Effect of Gamma Radiation on Aqueous Ethylene-oxygen Solutions

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Mixtures of ethylene and oxygen dissolved in water under pressures ranging from 200 to 700 lb./sq. in. were irradiated with Co^{60} gamma rays at a dose rate of 180,000 r./hr. *G* values (molecules/100 ev.) for aldehyde production as high as 200 were observed. Increasing total pressure and dose were found to decrease these *G* values. Alcohol, acids, hydrogen peroxide, and organic peroxide are also products of the reaction; however, the yields are much smaller.

Large-scale industrial use of ionizing radiation will certainly be limited to exothermic reactions in which the radiation serves to initiate long reaction chains (*1*). Processes in which ionizing radiation does not give large product yields per unit energy input will be excluded by the high cost of energy in this form. The reaction of hydrocarbons with oxygen is an exothermic reaction which, if controlled, yields products of commercial importance.

Recent studies with saturated hydrocarbons and oxygen (*2*) and with saturated hydrocarbon gases in aqueous solution (*3*) have clearly indicated that the oxidation initiated by gamma rays proceeds with a very poor yield of product per energy expenditure. In terms of molecules per 100 ev. (*G* units) yields of approximately unity have been observed for these oxidations. In the work reported here it has been found that when aqueous solutions of ethylene and oxygen under pressure are irradiated with gamma rays from cobalt-60, *G* values for the production of aldehyde as high as 200 are observed.

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The difference in yield values obtained from ethylene in contrast to saturated hydrocarbons would be due to the high heat content of the vinyl bond. This makes all reactions of ethylene which involve additions across the double bond potential chain reactions. The best example of this, and the only one that has captured the attention of radiation chemists, is polymerization of ethylene to form polyethylene. Yale and Michigan groups (*4, 5*), among others, have recently studied this reaction. The polymerization is reported to proceed readily under gamma-ray catalysis, chain lengths over one thousand having been observed at higher pressures and slightly elevated temperatures.

Reported in this paper are results obtained under a variety of experimental conditions, and an attempt is made to correlate these with the presently accepted picture of radiation chemical reactions in aqueous solutions.

DESCRIPTION OF APPARATUS

Figures 1 and 2 show the apparatus used. The reactor is a stainless steel cylinder of approximately 150-ml. capacity with gas entrance and exit lines extending through the nut. The entrance line, reaching almost to the bottom of the reactor, is connected externally through the piping shown to the ethylene-oxygen feed mixture. The entrance tube extends back and is connected in series to a cross, a needle valve, and a tee. To the cross are attached a blow-out disk assembly and a needle valve for filling and sampling. The exit tube extends back to the tee into which the by-pass valve enters, the other connections being used for a needle valve to control gas flow rate. For sampling, the by-pass and sampling valves are open, the other two closed. A standard gas cylinder with a pressure regulator is attached to the other connection of the tee on the entrance line.

IRRADIATION TECHNIQUE

The irradiations are carried out by lowering the reactor into the source; a hollow cobalt-60 cylinder of the type described by Henley (*6*) was used for these runs. The dose rate was determined by means of a cellophane dosimeter (*7*) and found to be 180,000 r./hr.

The high-pressure reactor is charged with 150 ml. of distilled water by opening the exit line and adding water at the sampling valve.

