teristics similar to those of the bulk metals. This is quite reasonable because the bonding characteristics of the metal surface are interpreted well by the knowledge of electronic states obtained for the bulk metal. Further quantitative discussion will be carried out on the basis of the density-of-states curves of metals, especially the degree of occupation of bonding or antibonding bands.

Acknowledgment. The authors thank Professor Noboru Mataga, Faculty of Engineering Science, Osaka University, for his kind discussion about the spectral data.

Radiolysis of HCOOH + O_2 at pH 1.3–13 and the Yields of Primary Products in γ Radiolysis of Water

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The radiation yields of carbon dioxide, hydrogen peroxide, and hydrogen from oxygenated ($[O_2] = 1 \times 10^{-3}$ M) aqueous formic acid solutions have been determined over the pH range 1.3 to 13. The formic acid concentration was varied between 1×10^{-4} and 5×10^{-2} M and the absorbed doses ranged from 3 to 16 krads. The radiation chemical behavior of solutes is discussed paying particular attention to secondary reactions which may influence the measured initial yields of radiolytic products. Since these yields depend on solute reactivity they were corrected, before employing them to calculate the primary yields, using the Flanders–Fricke method and Kuppermann's diffusion-kinetic theoretical curves. The contribution of the reaction $HCOO^- + H$ to the measured yields of CO_2 and H_2 has also been taken into account. From the results obtained, one can calculate at pH between 3 and 13: $G_{-H_2O} = 4.09$, $G_H + G_{e_{aq}^-} = 3.18$, $G_{OH} = 2.72$, $G_{H_2} = 0.45$, and $G_{H_2O_2} = 0.68$. The increase in acidity induces an increase in water decomposition. At pH 1.3 the following values were derived: $G_{-H_2O} = 4.36$, $G_H + G_{e_{aq}^-} = 3.49$, $G_{OH} = 2.85$, $G_{H_2} = 0.43$, and $G_{H_2O_2} = 0.76$. These figures are discussed in the light of some uncertainties in corrections applied to measured values, as well as in reactions of formate ion at pH 12–13.

Introduction

Three recent rather comprehensive analyses have shown that we still have no satisfactory answer concerning the pH dependence of primary yields in γ radiolysis of water.[1-3] These analyses serve to accentuate the following points concerning the use of a given chemical system for primary radical and molecular yield determination.

(a) It is necessary to know the yields of all the stable radiolytic products of the system studied; it is of special importance that the G values should be true initial yields.

(b) The reaction scheme must be complete, *i.e.*, must take into account all possible secondary reactions. This condition is the more significant the less the condition of item (a) is satisfied.

(c) The effect of the solute concentration in general and the reactivity in particular should be reliably established. The reactivity is defined here as $k_{R+S} \times [S]$, where [S] is the concentration (in M) of the scavenger for the radical R and k_{R+S} the corresponding rate constant (in M^{-1} sec^{-1}).

The purpose of the present work is the determination of the primary yields in the γ radiolysis of water at pH 1.3 to 13 using the system HCOOH + O_2. The radiation chemical behavior of HCOOH, $HCOO^-$, O_2, and products of their reactions with species formed in irradiated water have been the subject of many studies;[4-12] from them we have detailed information on

[1] M. Haissinsky, Rendements radiolytiques primaires en solutions aqueuses neutre ou alcaline, in "Actions chimiques et biologiques des radiations," Vol. 11, M. Haissinsky, Ed., Masson et Cie, Paris, 1967.

[2] E. Hayon, *Trans. Faraday Soc.*, **61**, 723 (1965); in "Radiation Chemistry of Aqueous Systems," G. Stein, Ed., Interscience Publishers, London, 1968, p 157.

[3] G. Czapski, Advances in Chemistry Series, No. 81, American Chemical Society, Washington, D. C., 1968, p 106.

[4] E. Hart, *J. Amer. Chem. Soc.*, **76**, 4198 (1954).

[5] E. Hart, *ibid.*, **76**, 4312 (1954).

[6] E. Hart, *Radiat. Res.*, **1**, 53 (1954).

[7] E. Hart and R. L. Platzman, "Radiation Chemistry," in "Mechanisms in Radiobiology," Vol. I, M. Errera and A. Forssberg, Ed., Academic Press, New York, N. Y., 1961, Chapter 2.

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mechanisms, rate constants, and the nature of intermediates. The establishment of a valid reaction scheme is especially important since it is not quite certain that condition (a) is fully satisfied here, *i.e.*, that the real initial yields are measured. This is because the sensitivities of the methods of microanalysis impose limits on absorbed doses; in our experiments these doses ranged from 3 to 16 krads.

Fifteen years ago, Hart[4-6] studied the radiolysis of HCOOH + O_2 in aqueous solution and used the measured yields to calculate the yields of "primary reactions" and, later,[7] the primary yields of water radiolysis. However, it seemed to us that more recent data from other systems, as well as new information on the properties of certain intermediate species made available by pulsed radiolysis, justify the reinvestigation of this system. We consider that the system satisfies the conditions of item (b) and we present new results which show the influence of the reactivity on the measured yields as required under item (c).

