Gamma-Ray Induced Oxidation of Aqueous Formic Acid–Oxygen Solutions. Effect of Oxygen and Formic Acid Concentrations

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Radiation yields of carbon dioxide, hydrogen and hydrogen peroxide formed and oxygen reacted have been measured over the formic acid concentration range 0.0001 to 1.0 M and the oxygen concentration range 0.005 to 1.2 mM. In the range 0.005 to 0.05 M formic acid, the reaction kinetics are fairly simple, and a ratio of rate constants of 540 for $k_{(H + O_2)}/k_{(H + HCOOH)}$ is found. At higher formic acid concentrations there is evidence that formic acid is competing with water for the capture of electrons ejected from the water. The results are interpreted in terms of radical pair and molecular product yields of the γ-rays.

Several chemical systems have been used to measure the molecular product and free radical pair yield of ionizing radiations in aqueous systems,[1-7] and the results have been reviewed by Allen[8] and Hart.[9] The lack of quantitative agreement between the results obtained in different systems is doubtless due to a scarcity of adequate detailed information regarding the influence of variables such as concentration of solute and pH on the decomposition of the water by the radiation. The formic acid–oxygen system studied in this Laboratory has proved a most versatile one for these studies since wide ranges in hydrogen ion and formic acid concentrations may be covered. The present paper provides new data on the influence of oxygen concentration on molecular product and free radical yields of Co^{60} γ-rays at formic acid concentrations in the range from 10^{-4} to 1.0 M. The mechanism of the γ-ray induced oxidation in the aqueous system formic acid–oxygen–hydrogen peroxide is also discussed.

Experimental

Matheson 98–100% formic acid was distilled at 20 cm. pressure through a 30-plate fractionation column at 59° to give a product having an n^{20}D of 1.3715 which was used without further treatment. Tank oxygen was condensed with liquid nitrogen, and gaseous oxygen from the middle fraction was dissolved in aqueous formic acid prepared using triply-distilled water.[10] Reagent grade sulfuric acid was used in one millinormal concentration to buffer the solutions.
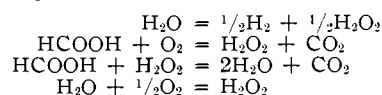
The "syringe technique" was used for preparing, irradiating and analyzing solutions containing as low as 10^{-2} mM oxygen with the production of micromolar amounts of carbon dioxide and hydrogen. This method has been described[11] and provides a major improvement over the technique previously used in the study of the formic acid–oxygen reaction.[4] The solutions were irradiated in 100-ml. syringes with Co^{60} γ-rays at room temperature (25 ± 3°). Gamma-ray energy absorption was measured in the solutions by the use of the ferrous sulfate actinometer, and a value of 15.5 Fe^{+++}/100 e.v. was used to convert chemical yield to electron volts/liter. Gas analyses were carried out using the Van Slyke apparatus. The residual gas, after removal of carbon dioxide and oxygen, consisted normally

(1) M. Lefort and M. Haissinsky, *J. chim. phys.*, **48**, 368 (1951).
(2) F. S. Dainton and J. Rowbottom, *Nature*, **169**, 370 (1952).
(3) C. J. Hochanadel, *J. Phys. Chem.*, **56**, 587 (1952).
(4) E. J. Hart, *ibid.*, **56**, 594 (1952).
(5) T. J. Sworski, private communication.
(6) M. G. Alder and H. E. Eyring, *Nucleonics*, **10**, No. 4, 54 (1952).
(7) E. R. Johnson and J. Weiss, Brookhaven National Laboratory Report BNL-1503 (1953); Nuclear Science Abstracts, 7-5032 (1953).
(8) A. O. Allen, Brookhaven National Laboratory Report BNL-1498 (1953).
(9) E. J. Hart, *Radiation Research*, **1**, 53 (1954).
(10) E. J. Hart, THIS JOURNAL, **73**, 68 (1951).
(11) E. J. Hart, S. Gordon and D. A. Hutchison, *ibid.*, **75**, 6165 (1953).

of hydrogen. In 10 mM formic acid irradiations, this residual gas was transferred to a Saunders–Taylor gas analysis system. Combustion over copper oxide showed that 85% of the gas was hydrogen, 1% carbon monoxide and 13% residual. At this concentration of formic acid, carbon monoxide is therefore a negligible product of the irradiation. The residual gas was shown to consist of 30% oxygen and is concluded to be air-introduced during the transfer of gas from the Van Slyke to the Saunders–Taylor apparatus since oxygen was removed prior to the transfer.