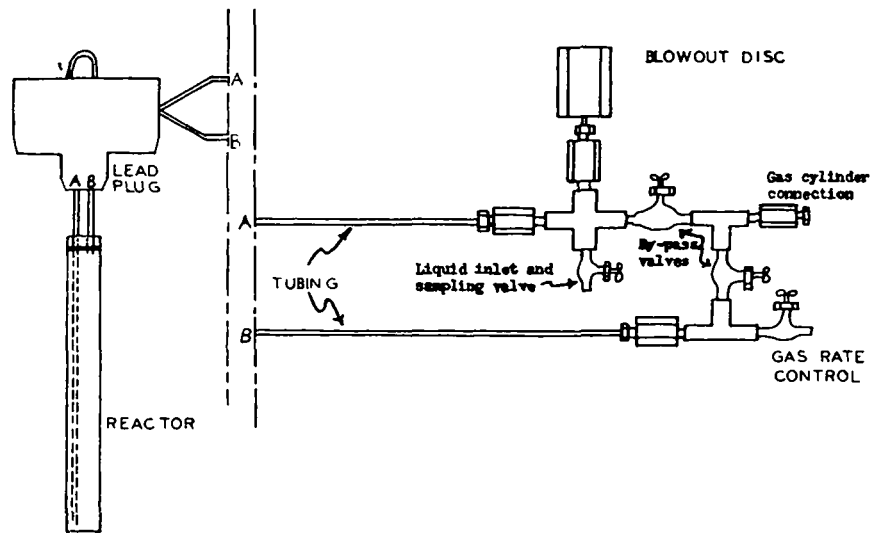


Fig. 1. Diagram of apparatus.

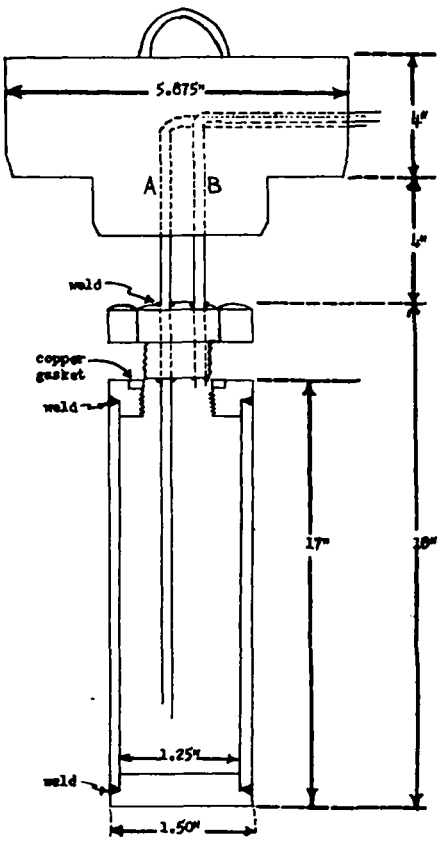
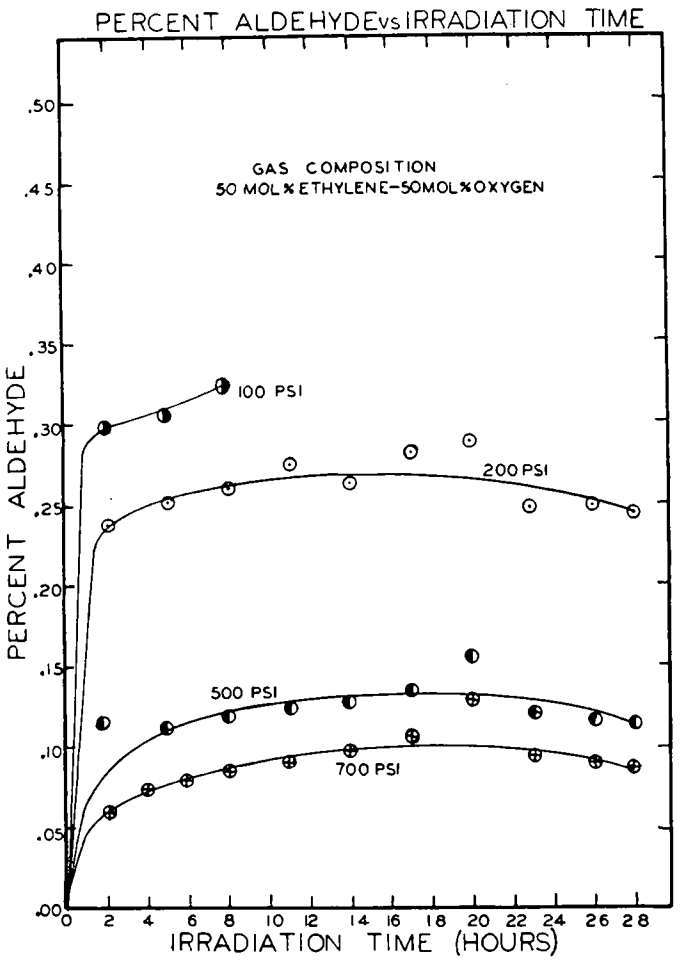


