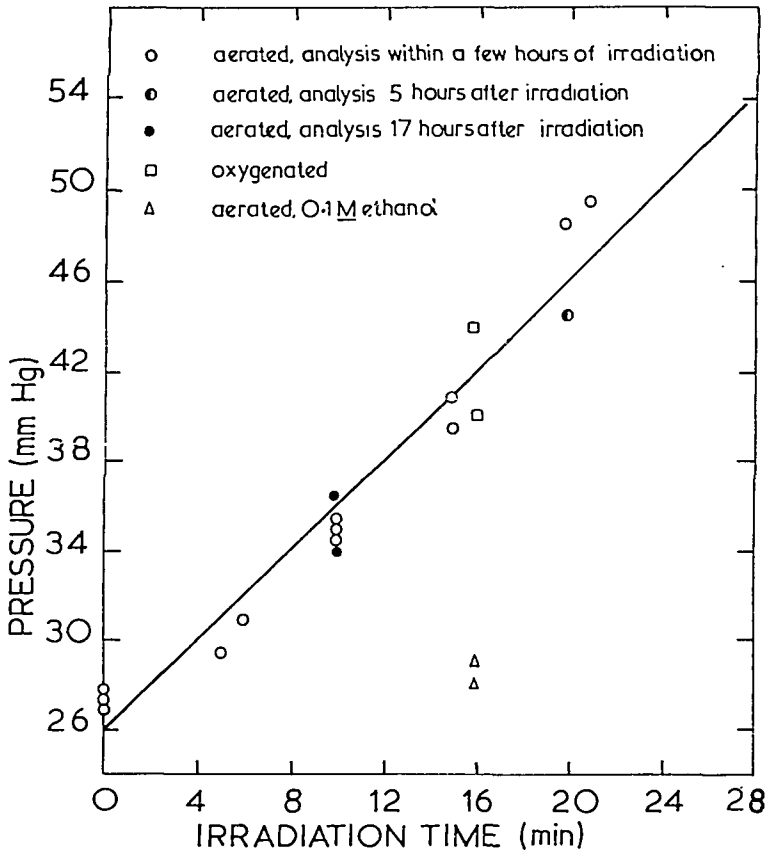

FIGURE 7. CARBON DIOXIDE YIELD vs. ABSORBED DOSE. 10^{-3}M SODIUM TEREPHTHALATE IN 2.4×10^{-3}M SODIUM HYDROXIDE. DOSE RATE ~700 rad min^{-1}

