THE EFFECT OF ACRYLAMIDE ON THE X- AND γ-RAY YIELDS OF HYDROGEN PEROXIDE FROM DE-AERATED WATER

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The yields of hydrogen peroxide obtained by irradiating air-free aqueous solutions of acrylamide with 220 Kvp or 50 Kvp X-rays are dependent upon the initial concentration of acrylamide. The value of $G_{H_2O_2}$ rises from almost zero to a maximum of $0{\cdot}90 \pm 0{\cdot}05$ at a concentration of monomer lying between 10^{-3} and 10^{-2} M, and subsequently falls again to about 0·25 in 0·4 M monomer solutions. This result, and the shapes of the hydrogen peroxide yield against dose curves at different monomer concentrations, are consistent with the view that acrylamide can react with the H atoms and OH radicals which would otherwise induce the reaction between the "molecular" hydrogen and hydrogen peroxide produced; and that at concentrations $> 10^{-2}$ M it can also remove some of the precursors of molecular hydrogen peroxide, thereby reducing the yield of the latter.

On the assumption that the net effect of ionizing radiations on water is

$$H_2O \xrightarrow{100eV} G^R_H H + G^R_{OH} OH + G^M_{H_2} H_2 + G^M_{H_2O_2} H_2O_2,$$

many estimates of the radical and molecular yields for various radiations have now been made, and it appears that in dilute solutions, over a wide range of solute concentration, the molecular yields $G^M_{H_2}$ and $G^M_{H_2O_2}$ remain constant. Nevertheless there is also evidence that with sufficiently high concentrations of solutes which react readily with H atoms or OH radicals, the yields of molecular hydrogen peroxide or hydrogen from hard X-ray, γ-ray, or electron irradiations decrease.[1] In this paper we present evidence of the variability of the molecular yield of hydrogen peroxide with change in concentration of acrylamide in aqueous solution. Acrylamide is a particularly appropriate solute to use in measuring molecular yields in water since (i) it does not react with either hydrogen or hydrogen peroxide, (ii) molecular products are unlikely to result from the reaction of radicals with it, and (iii) it is known to be a very efficient scavenger for hydroxyl radicals,[2] and is likely to be so for hydrogen atoms, thereby interfering to a degree dependent on its concentration with the back reactions between these radicals and the molecular products.

EXPERIMENTAL

Apparatus.—Details of the radiations employed and their dosimetry, the method of preparing solutions for irradiation, and the technique of irradiation are given elsewhere.[3]

Reagents.—A stock of hydrogen peroxide in 0·1 N perchloric acid was prepared by diluting the product from the vacuum distillation of a 90 % commercial sample. Very dilute hydrogen peroxide solutions were made by irradiating pure aerated water with 220 Kvp X-rays. Other materials used were prepared as described elsewhere.[3]

Analytical techniques.—Three methods were employed for the determination of hydrogen peroxide concentrations. Stock solutions (about 2×10^{-3} M H_2O_2) were standardized by reacting with excess ceric sulphate solution. The change in ceric concentration was determined by titration against ferrous ammonium sulphate.

Lower concentrations of hydrogen peroxide were estimated by the use of titanium sulphate or potassium iodide. Titanic sulphate solutions were prepared by slowly heating together 10·6 g of A.R. potassium oxalate, 18 g of ammonium sulphate, and 140 ml of concentrated sulphuric acid. The mixture was finally boiled to destroy the oxalate, and was subsequently made up to 1 l. with water. It was then about 3×10^{-2} M in titanium, and 5 N in sulphuric acid. 5 ml of this solution were added to a suitable volume of hydrogen peroxide solution, and the whole was made up to 50 ml. The optical density of the solution was measured against a water/titanium blank at 408 mμ on a Unicam S.P. 500 spectrophotometer. Experiment showed that the colour of the titanium + hydrogen peroxide complex did not reach its maximum value unless the titanium was in at least ten times molar excess. Under these conditions the molar decadic absorption coefficient of the complex (based on hydrogen peroxide concentration) was found to be 740 ± 5. It was shown by this method that the concentration of 3×10^{-3} M hydrogen peroxide in the presence of 0·2 M acrylamide remained the same within experimental error for at least 18 h.