In oxygenated 1000 mM formic acid solutions, carbon monoxide was not found initially in the irradiated solution by the cuprous chloride absorption method. Carbon monoxide was, however, found to the extent of 20% of the hydrogen produced in oxygen-free 1000 mM formic acid solutions. In view of the difficulties of obtaining sufficiently large samples of gas at low oxygen concentrations, analyses for carbon monoxide were not generally run.

Results and Discussion

Aqueous formic acid–oxygen solutions irradiated with γ-rays yield hydrogen peroxide, hydrogen and carbon dioxide as primary products. It was standard practice to measure oxygen consumed in addition to the three above-mentioned products. In accordance with established stoichiometry, the net reactions leading to the formation of these primary products are

$$\begin{align} H_2O &= {}^1/_2H_2 + {}^1/_2H_2O_2 \\ HCOOH + O_2 &= H_2O_2 + CO_2 \\ HCOOH + H_2O_2 &= 2H_2O + CO_2 \\ H_2O + {}^1/_2O_2 &= H_2O_2 \end{align}$$

Hydrogen and carbon dioxide are final products undergoing no subsequent reactions. However, hydrogen peroxide does react further with formic acid, producing carbon dioxide. Consequently, it is necessary to measure initial rates of formation of carbon dioxide and hydrogen peroxide in order to avoid complex secondary reactions. At concentrations of oxygen above 0.05 mM, the amounts of hydrogen, hydrogen peroxide and carbon dioxide formed and oxygen consumed are usually directly proportional to the dosage. At lower concentrations of oxygen, the dosage curves are non-linear indicating that the depletion of oxygen is affecting the rate of reaction. Normally the amounts of products formed and analyzed varied from 0.005 to 0.05 mM.

For the sake of simplicity it will be assumed that the gas remaining after removal of carbon dioxide and oxygen from the irradiated solution is hydrogen. This assumption will introduce no error in the conclusions drawn in the important concentration range below 10 mM formic acid and only modify to a slight extent, if at all, the conclusions based on work at 1000 mM formic acid.

Table I

Effect of Oxygen and Formic Acid Concentration on the Oxidation of Formic Acid[a]

Exp. no.	pH	Dosage rate, 10^{20} e.v./l. min.	Concn. HCOOH, mM	Concn. O2, mM	$G_{(CO_2)}$	$G_{(-O_2)}$	$G_{(H_2)}$	$G_{(H_2O_2)}$	k_7/k_4
1		2.10	0.10	1.117	2.58	2.58	0.34	3.00	
2		2.10	.10	0.54	2.45	2.45	.32	3.02	
3	3.03	2.10	.10	.209	2.35	2.35	.34	2.94	
4		2.09	.10	.111	2.24	2.45	.39	3.02	
5	3.02	2.09	.10	.070	2.35	2.66	.37	3.10	
6	3.03	0.054	.10	.039	2.56	2.73	.46	3.52	
7		0.054	.10	.013	2.53	2.84	.50	3.32	180
8		2.09	.10	.000	2.63	0.00	2.63	0.00	
9	2.92	2.18	1.00	1.20	2.38	2.52	0.45	3.16	
10	3.00	2.10	1.00	1.20	2.53	2.73	.38	3.25	
11	3.38	0.60	1.00	0.386	2.62		40	3.13	
12		.052	1.00	.043	2.80	2.72	.72	3.27	225
13		.052	5.00	.0053	3.1	2.0	2.3	3.10	479
14	3.02	.60	10.0	1.24	2.77	2.87	0.39	3.40	
15	2.75	2.03	10.0	1.23	2.75	2.75	.43	3.34	
16		1.92	10.0	0.441	2.78	2.78	.57	3.06	230
17	3.12	0.60	10.0	.384	2.80	2.82	.50	3.23	788
18		.052	10.0	.223	3.2	2.88	.65	3.54	531
19		.595	10.0	.172	2.89	2.79	.67	3.26	624
20		.052	10.0	.105	3.64	2.94	.85	3.46	542
21		.052	10.0	.072	3.38	2.70	.98	3.38	574
22		.052	10.0	.054	3.3	2.84	1.23	3.32	466
23		.052	10.0	.0204	3.72	2.88	1.80	3.72	518
24		.052	50.0	.051	4.35	2.93	2.26	3.50	530
25	2.35	2.18	100.0	1.200			0.66	3.71	942
26	2.32	2.10	100.0	1.200	2.96	3.13	0.55	3.71	1875
27	1.83	2.18	1000.0	1.200	3.79	3.86	0.79	4.29	5690
28		2.10	1000.0	1.130	3.49	3.32	0.78	3.93	6245
29		2.10	1000.0	0.212	4.3	3.14	1.81	3.32	4920
30	1.71	2.01	1000.0	1.147	3.33	3.13	0.94	3.91	3950