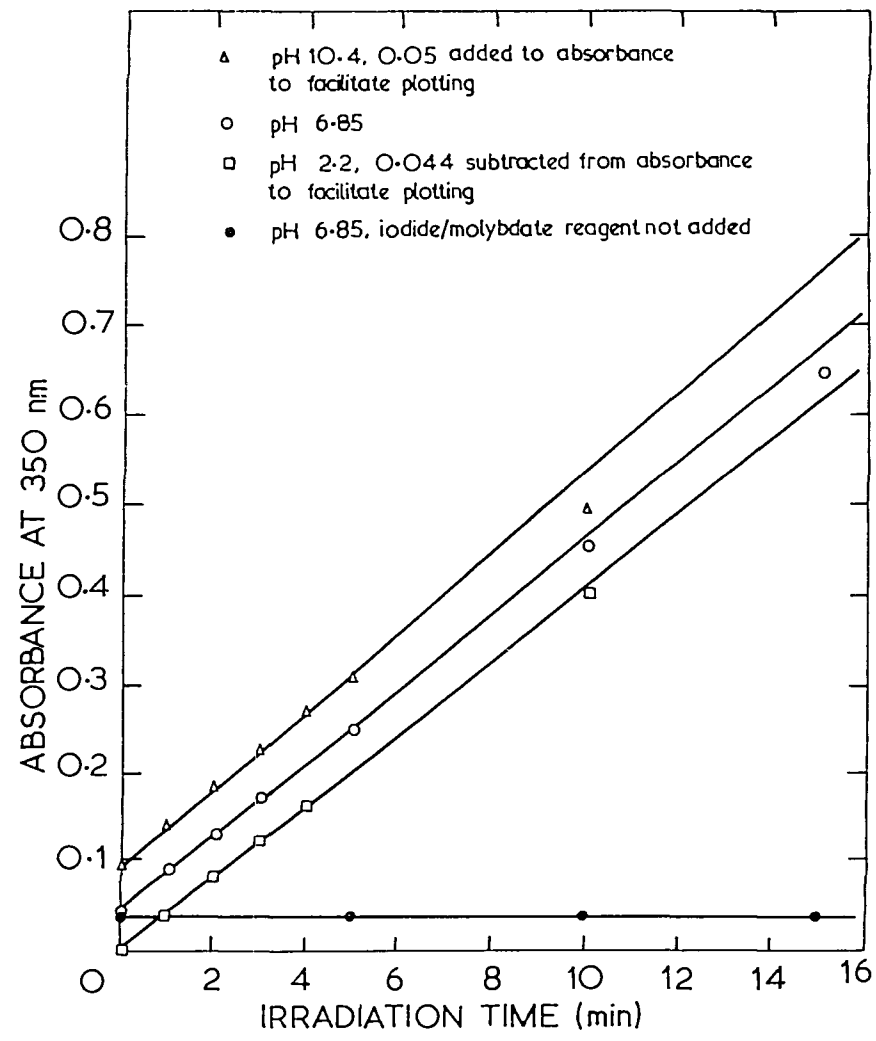

FIGURE 8. TRIIODIDE ABSORBANCE vs. IRRADIATION TIME. 2 cm CELL AT 350 nm, 1×10^{-4}M SODIUM TEREPHTHALATE IN AERATED SOLUTIONS. DOSE RATE 827 rad min^{-1}

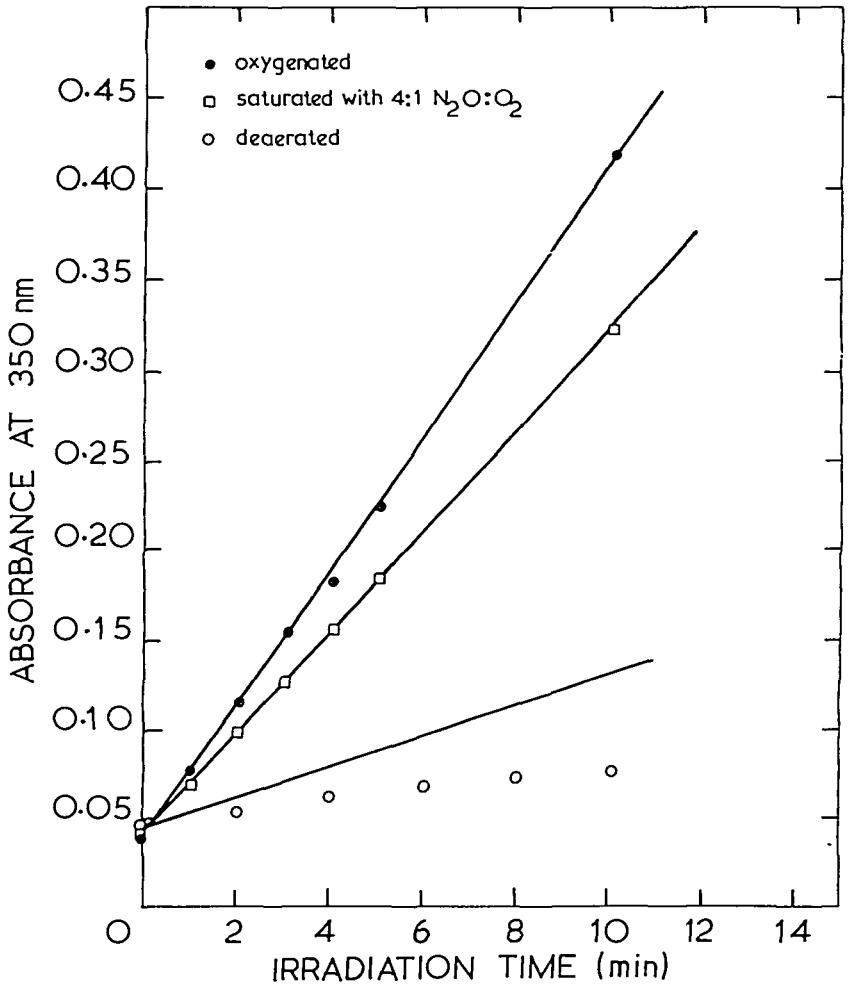

FIGURE 9. TRIIODIDE ABSORBANCE vs. IRRADIATION TIME. 2 cm CELL AT 350 nm, 1×10^{-4} M SODIUM TEREPHTHALATE IN AERATED 0.01 M PHOSPHATE SOLUTION, pH 6.85. DOSE RATE ~830 rad min^{-1}