Fig. 2. Detailed diagram of reactor and plug



The previously filled gas cylinder is attached through the pressure regulator to the entrance line of the reactor and the pressure set at some predetermined value. In this case once the gas flow rate is set, by the exit valve, it will remain constant. The gas flow was adjusted to give a slow sparge. To take a sample it is necessary only to open the by-pass valve and close the valve in the entrance line. The sample is then collected at the sampling valve. The sampling operation can be carried out in less than 10 sec. with no loss of pressure in the reactor.

ANALYTICAL PROCEDURE

The following methods of analysis have been employed for the quantitative determination of acid, aldehyde, alcohol, hydrogen peroxide, and formaldehyde (*8, 9, 10, 11, 12*).

Acid

The sample is a very dilute solution of a weak acid and direct titration cannot be used because the end point is obliterated by dissolved carbon dioxide.

The weighed sample is added to 5 ml. of standard 0.05 *N* KOH and the excess KOH is titrated with standard 0.05 *N* HCl to a *p*H of 6.7. This value of the *p*H has been experimentally determined to give the stoichiometric end point most accurately.

Fig. 4. Percentage of acid vs. irradiation time. →

Aldehyde

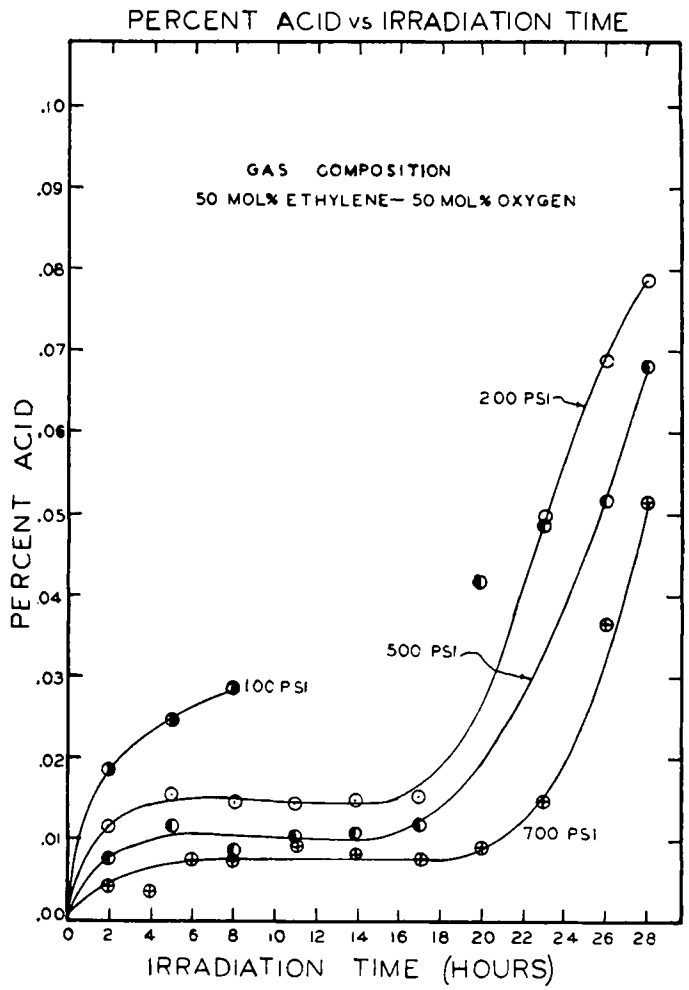
The sample is added to 25 ml. of approximately 7 wt. % H_2O_2 and after it stands for 10 min. 5.0 ml. of standard 0.05 *N* KOH is added. The presence of ethanol in the sample does not interfere, as more stringent oxidizing conditions are required for alcohols to go to acids. The excess KOH is titrated with standard 0.05 *N* HCl to a *p*H of 6.7.