[a] 1 mN sulfuric acid present in all irradiations except No. 11.

The effect of oxygen concentration on the γ-ray initiated oxidation has been studied in detail at 10 and 0.1 mM formic acid concentrations. The concentration of oxygen was varied from 0.013 to 1.117 mM at 0.10 mM formic acid (see exp. 1–7) and from 0.020 to 1.24 mM at 10 mM formic acid (see exp. 14–23). Additional irradiations were carried out at concentrations up to 1000 mM in formic acid. The data appear in Table I. The yield is expressed in units of molecules of product/100 e.v. The yields of carbon dioxide, hydrogen and hydrogen peroxide formed and oxygen consumed are written as $G_{(CO_2)}$, $G_{(H_2)}$, $G_{(H_2O_2)}$ and $G_{(-O_2)}$, respectively. These yields are obtained from plots of molecules of product formed vs. γ-ray energy absorbed in the aqueous solution. Three to four experimental points per product are obtained per irradiation. Normally these four points lie on a straight line extrapolating into the origin. At low concentrations of oxygen or for long irradiations at high oxygen, curves of the type shown in Fig. 1 are obtained and in these cases, initial slopes are measured. In no case has an effect of dosage rate on the yield of products been noted (see Table I).

Two features are of interest in the data of Table I, namely, the constancy of $G_{(-O_2)}$ and the increase of $G_{(H_2)}$ with decreasing concentration of oxygen.

$G_{(-O_2)}$ is substantially constant at 0.1 mM formic acid over a hundredfold decrease in oxygen concentration. This constancy of yield with oxygen con-
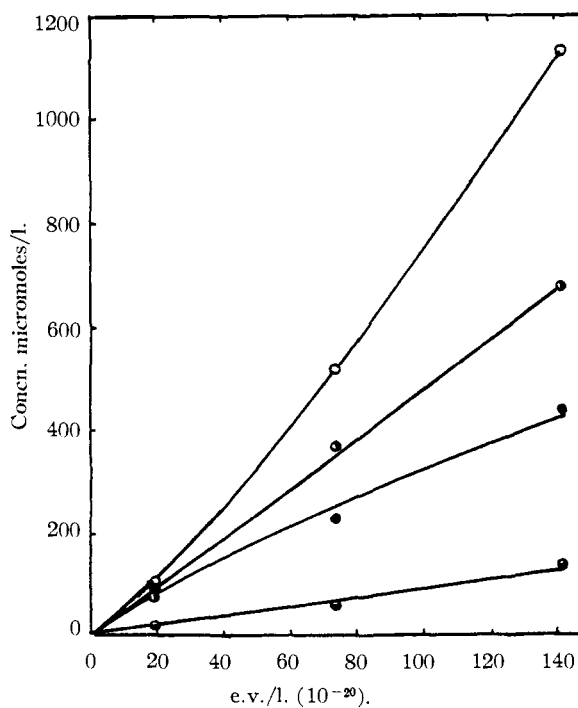