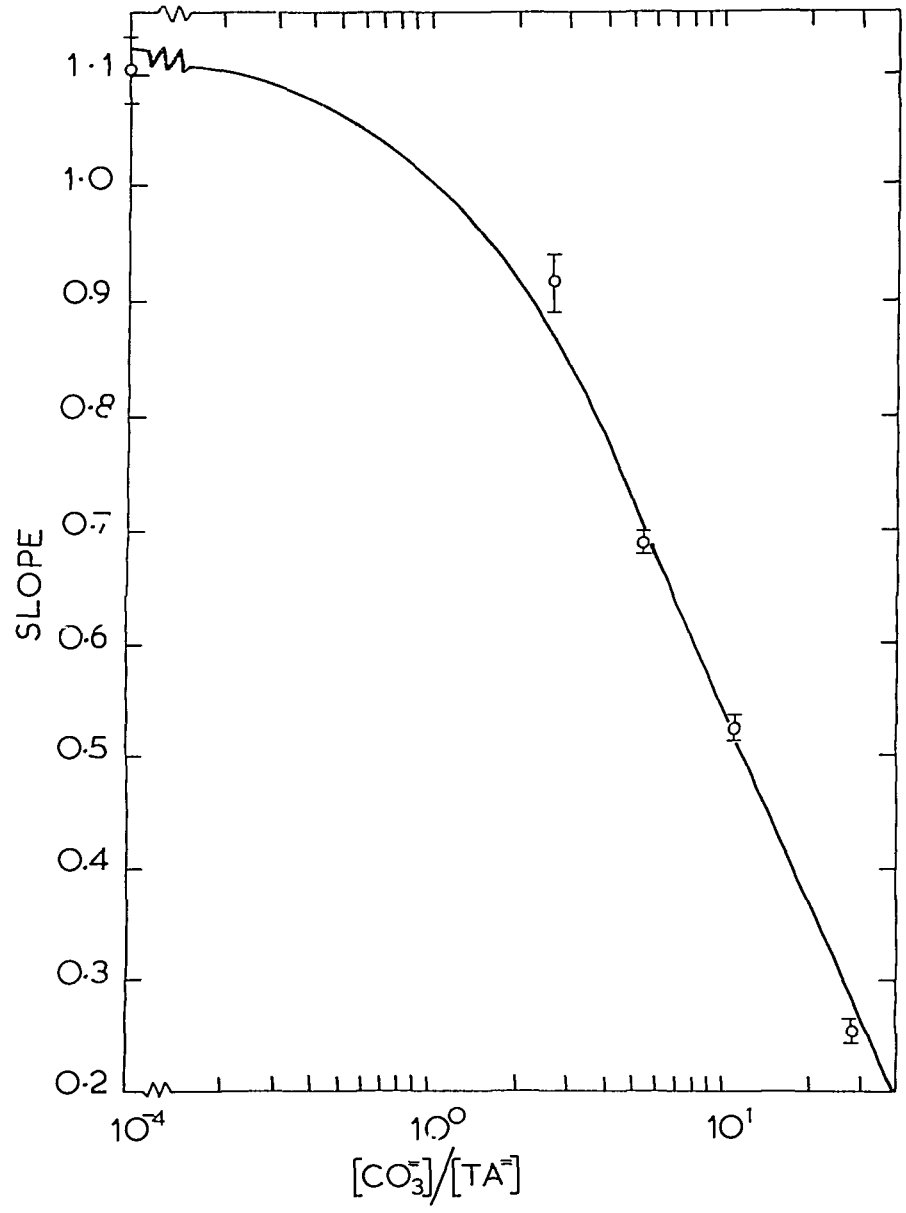

FIGURE 10. SLOPE OF FLUORESCENCE-INDUCED PHOTOCURRENT/min vs. RATIO (CARBONATE/TEREPHTHALATE CONCENTRATION) FROM THE DATA IN FIGURE 4.