The use of potassium iodide in the estimation of hydrogen peroxide has been described by Allen *et al.*[4] Hydrogen peroxide oxidizes iodide to iodine under the influence of a molybdate catalyst and the iodine, in the form I_3^- in 0·1 M potassium iodide, absorbs strongly at 350 mμ. The measured molar decadic absorption coefficient at this wavelength was $25,700 \pm 300$. The absorption due to I_3^-(2×10^{-5} M) decreased less than 2 % in 40 min in the presence of 0·5 M monomer solution, and consequently the method is satisfactory for measuring hydrogen peroxide in the presence of acrylamide. However, the apparent optical density at 350 mμ of an irradiated acrylamide solution is greater than that of an unirradiated solution. Consequently before analysing for hydrogen peroxide in an irradiated solution, the optical densities at 350 mμ of this solution, and of the reagent solution to be used for analysis, were measured. From these observations it was possible to make an appropriate correction to the optical density at 350 mμ subsequently obtained for the mixed irradiated solution and reagent solution, since the absorption of the polymer solution was found to be the same in pure water as in the potassium hydrogen phthalate buffer used for analysis.

PROCEDURE FOR THE MEASUREMENT OF HYDROGEN PEROXIDE YIELDS.—Cells were filled to fixed marks with de-aerated solutions of acrylamide as before,[3] except that for these experiments no dilatometer was necessary, and they were then sealed off under vacuum. The solutions were irradiated, and the hydrogen peroxide content was determined by one of the above methods.

RESULTS

50 Kvp X-RAYS

Evacuated solutions of acrylamide were irradiated at a dose rate of about $1·1 \times 10^{18}$ eV l.$^{-1}$ sec^{-1}, and the yields of hydrogen peroxide were studied as a function of dose up to about $1·3 \times 10^{21}$ eV l.$^{-1}$ total energy absorbed. The results are shown in fig. 1.

At monomer concentrations of about 10^{-5} M, a low stationary concentration was built up after a short irradiation. As the monomer concentration increased, the stationary concentration also increased, and was not attained until a greater total dose had been given. For solutions between 10^{-3} and 10^{-2} M, a maximum initial slope was reached, but any assumed stationary concentration was higher than the maximum concentration of peroxide ($9·3 \times 10^{-6}$ M) which was measured. At still higher concentrations of monomer, the yields of hydrogen peroxide fell off rapidly, until in 0·5 M solutions they were comparable with the yields found in 10^{-5} M solutions, and there was no indication of the attainment of a stationary concentration.

220 Kvp X-RAYS

The solutions were irradiated at $5·5 \times 10^{17}$ eV l.$^{-1}$ sec^{-1}. At this lower dose rate it was necessary to irradiate to 30-40 % conversion of the monomer in order to obtain a high enough concentration of hydrogen peroxide (i.e. about 4×10^{-6} M) for accurate measurement. The experimental data are given in fig. 2. All the hydrogen peroxide yields were linear with dose, within the experimental error, and the initial slopes showed the same dependence on monomer concentration as did those with 50 Kvp X-rays. There was no indication of the attainment of a stationary concentration of hydrogen peroxide at the lower total doses used. In fig. 3 are plotted the yields of hydrogen peroxide expressed as molecules per 100 eV absorbed, which were obtained at the highest total dose

given. The yields are plotted against monomer concentration, and the yields with 50 Kvp X-rays (obtained by interpolation at the same dose) have been included. The hydrogen peroxide yield, $G(H_2O_2)$, increases with increase of monomer concentration to

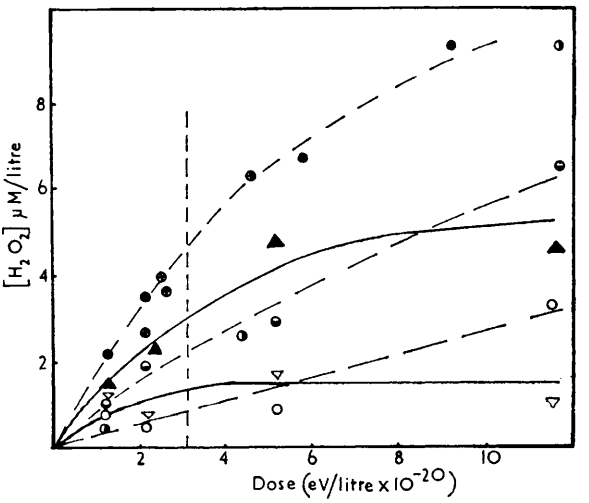

FIG. 1.—The formation of hydrogen peroxide by 50 Kvp X-rays in aqueous solutions of acrylamide. Dose rate approximately 10^{18} eV l.$^{-1}$ sec^{-1}.

○ 0·50, ◒ 0·30, ◑ 0·10, ● 0·01, ⊕ 0·001, ▲ 0·00005, ▽ 0·000005, [m_1], M.