Experimental Section

Solutions. Water was triply distilled in a continuous system (alkaline permanganate, acid dichromate, and finally without any additive) in an oxygen atmosphere. The formic acid and the formate were AR grade BDH products. The acid solutions were prepared by adding perchloric or sulfuric acid; the alkaline solutions were made up from sodium hydroxide freshly prepared by a special procedure.[13] The oxygen concentration in the solutions was 1×10^{-3} *M*, except in a few experiments, when it was varied down to 2×10^{-4} *M* on purpose for concentration effect studies. The ampoules were completely filled, leaving no gas space. The alkaline solutions were first degassed and then conditioned with oxygen.[13] Acid and neutral solutions were prepared with freshly distilled water directly conditioned with oxygen, in order to avoid the loss of formic acid by evaporation during degassing.

Irradiation. The samples were irradiated using a 3000-Ci ^{60}Co source. The dose rate, as determined with the Fricke dosimeter ($G(\mathrm{Fe}^{3+}) = 15.5$), was 3×10^{19} eV ml^{-1} hr^{-1}. The absorbed doses were between 2×10^{17} eV ml^{-1} and 1×10^{18} eV ml^{-1}.

Analyses. The gas products, CO_2 and H_2, and the O_2 initially present, were determined by gas chromatography.[14] In determining CO_2 we paid special attention to the blank corrections. Generally, six to eight ampoules were prepared as a series and two or three of them were not irradiated. The CO_2 content observed in these samples ($\leq 3.3 \times 10^{-6}$ and $\leq 1.6 \times 10^{-5}$ *M*, at pH ~7 and 13, respectively) was plotted at zero absorbed dose on the dosage curve. The accuracies in $G(CO_2)$ and $G(H_2)$ measurements were better than ±3% and ±2%, respectively. The H_2O_2 was determined spectrophotometrically by the potassium iodide method.[15] The acid and alkaline solutions were neutralized before adding the reagent. The molar extinction coefficient at 24° was 25,500 l. mol^{-1} cm^{-1}. The reference and irradiated samples were prepared and measured simultaneously. The accuracy in $G(H_2O_2)$ measurements was better than ±2%.

Calculations of the Initial Yields of H_2O_2, CO_2, and H_2. Concentration-dose plots were obtained by exposure of samples to five or six different doses. They were generally straight lines passing through the origin. The radiation chemical yields were calculated from their slopes; the errors did not exceed the maximal error of analysis given above.

At pH >3 the dosage curves for H_2O_2 showed a yield dependence on the absorbed dose; with increasing dose the yields decreased due to attack by hydrated electrons. In the worst case, *i.e.*, at largest dose where hydrogen peroxide concentration was at its maximum (6×10^{-5} *M*) and that of oxygen at minimum (9×10^{-4} *M*), this decrease was about 5%. In such cases the best line through the experimental points made an intercept with the ordinate and was not used for the yield calculations. On the other hand, the slope of the best line drawn through the origin always gave smaller yields than those calculated for the lowest doses. For this reason, we derived the initial $G(H_2O_2)$ by extrapolating the point by point yields to zero dose on a diagram where measured yields were plotted against doses. The error due to the extrapolation did not exceed the error in H_2O_2 determination. Figure 1 represents the treatment of data for sodium formate (5×10^{-3} *M*) and oxygen (1×10^{-3} *M*) in a solution at pH ~7. On the left side of the diagram the optical densities are plotted after corrections for blanks; on the right are given the corresponding yields, which were calculated by taking into account the dilution factor, the molar extinction coefficient, and the dose absorbed. As can be seen, with decreasing dose the calculated yields increase and at the zero dose the best line gives 3.78 for the initial $G(H_2O_2)$. This value should be compared with 3.64, which may be calculated in the usual way from the slope of the concentration-dose plot drawn through the origin.

Results

Figure 2 shows the yields of the stable radiolytic products as a function of formic acid concentration. The measurements were made at pH 1.3, where the dis-

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(15) A. O. Allen, C. J. Hochanadel, J. A. Ghormley, and T. W. Davis, *J. Phys. Chem.*, **56**, 575 (1952).

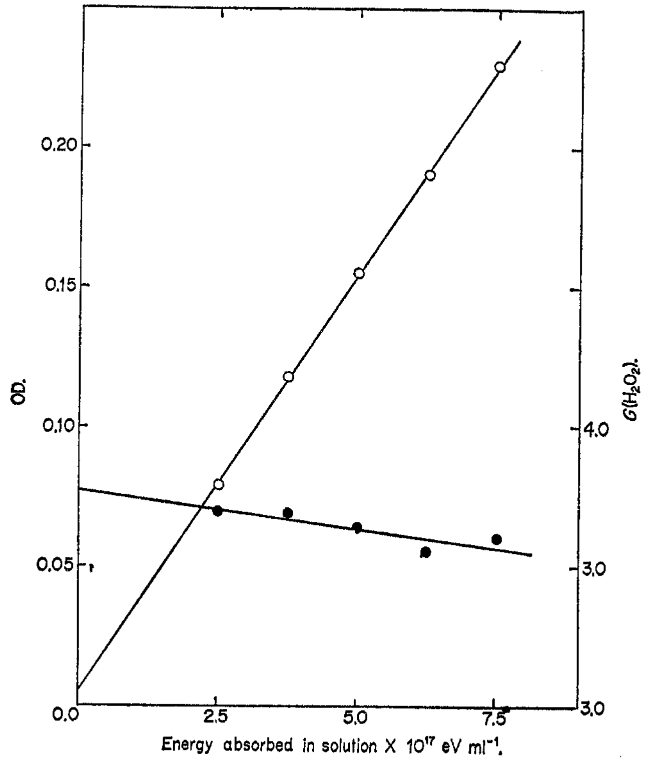

Figure 1. Hydrogen peroxide formation in 5 × 10^{-3} M HCOONa with 1 × 10^{-3} M O_2 present, pH ~7: ○, optical density of irradiated solution; ●, calculated $G(H_2O_2)$.