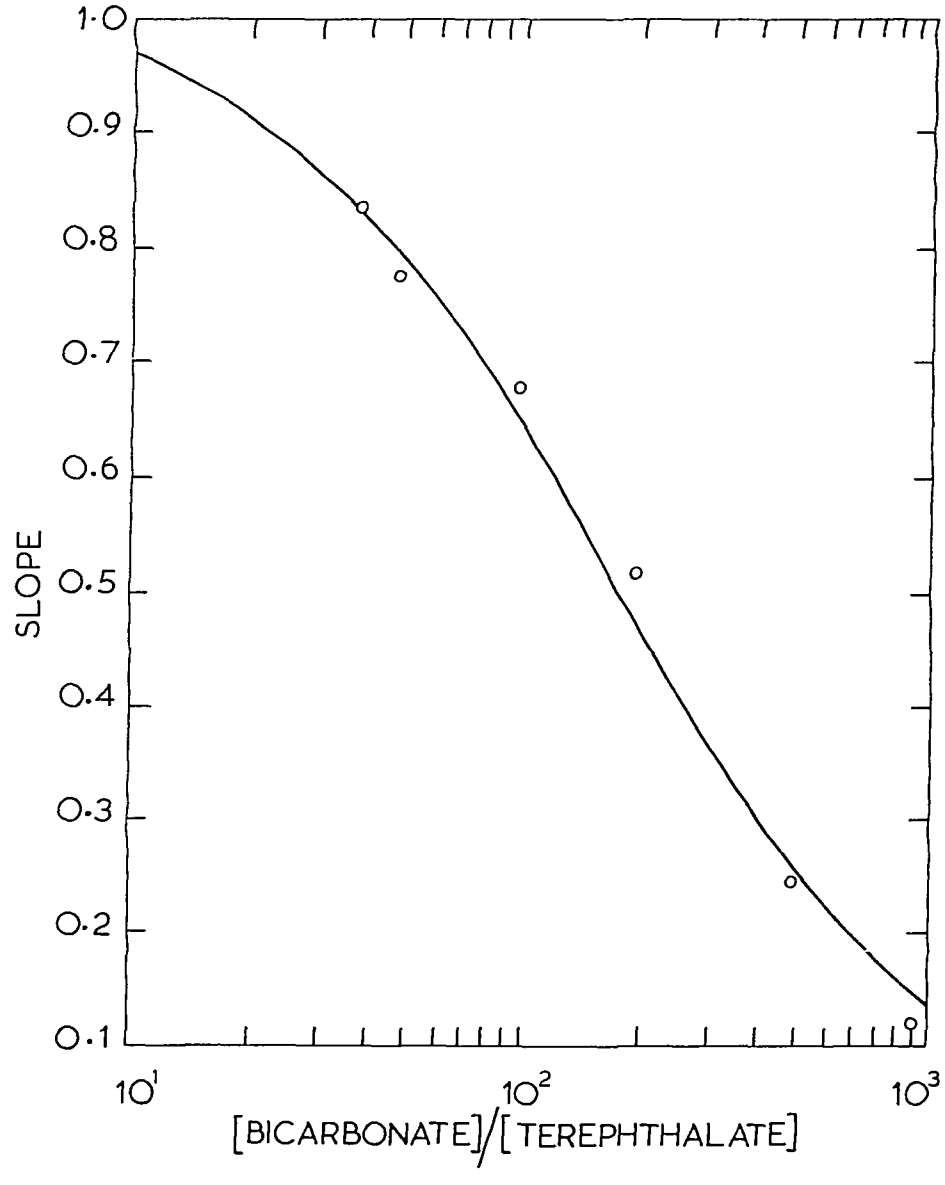

FIGURE 11. SLOPE OF FLUORESCENCE-INDUCED PHOTOCURRENT/min vs. RATIO (BICARBONATE/TEREPHTHALATE CONCENTRATION) FROM THE DATA IN FIGURE 5.