A correction for the acid originally present (assumed to be acetic) must be applied to the percentage of aldehyde calculated from the titration.

Alcohol

To 5.0 ml. of standard 0.05 *N* $K_2Cr_2O_7$ and 5 to 6 ml. of concentrated H_2SO_4 in an iodine flask a 1- to 2-g. sample is added and the solution brought slowly to boiling. After cooling, a small piece of dry ice and approximately 3 g. of potassium iodide (iodate free) are added and the solution is allowed to stand 10 min. The dry ice sublimes and the carbon dioxide displaces air from the flask to prevent air oxidation of potassium iodide. The excess of $K_2Cr_2O_7$ is found by titrating with standard 0.05 *N* $Na_2S_2O_3$ to a starch-iodide end point. A correction for the aldehyde present must be applied to the percentage of alcohol calculated from the titration.

← Fig. 3. Percentage of aldehyde vs. irradiation time.



Hydrogen Peroxide

Hydrogen peroxide is reacted with potassium iodide in the presence of a molybdate catalyst, and the triiodide ion produced is determined colorimetrically at 350 μ by use of a Beekman model DU spectrophotometer (*11*, *13*). Calibration curves using standardized H_2O_2 were straight lines when optical density differences were plotted against H_2O_2. Organic peroxides were determined by the method indicated by Weiss (*8*).

Formaldehyde

The method of Denige as described by Walker (*12*) was used. Schiff's reagent is added to the acidified sample, and the resulting color is read spectrophotometrically at 580 mμ. Peroxides are destroyed as suggested by Satterfield (*8*).

RESULTS

Figure 3 indicates the production of aldehyde as a function of irradiation time under a variety of experimental conditions. The aldehyde for the purpose of this calculation was considered to be acetaldehyde. Owing to the limited gas supply the pressure dropped somewhat during these runs. The magnitude of this drop was dependent upon the rate of sparging and was usually between 5 and 20 lb. Various sparging rates had no detectable effect, and no effect of temperature was noted in the range of 25° to 61°C.

Similar data for the production of acid are summarized in Figure 4. The acid present was assumed to be acetic.

The dependence of the steady state concentration of aldehyde on total pressure is indicated in Figure 5. The maximum concentration of aldehyde is seen to be inversely proportional to the log of the total pressure.

Alcohol and peroxide production as a function of dose for total pressures of 200, 500, and 700 lb./sq. in. is summarized in Figures 6 and 7. The alcohol was calculated as ethyl alcohol, the peroxide as hydrogen peroxide.

G values for the 200 lb./sq. in. runs as a function of dose are plotted in Figure 8.

DISCUSSION

The solute concentration in these solutions varies directly with total pressure. At the highest pressure used (700 lb./sq. in.) the total solute concentration is approximately 0.05M; consequently all the energy is absorbed in the solvent water. It is commonly postulated that the result of this energy absorption is the production of reactive radical pairs, H + OH, along with smaller quantities of H_2 + H_2O_2 (*14*). Each 100 ev. of energy absorbed by the water (1 r. = $6.08 \cdot 10^{13}$ ev./g.) produces 4.5 detectable water decomposition; 7.6 radicals are produced along with 0.8 molecule of H_2 + H_2O_2 (*15*).

As more than 200 molecules of aldehyde are produced per 100 ev. absorbed, it appears that the radicals are initiating a chain reaction between ethylene and oxygen.

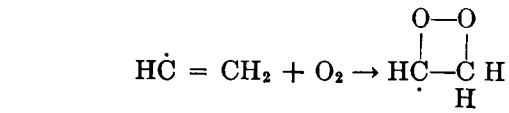
The initiation steps for this reaction could be

$$H\cdot + O_2 \rightarrow HO_2\cdot \quad (1)$$

$$HO_2\cdot + H_2C = CH_2 \rightarrow H_2O_2 + H\dot{C} = CH_2 \quad (2)$$

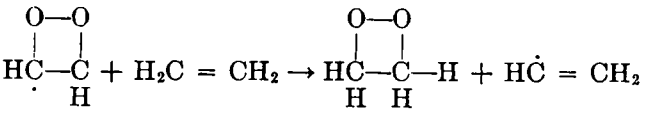
$$HO\cdot + H_2C = CH_2 \rightarrow H_2O + H\dot{C} = CH_2 \quad (3)$$

followed by



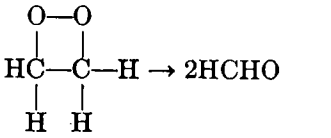
$$H\dot{C} = CH_2 + O_2 \rightarrow HC(-O-O-)C\cdot H \quad (4)$$