Fig. 1.—Oxidation of 0.01 M formic acid plus 1.19 mM oxygen by γ-rays at 0.052 × 10^{20} e.v./l. min.: O, CO_2; ◑, O_2; ◒, H_2; ●, H_2O_2.

centration holds also at each formic acid concentration as the formic acid is varied from 0.10 to 1000 mM. Since the generation of free radicals by the γ-rays is constant in these dilute solutions and in view of the fact that $G_{(-O_2)}$ is independent of oxygen concentration the conclusion is drawn that oxygen reacts with both hydrogen atoms and formate radicals (see eq. 5 and 7). The increase in $G_{(H_2)}$ is connected with the competition between formic acid and oxygen molecules for the hydrogen atoms produced in the water and is expressed by eq. 4 and 7. These statements will be considered in greater detail when the mechanism is discussed.

As mentioned above, hydrogen peroxide produced by the radiolysis reacts with formic acid in the presence of oxygen, although oxygen is a strong inhibitor for the formic acid–hydrogen peroxide reaction.[10] This effect was observed on long irradiations from the form of the dosage curves. The carbon dioxide curves were concave upward whereas the hydrogen peroxide curves were concave downward. Irradiations reported in Table II containing hydrogen peroxide and oxygen were carried out in order to determine the effect of initially added hydrogen peroxide. Initial rates of product formation were measured. Carbon dioxide formation increases with increasing initial hydrogen peroxide concentration whereas oxygen consumption is independent of peroxide concentration. The expected decrease in yield of hydrogen peroxide did not materialize. Measurements of small differences in hydrogen peroxide concentration become more difficult at the higher concentrations and it is possible that a small decrease could not be detected under the conditions of the irradiations.

TABLE II

THE EFFECT OF HYDROGEN PEROXIDE ON INITIAL YIELDS IN
THE FORMIC ACID–OXYGEN SYSTEMS

HCOOH (mM)	10.0	10.0	10.0
H$_2$SO$_4$ (mN)	1.0	1.0	1.0
Oxygen (mM)	0.441	0.450	0.503
H$_2$O$_2$ (mM)	0.000	0.480	1.079
$G_{(CO_2)}$	2.84	3.52	3.72
$G_{(-O_2)}$	2.84	3.06	2.7–3.0
$G_{(H_2)}$	0.58	0.57	0.48
$G_{(H_2O_2)}$	3.16	3.2	3.5

A mechanism capable of accounting for the behavior of formic acid–oxygen solutions in the concentration range from 5 to 50 mM formic acid is the following

$$H_2O = H + OH \qquad k_1 \qquad (1)$$
$$H_2O = {}^1/_2H_2 + {}^1/_2H_2O_2 \qquad k_2 \qquad (2)$$
$$OH + HCOOH = H_2O + HCOO \qquad k_3 \qquad (3)$$
$$H + HCOOH = H_2 + HCOO \qquad k_4 \qquad (4)$$
$$HCOO + O_2 = HO_2 + CO_2 \qquad k_5 \qquad (5)$$
$$HCOO + H_2O_2 = H_2O + CO_2 + OH \qquad k_6 \qquad (6)$$
$$H + O_2 = HO_2 \qquad k_7 \qquad (7)$$
$$HO_2 + HO_2 = H_2O_2 + O_2 \qquad k_8 \qquad (8)$$
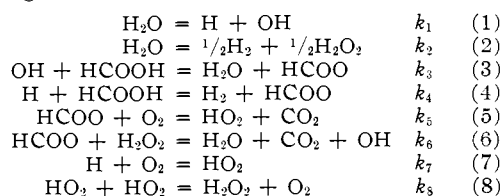
Equations 9 to 12, expressing the yield of products as a function of oxygen, hydrogen peroxide and formic acid concentration, are derived from the above mechanism by assuming only that a steady state between intermediate free radicals, H, OH, HCOO and HO$_2$ is readily established.