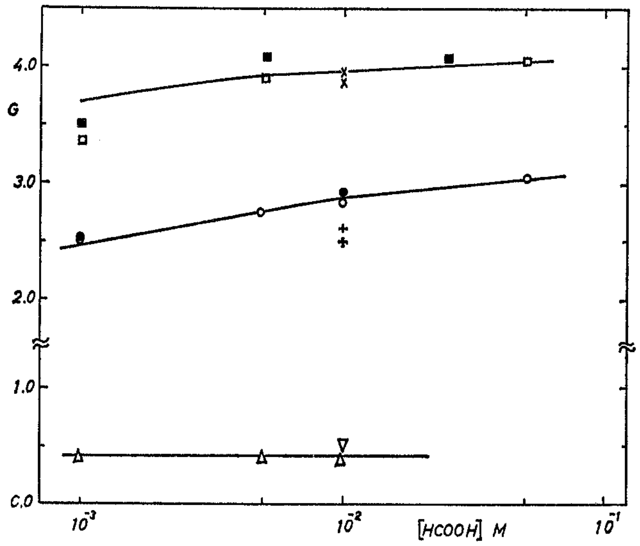

Figure 2. The formic acid concentration effect on the measured yields of the stable radiolytic products at pH 1.3, with 1 × 10^{-3} M O_2 present: measurements in the presence of H_2SO_4: □, H_2O_2; ○, CO_2; △, H_2. Measurements in the presence of $HClO_4$: ■, H_2O_2; ●, CO_2. Hart's values[4] at pH 1.28 with 0.42 × 10^{-3} M or 1.12 × 10^{-3} M O_2: ×, H_2O_2; +, CO_2; ▽, H_2.

sociation of the formic acid is negligible. The adjustment of pH with H_2SO_4 gave slightly smaller yields than with $HClO_4$, but within the experimental errors.

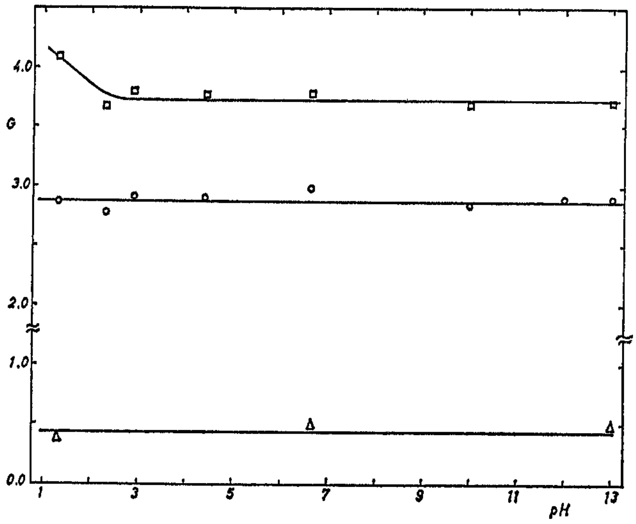

Figure 3. pH effect on the measured yields of the stable radiolytic products in 1 × 10^{-2} M HCOOH or 5 × 10^{-3} M $HCOO^-$ with 1 × 10^{-3} M O_2 present: □, H_2O_2; ○, CO_2; △, H_2.

In the concentration range studied, $G(H_2)$ values remain unchanged; $G(CO_2)$ and $G(H_2O_2)$ increase with increasing concentration of formic acid. For comparison, Hart's values[4] obtained under experimental conditions similar to ours are also plotted on the diagram.

It can be seen that the increase of $G(H_2O_2)$ follows the increase of $G(CO_2)$; the deviation of $G(H_2O_2)$ measured at 1 × 10^{-3} M HCOOH is larger than the possible experimental error.

Figure 3 represents the yields of CO_2, H_2O_2, and H_2 measured as a function of pH in solutions 1 × 10^{-3} M O_2 and 1 × 10^{-2} M HCOOH or 5 × 10^{-3} M $HCOO^-$.

The data indicate that at these concentrations of HCOOH and $HCOO^-$, only $G(H_2O_2)$ shows a slight pH dependence at pH <3. It is worthwhile to mention that a check by gas chromatography on the eventual presence of CO gave a negative result.

Figure 4 summarizes the radiolytic yields measured for different formate ion concentrations. The pH of solutions was between 4.4 and 13. It can be seen that the variation of pH has no influence on the yields measured; they depend on the formate concentration only. The trend is similar to that observed in acid medium (Figure 2) for increasing formic acid concentration. Here also Hart's values[4] are included.

At pH 13, where the reaction $O_2 + O^-$ might become significant, a series of $G(CO_2)$ determinations was performed in solutions having various O_2/formate concentration ratios. It was found that measured carbon dioxide yields follow only the concentration changes of formate ion and do not depend on $[O_2]/[HCOO^-]$ in the region studied (from 0.2 to 8). In experiments the results of which are shown in Figures 1–4, less than 10% of the initial oxygen concentration was consumed.