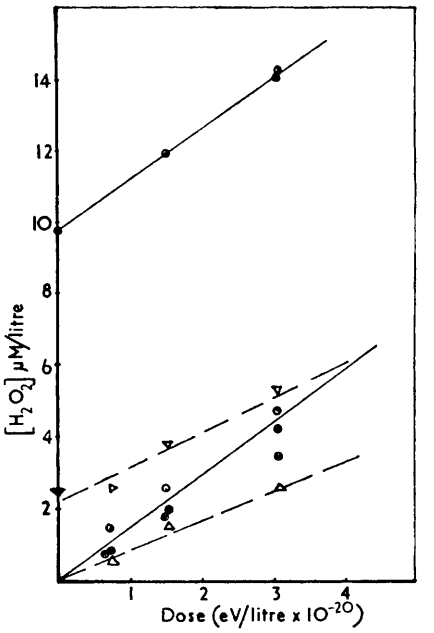

FIG. 2.—The formation of hydrogen peroxide by 220 Kvp X-rays in aqueous solutions of acrylamide. Dose rate = $5{\cdot}2_3 \times 10^{17}$ eV l.$^{-1}$ sec^{-1}.

● 0·02;
⊗ 0·10;
▽ 0·20 (H_2O_2 added initially);
△ 0·20;
◑ 0·01 (H_2O_2 added initially);
○ 0·0065, concentration in molarities.

a maximum value of 0·90 ± 0·05, and subsequently falls to about 0·3 in 0·4 M monomer solutions. At higher concentrations of monomer than this, the solutions became so viscous after irradiation that analysis for hydrogen peroxide was impracticable, and moreover the optical density of the polymer solution at 350 mμ became comparable with that of the I_3^- ion formed during the analysis.

The decrease in yield of the hydrogen peroxide at high monomer concentrations was not due to destruction of the hydrogen peroxide by the monomer, or any substance produced during the irradiation, since (i) the concentration of hydrogen peroxide measured by either the titanium method or the iodide method remained unchanged after standing for considerable periods of time in contact with acrylamide, (ii) the yields from identically treated solutions were the same whether they were analysed 2 min or 3 h after the irradiation ceased, (iii) in two experiments hydrogen peroxide was added to the system prior to irradiation, with no resultant effect on the yield of hydrogen peroxide formed, and no apparent destruction of that added (see fig. 2), and (iv) it was found that neither the intrinsic viscosity of the polymer, nor the rate of polymerization, were altered appreciably

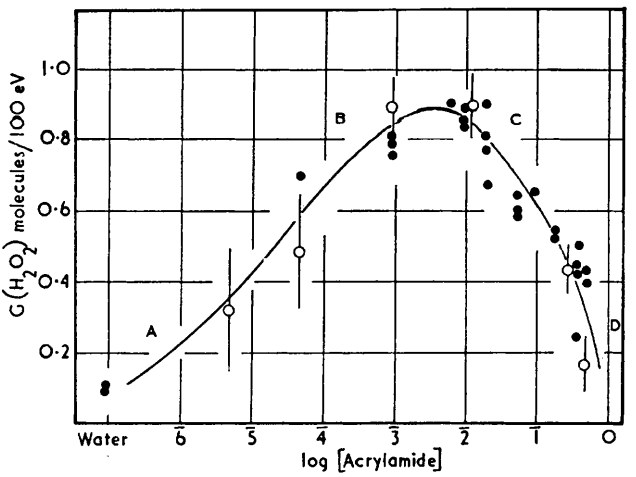

FIG. 3.—The formation of molecular hydrogen peroxide by X-ray irradiations of aqueous solutions of acrylamide. Dose: $3{\cdot}14 \times 10^{20}$ eV/l. (dotted line in fig. 1).
● 220 Kvp X-rays; ○ 50 Kvp X-rays.

by the addition of hydrogen peroxide at concentrations below 10^{-4} M. Since the measured concentrations of hydrogen peroxide formed did not exceed 10^{-5} M, the above results indicate that the fall in hydrogen peroxide yield with rise in monomer concentration is due to a decrease in the rate of *formation* of hydrogen peroxide.

DISCUSSION

The region of increasing hydrogen peroxide yield in fig. 3 (region AB) coincides with the monomer concentration range in which stationary concentrations of hydrogen peroxide were set up. It is thus reasonable to assume that the increase in yield of hydrogen peroxide is due to an increase in the proportion of free radicals captured by the monomer—free radicals which would otherwise tend to decompose the hydrogen peroxide. In view of the fact that at 25° C acrylamide is known to react with hydroxyl radicals about 50 times faster than do ferrous ions,[2] and that the yield of ferric ion formed by irradiating aerated ferrous sulphate solutions does not fall off until a ferrous ion concentration of 10^{-4} M is reached, it seems likely that acrylamide should capture hydroxyl radicals efficiently even in 10^{-5} M monomer solutions. Molecular hydrogen is unlikely to compete for hydroxyl radicals, since it reacts with them about 7 times more slowly than does ferrous ion.[2] From these arguments the most likely effective reaction leading to a decrease in $G(H_2O_2)$ at low monomer concentrations seems to be

$$H + H_2O_2 \rightarrow OH + H_2O \qquad 1)$$

at any rate for monomer concentrations only just less than 10^{-3} M.