Chain propagation must thus involve the reaction of this radical with ethylene.



$$HC(-O-O-)C\cdot H + H_2C = CH_2 \rightarrow HC(-O-O-)C(H)H + H\dot{C} = CH_2 \quad (5)$$

followed by



$$HC(-O-O-)C(H)H \rightarrow 2HCHO \quad (6)$$

This postulated mechanism leads to the formation of formaldehyde. If one chose to use the oxidative scheme of Bell et al., one could predict that acetaldehyde would be the primary product (*16*). The initiation and propagation steps could be similar; however, instead of reaction (6) one would have

$$H_2C = CHO_2H \rightarrow H_2C = CHO\cdot + OH\cdot \quad (7)$$

followed by

$$H_2C = CHO\cdot + H_2C = CH_2 \rightarrow CH_3{-}CHO + H\dot{C} = CH_2 \quad (8)$$

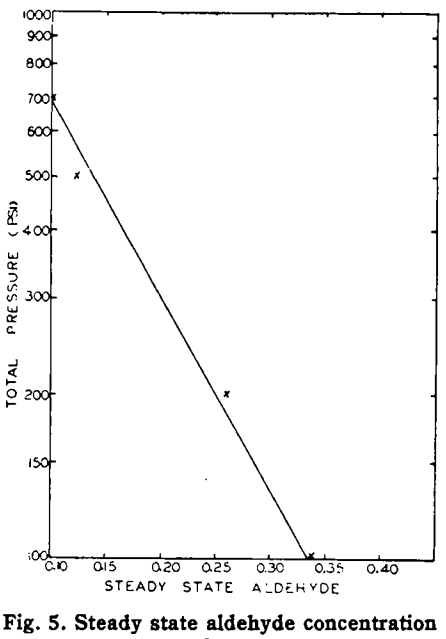


Fig. 5. Steady state aldehyde concentration vs. total pressure.

These reactions are observed in the low-temperature oxidation of paraffins.

The initial high G value for aldehyde production falls rapidly with dose (Figure 8). After an initial rapid increase the concentration of the aldehyde remains constant with dose. The molar concentration of the labile aldehyde is at this point greater than the concentration of dissolved ethylene. As no carbon dioxide was detected in the effluent gas stream, it does not appear likely that aldehyde is being destroyed at a rate equal to its rate of production by another chain process. Most probably the aldehyde and other reaction products (hydrogen peroxide, organic peroxide, and alcohols) are preventing initiation and propagation steps in the reaction of ethylene with oxygen.

The fact that increased total pressure decreases the maximum concentration of aldehyde is not easily explainable, for it indicates that O_2 is involved in a termination step to a higher power than in the initiation and propagation steps.

The other reaction products are produced with much smaller G values. The constant G value for total peroxide production may be accounted for by the molecular yield for H_2O_2 (G = 0.8) and that produced in reaction (2) (G = 1.7).

Acid is apparently produced in a nonchain oxidation by further oxidation of the aldehyde.

It is interesting to compare these results with those initially reported by Henley et al. (*17*) for the same system at lower