Discussion

Primary and Secondary Reactions of Scavengers in

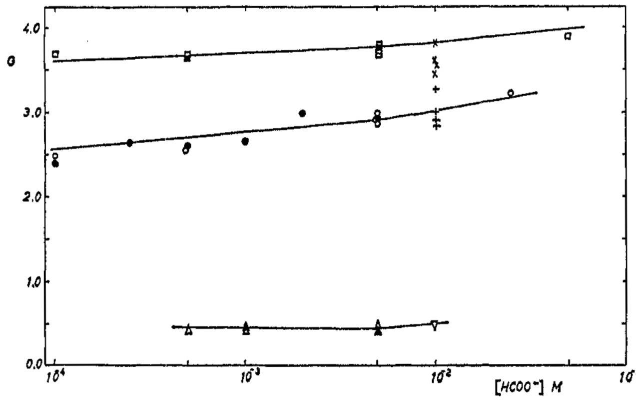

Figure 4. The $HCOO^-$ concentration effect on the measured yields of the stable radiolytic products with 1×10^{-3} M O_2 present: pH 4.4–11.9: □, H_2O_2; ○, CO_2; △, H_2; pH 13: ■, H_2O_2; ●, CO_2; ▲, H_2. Hart's values[4] at 4.92–11.58 in the presence of 0.4×10^{-3} M or 1.2×10^{-3} M O_2: ×, H_2O_2; +, CO_2; ▽, H_2.

Studied Solutions. In the irradiated aqueous solution oxygen and formic acid react with the free radicals formed from water during irradiation. If not otherwise indicated, the rate constants of these reactions were taken from Anbar and Neta.[16]

Under our experimental conditions the reducing species are efficiently scavenged by molecular oxygen

$$O_2 + H = HO_2; \quad k_1 = 1.9 \times 10^{10}\ M^{-1}\ \text{sec}^{-1} \quad (1)$$

$$O_2 + e_{aq}^- = O_2^- + H_2O; \quad k_2 = 1.88 \times 10^{10}\ M^{-1}\ \text{sec}^{-1} \quad (2)$$

Undissociated formic acid does not compete with oxygen for H atoms since $k_{H+HCOOH} \sim 10^{-4}k_1$; this is not the case with hydrated electrons, however.

$$HCOOH + e_{aq}^- = HCOOH^- + H_2O; \quad k_3 = 1.4 \times 10^8\ M^{-1}\ \text{sec}^{-1} \quad (3)$$

Taking into consideration the concentrations of O_2, H^+, and HCOOH, it is obvious that the contribution of this reaction will be most important at pH about 3. However, even here, its competition with reaction 2 is insignificant, as only 4% of the hydrated electrons can participate in reaction 3. In addition, since the formed intermediate reacts efficiently with oxygen producing $HCOOH + O_2^-$, the final results will be the same as if only reaction 2 occurs. The evidence for this conclusion may be obtained from the similarity in behavior of oxygenated solutions of oxalic acid[13] as well as from Figure 2 where it can be seen that the increase of $G(H_2O_2)$ follows the increase of $G(CO_2)$.

The formate ion does not compete with oxygen for hydrated electrons as $k_{e_{aq}^- + HCOO^-} < 10^6\ M^{-1}\ \text{sec}^{-1}$. However, the reaction

$$HCOO^- + H = H_2 + COO^-; \quad k_4 = 2.5 \times 10^8\ M^{-1}\ \text{sec}^{-1} \quad (4)$$

should be taken into account for $[HCOO^-] \geqslant 1 \times 10^{-3}$ M as, under our working conditions, $[O_2] = 1 \times 10^{-3}$ M.

Both formate ions and formic acid react very efficiently with hydroxyl radicals

$$HCOOH + OH = H_2O + HCOO\ (\text{or } COOH); \quad k_5 = 2.5 \times 10^8\ M^{-1}\ \text{sec}^{-1} \quad (5)$$

$$HCOO^- + OH = OH^- + HCOO\ (\text{or } H_2O + COO^-); \quad k_6 = 2.5 \times 10^9\ M^{-1}\ \text{sec}^{-1} \quad (6)$$

Measured H_2O_2 and CO_2 yields indicate the high efficiency of the reaction

$$O_2 + COOH\ (\text{or } HCOO \text{ or } COO^-) = CO_2 + HO_2\ (\text{or } O_2^-) \quad (7)$$

The carboxyl radical reacts with formic acid and hydrogen peroxide but these reactions do not proceed in the presence of oxygen. This was shown by the absence of CO as a radiolytic product,[17] confirmed also in this work, and the inhibitory action of oxygen on the chain reaction in the $HCOOH + H_2O_2$ system.[18] Likewise, it is known that carboxyl ion radicals dimerize efficiently to give oxalic acid ($2k = 1 \times 10^9\ M^{-1}\ \text{sec}^{-1}$).[10] However, measurements using ^{14}C-labeled formate[19] have shown that oxalic acid is not formed in the presence of oxygen. Hence, it follows that the radicals produced in reactions 4, 5, and 6 disappear only *via* reaction 7.