In the monomer concentration region 10^{-3} to 10^{-2} M (region BC in fig. 3), $G(H_2O_2)$ is almost independent of the monomer concentration, and the plots of hydrogen peroxide concentration against dose are linear. Hence it seems probable that the yield of hydrogen peroxide in this region is the true maximum molecular yield, the same value, $0{\cdot}90 \pm 0{\cdot}05$, being obtained with both 220 Kvp and 50 Kvp X-rays. Under these conditions it follows that the monomer must be reacting efficiently with H atoms in order to prevent destruction of hydrogen peroxide by reaction (1).

In the remaining region of acrylamide concentration (CD in fig. 3) there is some scatter of the experimental points, but in no case was there any indication of the attainment of a stationary concentration of hydrogen peroxide, in marked contrast to the results at lower monomer concentrations. Since the evidence quoted in the previous section supports the view that there is in this region a decrease in the rate of formation of hydrogen peroxide, it is suggested that at these concentrations of acrylamide not only all the radicals from the water but also some of the precursors of the " molecular " hydrogen peroxide are captured by the monomer. It is not known with certainty from this work whether precursors of the " molecular " hydrogen are also captured, though the values obtained for the rates of polymer initiation [3] suggest that this may not be the case.

The maximum value observed for $G^{M}_{H_2O_2}$, $0{\cdot}90 \pm {\cdot}05$, was the same for both 220 Kvp and 50 Kvp X-rays. It is higher than the values between 0·48 and 0·68 found from other systems in neutral solution,[5] though a value of 0·76 has also been quoted.[7] Values of $G^{M}_{H_2O_2}$ nearer to 0·9 have been found from a variety of systems at higher acidities. Though we are not able rigorously to exclude the possibility of the formation of organic hydroperoxides, which would oxidize iodide ion in the same way as does hydrogen peroxide, we incline to the view that the peroxide occurring is indeed hydrogen peroxide alone. Our reasons are (i) that both the iodide and titanium method gave the same results whenever both methods were used, and (ii) that the curve in fig. 3 would not be expected to have this form if the peroxide concerned were an organic one.

From the results here presented, and from similar findings with other solutes,[1] it seems clear that the molecular yield of hydrogen peroxide from irradiated water can be reduced by the use of a suffic ently high concentration of solute. The same effect has also been reported for α-particle irradiations.[8] In no case so far has the yield of hydrogen peroxide been reduced to zero, and in this system it was not possible to work at a very high solute concentration owing to the resulting high viscosity of the solution. However, neither in this system, nor in aerated alkali halide solutions, was there any indication that a residual yield of hydrogen peroxide would remain at the highest solute concentrations. On the other hand it has been claimed that for neutral solutions of nitrite in concentrations greater than 2×10^{-3} M the yield of hydrogen peroxide is constant.[6]

It is not possible at this stage to draw any definite conclusion regarding the mechanism of formation of molecular hydrogen peroxide, but it is worth noting how well these results fall into line with the original postulates of Allen,[9] to whom the concept of an initial yield of radical and molecular products is due. It has never before been demonstrated using one solute, that as the concentration of solute is increased the yield of molecular product is first enhanced, presumably by suppression of the chain back reaction between radicals and molecular products,[9] and later diminished, probably by capture of molecular product precursors.

If subsequent investigation reveals that the precursors of molecular hydrogen are not captured by the monomer, as the present results seem to imply, then the following reaction may be responsible for the formation of molecular hydrogen

$$H_2O^* \rightarrow H_2 + O(^1D).$$

The reaction

$$O(^1D) + H_2O \rightarrow H_2O_2$$

is known to be a very efficient process,[10] and may indeed contribute to the yield of molecular hydrogen peroxide, though it cannot be entirely responsible for it since $G^M_{H_2O_2} > G^M_{H_2}$. Acrylamide (m_1) could interfere with this process in the following way:

$$O + H_2O + m_1 \rightarrow HOm_1^* + OH.$$

Even if the molecular hydrogen yield is altered by changing monomer concentration, the above processes are not ruled out, for the monomer may react with the excited water molecule

$$H_2O^* + m_1 \rightarrow HOm_1^* + H \text{ (or } Hm_1^* + OH).$$

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