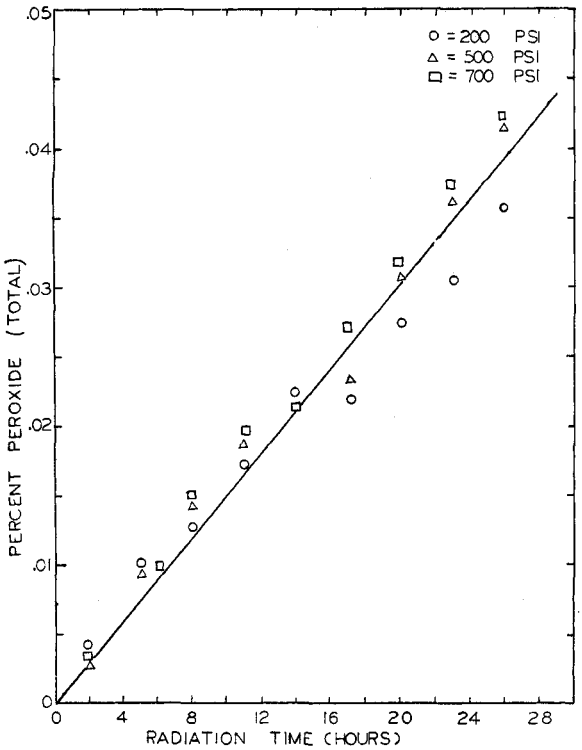


Fig. 6. Percentage of peroxide vs. irradiation time.

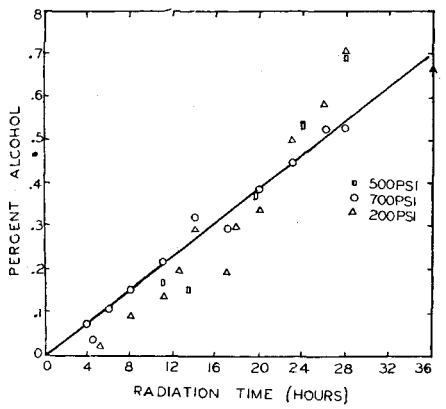


Fig. 7. Percentage of alcohol vs. irradiation time.

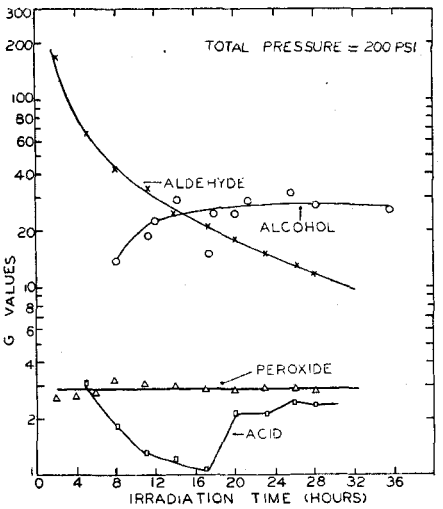


Fig. 8. *G* values for 200 lb./sq. in. run vs. irradiation time.

pressures. The results differ in some respects, the most notable being the difference in peroxide and aldehyde yields. The latter is probably due to the fact that in the low-pressure apparatus the gas storage tank was too small and so the gas pressures varied continuously during the runs, no steady state being achieved. The difference in peroxide concentrations is not easily explained except in terms of materials used and of pressures.

Differences in alcohol and acid concentrations reported here and in previous papers are not great. The acid determination is relatively unreliable at these low concentrations, as may be inferred from Figure 8. As for the alcohol determination, this also is less precise at low-alcohol and high-aldehyde concentrations. This is the reason little weight can be given to the lower part of the data in Figure 7. Also there is an error in reference *17*; the alcohol and acid curves are interchanged.

It should also be mentioned that polarographic measurements of oxygen uptake rates for the ethylene-oxygen system at atmospheric pressure showed the absence of a chain reaction. This has since been confirmed by British workers (*18*).

The origin of the alcohol, which is produced with a constant *G* value of approximately 25, is as yet not completely known. It is hoped that experiments now in progress on higher olefins will help in the achievement of an understanding both of the hydration process and the effect of pressures. Refinements in analytical techniques are also desirable.

Originally qualitative analysis and the reports of others led to the conclusion that all hydrocarbons would be of the two-carbon variety. From the gas-analysis mechanism, and an analysis for total carbon (*19*), it became apparent that a good deal of the aldehyde was formaldehyde rather than acetaldehyde. This was confirmed by a separate analysis which showed that in the case of the 20-hr. sample of the 500 lb./sq. in. run about 25% of the aldehyde was formaldehyde.

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