Hydroperoxyl radicals formed in reactions 1, 2, and 7 undergo disproportionation

$$2HO_2\ (\text{or } 2O_2^-) = H_2O_2 + O_2 \quad (8)$$

where $k_{HO_2+HO_2} = 2.7 \times 10^6\ M^{-1}\ \text{sec}^{-1}$ and $k_{O_2^-+O_2^-} = 1.7 \times 10^7\ M^{-1}\ \text{sec}^{-1}$, according to Czapski and Dorfman.[20] Reaction 8 explains the large yields of H_2O_2 in the irradiated solutions. It should be pointed out that reaction 1 efficiently protects H_2O_2 from H atom attack, as $k_{H+H_2O_2} = 5 \times 10^7\ M^{-1}\ \text{sec}^{-1}$ and $[H_2O_2] \ll [O_2]$. However, as mentioned above, calculation shows the possibility of some peroxide loss due to attack by hydrated electrons. This was, indeed, found on dosage curves for pH >3. The decrease is small, not exceeding 5% even under the worst conditions, and we consider that the method employed above to obtain the initial yields has eliminated this source of error. The corresponding gain in $G(CO_2)$ was within

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(16) M. Anbar and P. Neta, *Int. J. Appl. Radiat. Isotopes*, **18**, 493 (1967).

(17) G. E. Adams and E. Hart, *J. Amer. Chem. Soc.*, **84**, 3994 (1962).

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experimental error. It can also be shown that under the present working conditions other known reactions of H_2O_2 (with OH or O^-) cannot compete with reactions 5 or 6.

The concentration of H_2 in the solutions is smaller than 10^{-5} M which, since $k_{OH+H_2} = 4.5 \times 10^7$ M^{-1} sec^{-1}, excludes a competition with reactions 5 or 6.

The concentration of CO_2, or HCO_3^-, and CO_3^{2-} at higher pH, in irradiated solutions is considerable (from 2×10^{-5} to 1×10^{-4} M). Some fast reactions of these species with the primary products of water radiolysis are known.[8,10] Still, as can be seen, their presence has no essential influence on the scheme given in reactions 1 to 8. The reaction $CO_2 + e_{aq}^- = COO^- + H_2O$ with $k = 7.7 \times 10^9$ M^{-1} sec^{-1}, in the most inconvenient case, can consume 4% of hydrated electrons in competition with reaction 2. Since the fate of the formed COO^- is in reaction 7, it still holds stoichiometrically that only reaction 2 takes place. Bicarbonate and carbonate ions react rapidly with OH radicals (1×10^7 M^{-1} sec^{-1} and 3×10^8 M^{-1} sec^{-1}, respectively) but their concentrations are insufficient to compete with reaction 6 for OH radicals. The reactions of HCO_3^- and CO_3^{2-} with hydrogen atoms or hydrated electrons are slow ($<10^6$ M^{-1} sec^{-1}), as are the CO_2 reactions with H or OH radicals. Hence, it follows that the stable radiolytic products in the system $HCOOH + O_2$, under appropriately chosen conditions, may not affect the simple reaction mechanism even in the case where the irradiation conditions are not strictly initial.

It should be added that in alkaline media where reaction $OH^- + OH = O^- + H_2O$ ($k = 3.6 \times 10^8$ M^{-1} sec^{-1}) also occurs, there is no change in the measured yields of the stable radiolytic products. As is seen in Figure 4, the yields are the same as in a neutral medium. This implies that reaction 9 occurs.

$$HCOO^- + O^- = OH^- + COO^- \qquad (9)$$

Since k_9 is not known, we have tried to measure it from the competition with

$$O_2 + O^- = O_3^-; \quad k_{10} = 2.6 \times 10^9\ M^{-1}\ sec^{-1} \qquad (10)$$

However, no competition could be observed, $G(CO_2)$ measured at pH 13 being independent of oxygen to formate concentration ratios between 0.2 and 8. This indicates that reaction 11 most probably occurs

$$HCOO^- + O_3^- = COO^- + HO_3^- \qquad (11)$$

As $HO_3^- \rightarrow OH^- + O_2$,[21] reactions 10 and 11 lead to the same yield as reaction 9. No other O^- radical reactions can influence the observed radiolysis mechanism. This can be easily checked if one takes into account the concentration of the substances in the solution and the rate constants: $k_{O^-+H_2} = 1.6 \times 10^8$ M^{-1} sec^{-1} $k_{O^-+HO_2^-} = 7 \times 10^8$ M^{-1} sec^{-1}; $k_{O^-+CO_3^{2-}} = 4.4 \times 10^7$ M^{-1} sec^{-1}

Expressions for Primary Yield Calculations. The usual kinetic treatment of reactions 1 to 11 gives, independently of pH, the known relations

$$G(CO_2) = G_{OH} \qquad (12)$$

$$G(H_2O_2) = G_{H_2O_2} + 0.5(G_H + G_{e_{aq}^-} + G_{OH}) \qquad (13)$$

$$G(H_2) = G_{H_2} \qquad (14)$$

The equation for material balance

$$G_{OH} + 2G_{H_2O_2} = G_H + G_{e_{aq}^-} + 2G_{H_2} \qquad (15)$$

used with eq 13 and 14 gives, upon some rearrangement

$$G_H + G_{e_{aq}^-} = G(H_2O_2) - G(H_2) \qquad (16)$$

Hence to calculate free radical yields, eq 12 and 16 were used. The yield of primary molecular hydrogen is given by eq 14. The yield of primary hydrogen peroxide was calculated from eq 15.

Corrections of Measured Values. Experimental yields (Figures 2–4) were not used directly in the above expressions; they were corrected beforehand for scavenging in the spur and, when necessary, also for the contribution of reaction 4 to the H_2 and CO_2 formation.

Among the various ways of carrying out the corrections due to the scavenging within the spur the most convenient seemed to be that given by Flanders and Fricke[22] as used by Fielden and Hart.[23,24]

In this case we assumed that

$$G(CO_2)_{cor} = G(CO_2)_{measd} \times \frac{0.551}{I_S}$$

where I_S is the fraction of radicals combining with the solute S. The values $0.551/I_S$ were taken from Table I of ref 22, for $E = 2.5$ and the corresponding values of B, a dimensionless parameter derived from the expression

$$B = \frac{b^2}{4D} \times k_{OH+S} \times [S]$$

Here b (= 5.8 Å) is the radius of the spur for OH radicals (considered to be 2.7 times smaller than that for e_{aq}^- [25,26]), $D = 2 \times 10^{-5}$ cm^2 sec^{-1} is the diffusion coefficient for the OH radical,[25] k_{OH+S} the rate constants of the reactions 5 and 6, and [S] is the formic acid or

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(24) E. M. Fielden and E. Hart, *ibid.*, **33**, 426 (1968).

(25) A. Kuppermann, "Radiation Research, 1966," G. Silini, Ed., North-Holland Publishing Co., Amsterdam, 1967, p 212.

(26) H. Schwarz in Proceedings of the Fifth Informal Conference on the Radiation Chemistry of Water, University of Notre Dame, Radiation Laboratory, AEC Report COO-38-519, Notre Dame, Ind., Oct 1966.

Table I: Summary of Stable Product Yields in γ Radiolysis of HCOOH + O_2 at Different Formic Acid Concentrations and Various pH. $[O_2] = 1 \times 10^{-3}$ *M*. Measured Yields Corrected for Scavenging in the Spur

pH	Concn, *M*	$G(CO_2)$			$G(H_2O_2)$			$G(H_2)$	
		a	*b*	*c*	*a*	*b*	*c*	*a*	*c*
1.3	1×10^{-3}	2.51^d	...	...	3.35^d	...	...	0.42	0.43
		2.54^d	...	...	3.50^d	...	...	...	...
	5×10^{-3}	2.77	2.74	2.77	3.90	3.80	3.81	0.42	0.43
		...	...	...	4.07	3.97	3.98	...	...
	1×10^{-2}	2.83	2.79	2.83	...	...	...	0.40	0.41
		2.91	2.87	2.91	...	...	...	...	...
	2.5×10^{-2}	...	...	...	4.07	3.97	3.94	...	...
	5×10^{-2}	3.05	2.96	2.92	4.05	3.96	3.90	...	...
2.3	1×10^{-2}	2.77	2.72	2.77	3.67	3.58	3.57	...	...
2.9	1×10^{-2}	2.91	2.83	2.81	3.78	3.69	3.65	...	...
4.4	5×10^{-3}	2.90	2.77^e	2.80^e	3.76	3.67	3.63	...	...
~7	1×10^{-4}	2.48^d	...	...	3.69^d	...	...	...	...
	5×10^{-4}	2.56	2.53	2.56	3.68	3.59	3.60	0.43	0.44
	1×10^{-3}	...	...	...	...	...	...	0.43	0.43^e
	5×10^{-3}	2.98	2.85^e	2.82^e	3.78	3.69	3.64	0.50	0.48^e
	2.5×10^{-2}	3.22	2.82^e	2.72^e	...	...	...	...	...
	5×10^{-2}	...	...	...	3.87	3.78	3.56	...	...
10	5×10^{-3}	2.85	2.72^e	2.69^e	3.70	3.61	3.56	...	...
11.9	5×10^{-3}	2.90	2.77^e	2.74^e	...	...	...	...	...
13	1×10^{-4}	2.40^d	...	...	...	...	...	...	...
	2.5×10^{-4}	2.64	2.64	2.64	...	...	...	...	...
	5×10^{-4}	2.58	2.56	2.58	3.68	3.59	3.60	...	...
	1×10^{-3}	2.66	2.61^e	2.64^e	...	...	...	0.44	0.44^e
	2×10^{-3}	2.98	2.91^e	2.92^e	...	...	...	...	...
	5×10^{-3}	2.90	2.77^e	2.74^e	3.77	3.68	3.63	0.49	0.47^e

[a] Measured yield. [b] Measured yield corrected according to Flanders and Fricke.[22] [c] Measured yield corrected according to Kuppermann.[25] [d] No correction, low hydroxyl radical reactivity. [e] Corrected also for the contribution of reaction 4.

formate ion concentration in moles per liter. The substitution gives

$$B = 1.05 \times 10^{-2} \times [\text{HCOOH}] \text{ (for formic acid)}$$

and

$$B = 1.05 \times 10^{-1} \times [\text{HCOO}^-] \text{ [for the formate ion)}$$

where the concentration is expressed in moles per liter. $G(CO_2)$ values obtained at $[\text{HCOO}^-] \geq 1 \times 10^{-3}$ *M* are also corrected for reaction 4.

The oxygen concentration (1×10^{-3} *M*) is such that reactions 1 and 2 also occur to some extent in the spur. As these influence the yields of $G(H_2O_2)$, we made corrections before introducing the measured values into eq 16. The corrections were calculated in the way described above. Parameter *B* was calculated as

$$B = 2.44 \times [O_2]$$

by taking from Fielden and Hart[28] the data for hydrated electrons: $b = 15.8$ Å and $D = 4.8 \times 10^{-5}$ cm^2 sec^{-1}; the oxygen concentration is in moles per liter.

Table I presents all our experimental values for the stable product yields and the values obtained after corrections described above. It gives also the measured values corrected according to Kuppermann's diffusion-kinetic theoretical curves.[25]

It is certain that the corrections derived from diagrams are less precise than those obtained by using the Flanders and Fricke method of calculation.[22] This may be especially true in the relatively low reactivity region, studied in the present work, where the effect of scavenging within the spur is not very significant. However, Kuppermann's curves offer greater possibilities for estimating the various corrections as they were derived from a more elaborate model of water radiolysis (seven primary species in a mechanism involving 20 reactions). The need for the different corrections can be seen from the following considerations. The increase in formic acid concentration leads not only to an apparent increase of G_{OH} but, by preventing the hydroxyl radical recombination, also to an apparent decrease in $G_{H_2O_2}$. The efficient scavenging of primary reducing species by oxygen leads not only to an apparent increase of G_{red} but also to a corresponding decrease in G_{H_2}. Also larger reactivities toward hydrated electrons (1.9×10^7 sec^{-1} in the case of 1×10^{-3} *M* of oxygen) and hydroxyl radicals (in the present work up to 1×10^8 sec^{-1}), prevent the water-forming reaction between OH + e_{aq}^- (or H) in the spurs and so leave in excess a certain number of primary oxidizing and reducing species, respectively.

As can be seen, the measured yields (column *a*) corrected according to the two methods (columns *b* and *c*) agree very well although the corrections differ, in some cases quite considerably, among themself. This is not surprising as in both cases the corrections are small compared to the measured yields to which they are applied; hence the fact that they differ is without particular importance in the present working conditions. In the primary yield calculations (eq 12, 14–16) we have used the mean values obtained by correcting the measured yield in the two ways mentioned above. Table I shows that only in a few cases do the corrections exceed 0.1 G unit, and that in most cases the uncertainty introduced into the stable products measurements by the corrections exceeds only marginally the experimental error.

Primary Yields in Water γ-Radiolysis Calculated for Various pH. Figure 5 summarizes the values obtained from measurements in $HCOOH + O_2$, by using the corrected data given in Table I and the eq 12, 14, 15, and 16.

It can be seen that the yields of primary products in the γ radiolysis of water do not change in the range $3 < pH < 13$: $G_{-H_2O} = 4.09$, $G_H + G_{e_{aq}^-} = 3.18$, $G_{OH} = 2.72$, $G_{H_2} = 0.45$, and $G_{H_2O_2} = 0.68$. The increase in acidity induces an increase in water decomposition. At pH 1.3 the following values are derived: $G_{-H_2O} = 4.36$, $G_H + G_{e_{aq}^-} = 3.49$, $G_{OH} = 2.85$, $G_{H_2} = 0.43$, and $G_{H_2O_2} = 0.76$.

It is certain that the improvement in the diffusion radical model will require some changes in the parameters used in calculating the corrections. Nevertheless, such changes may not lead to significant variations in the values for the primary yields given above, as they were mostly derived from measurements in a reactivity range where the contribution of intraspur reactions is not very significant.

Concluding Remarks

Primary Yield Increase in Acid Medium. In contrast with other published results, the data presented here show a relatively small increase (~7%) in G_{-H_2O} when the pH is varied from 3 to 1.3. The corresponding increase in the total reducing radical yield is of the same order (~10%). This finding eliminates Hayon's explanation of the pH effect[2] in acid medium: if only the reactivity of H^+ were in question, the increase in yield should be almost tripled. The figures given here indicated that only about one-third of the H atoms formed in the spur reaction

$$H_3O^+ + e_{aq}^- = H + H_2O \qquad (17)$$

reach the bulk of the solution and the rest disappear in recombination reactions inside the spur.

The Constancy of Primary Yields at $3 < pH < 13$. Data from a number of published systems show the constancy of primary yields when the pH changes from neutral to alkaline: $HPO_3^{2-} + NO_3^-$,[27] $HCOO^- + Fe(CN)_6^{3-} + Fe(CN)_6^{4-}$,[12] $C_2O_4^{2-} + O_2$,[13] $CO + O_2$,[28] and BrO^-.[29,30] However, with the exception of the phosphite–nitrate system[27] the calculated primary radical yields as well as the G_{-H_2O} values are considerably lower than those obtained in the present work. The cause for this is more likely to lie in the incomplete fullfilment of the conditions, (a), (b), and (c) cited in the Introduction, rather than in some unknown primary processes which could occur with different efficiencies in the presence of different solutes. This conclusion is also reached in a critical analysis of some published values made recently by Czapsky.[3] Considering his own data[27] and also reviewing published results[1] on the influence of pH on primary yields, Haissinsky draws the conclusion that the decomposition of water is the same over the whole pH scale; secondary reactions contribute to an increase of G_{-H_2O} in acid medium (about 10%) without influencing it appreciably in alkaline solution.

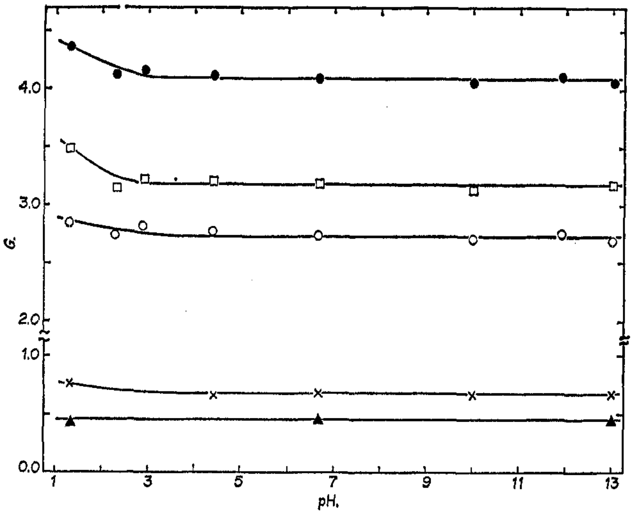

Figure 5. The pH effect on the radiation chemical yields of water decomposition and the primary radiolytic products: ●, H_2O: □, $e_{aq}^- + H$; ○, OH; ×, H_2O_2; ▲, H_2.

It is worth mentioning that the results presented here for neutral media are in a good agreement with recent measurements using the systems $CO + O_2$,[31] tetranitromethane $+ O_2$,[32] air-saturated solutions of ferrous sulfate at low acidities, and neutral air-saturated solutions of ethanol and of sodium formate.[33]

The primary yields calculated for pH 12–13 should be

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regarded with some reserve since the rate constants and the products for the reactions 9 and 11 are not completely established. However, on the basis of our present knowledge, it is unlikely that these values will vary much, as the increase of pH and the conversion of OH to O^- does not change the measured yields of CO_2 and H_2O_2. Also, it is difficult to expect that the increase in hydroxyl ion concentration in this pH range (reactivities 3.6×10^6 to 3.6×10^7 sec^{-1}) increases the yield of water decomposition.

$G_{e_{aq}^-}$ at $3 < pH < 13$. If we take as $G_H = 0.55$,[27] we can obtain for the yield of hydrated electrons in the studied pH region $G_{e_{aq}^-} = 2.63$. In a recent publication Fielden and Hart,[23] analyzing the published values as well as their own, conclude that the figure 2.63 ± 0.1 can cover the results for hydrated electron yields obtained from four different systems at neutral pH. The value obtained from oxygenated formic acid solutions in the present work is in perfect agreement with Fielden and Hart's figure. At pH 13, these authors find a higher electron yield, which is at variance with the data presented here. Another interesting conclusion drawn from the primary yields derived at $3 < pH < 13$ is that $G_{e_{aq}^-} \simeq G_{OH} \simeq 2.67$.

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On the Origin of Primary Hydrogen Peroxide Yield in the γ Radiolysis of Water

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In an attempt to throw light on the origin of $G_{H_2O_2}$, hydrogen peroxide yields were determined in deaerated aqueous solutions (pH 1.3–13) of different substances, irradiated with ^{60}Co γ-rays. Only those systems for which the reaction mechanism enables the direct measurement of $G_{H_2O_2}$ were chosen: 1-propanol, ethanol, acrylamide, acetone, and potassium nitrate. Particular care was taken to ensure that the values derived represent the initial yields. It was shown that homogeneous kinetics can be used to express the dependence of $G_{H_2O_2}$ on hydroxyl radical scavenger concentration, and the origin of intraspur H_2O_2 in a pseudo-first-order process was considered. However, all experimental data obtained in this work demonstrate that $G_{H_2O_2}$ values depend on the reactivities as required in the diffusion kinetic model; the fractional lowering of primary peroxide yield decreases with increasing reactivity of the OH scavenger and increases with increasing e_{aq}^- scavenger reactivity. Theoretical kinetic curves calculated by Kuppermann and by Mozumder and Magee, using the same parameters which furnish good agreement with LET effects, satisfy reasonably well the results presented here, hence the conclusion that the origin of $G_{H_2O_2}$ lies in the recombination of OH radicals within the spur. The experimental results also enable the determination of the primary hydrogen peroxide yields from the γ radiolysis of water: 0.76 ± 0.01 and 0.67 ± 0.01 at pH 1.3 and about 6, respectively. At pH 13 acrylamide solutions give $0.56 < G_{H_2O_2} < 0.67$ and other studies are desirable before a definite conclusion is made.

Introduction

The radical diffusion model for the radiolysis of water assumes that OH radicals are produced in localized regions in the irradiated medium and that the primary hydrogen peroxide yield is formed by combination of these species as they diffuse from the spurs, short tracks, and blobs

$$OH + OH = H_2O_2 \qquad (1)$$

In the case that the reaction

$$OH + S \neq H_2O_2 \qquad (2)$$

competes efficiently with reaction 1, the formation of hydrogen peroxide is suppressed: $G_{H_2O_2}$ should decrease with increasing [S]. The diffusion model predicts that the ratio of peroxide yields, measured in the presence of hydroxyl radical scavenger ($G_{H_2O_2}$) to that observed in dilute solution when the solute has no effect ($G°_{H_2O_2}$), should depend chiefly on the reactivities ($v = k_{OH+S} \times [S]$) of the scavengers used.

After Sworski's original observations on aerated bromide solutions,[1] other results were published con-

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