$$G_{(CO_2)} = \left[G_{(1)} + \frac{G_{(1)}}{1 + k_7(O_2)/k_4(HCOOH)} \right] [1 + k_6(H_2O_2)/k_5(O_2)] \quad (9)$$

$$G_{(-O_2)} = G_{(1)} \quad (10)$$

$$G_{(H_2)} = G_{(2)}/2 + \frac{G_{(1)}}{1 + k_7(O_2)/k_4(HCOOH)} \quad (11)$$

$$G_{(H_2O_2)} = G_{(1)} + G_{(2)}/2 - G_{(1)}\frac{k_6}{k_5}\frac{(H_2O_2)}{(O_2)}\left[1 + \frac{1}{1 + k_7(O_2)/k_4(HCOOH)}\right] \quad (12)$$

where $G_{(1)}$ and $G_{(2)}$ are the yields of water molecules decomposed/100 e.v. in reactions 1 and 2, respectively.

Since initial yields are reported, a simplification of the above equations can be made by setting (H$_2$O$_2$) = 0. Thus we have

$$G_{(CO_2)} = G_{(1)} + \frac{G_{(1)}}{1 + k_7(O_2)/k_4(HCOOH)} \quad (9')$$

and

$$G_{(H_2O_2)} = G_{(1)} + G_{(2)}/2 \quad (12')$$

The yield of free radicals produced in eq. 1 is given by $G_{(-O_2)}$ and equals 2.82 ± 0.06 in 10 mM formic acid. $G_{(2)}$ may be obtained from either eq. 11, 12 or 12'. Since eq. 12 involves two pairs of constants, k_6/k_5 and k_7/k_4, and eq. 12' is based on an approximation, $G_{(2)}$ has been calculated from eq. 11 and the average values appear in Table III.

TABLE III

AVERAGE FREE RADICAL AND MOLECULAR PRODUCT YIELDS
IN FORMIC ACID–OXYGEN SOLUTIONS

	0.100	mM HCOOH 10.0	1000.0
$G_{(-O_2)}$	2.58 ± 0.17	2.82 ± 0.06	3.44 ± 0.37
$G_{(H_2)}{}^a$	0.32 ± 0.03	0.43 ± 0.03	0.43 ± 0.03
$G_{(H_2O_2)}$	3.13 ± 0.20	3.39 ± 0.22	3.85 ± 0.49
$G_{(H_2O_2)}{}^b$	2.90	3.25	3.87
$G_{(1)}$	2.58 ± 0.17	2.82 ± 0.06	3.44 ± 0.37
$G_{(2)}$	0.64 ± 0.06	0.86 ± 0.03	0.86 ± 0.03

^{a} $G_{(H_2)}$ extrapolated to infinite oxygen concentration.
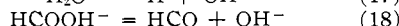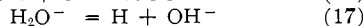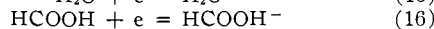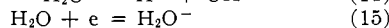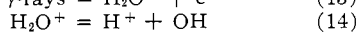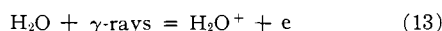^{b} Calculated from eq. 12'.

A plot of $G_{(H_2)}$ vs. $1/(O_2)$ yields a straight line for the range of concentration from 0.054 to 1.24 mM oxygen at 10 mM formic acid (see Fig. 2). $G_{(2)}/2$ is given by the intercept of this line with the ordinate and has the value 0.43. Therefore $G_{(2)}$ equals 0.86 for these solutions. Inserting these constants in eq. 11 one obtains

$$G_{(H_2)} = 0.43 + \frac{2.82}{1 + k_7(O_2)/k_4(HCOOH)} \quad (11')$$

The value of k_7/k_4 for the data of Table I can be calculated from eq. 11' by using the experimental values of $G_{(H_2)}$ and oxygen and formic acid concentrations. These ratios of rate constants appear in column 9 of Table I. The deviation of k_7/k_4 from constancy is appreciable outside the concentration range 5 to 50 mM formic acid where an average value of 530 is obtained. For example, in the experiments carried out at 10 mM formic acid at concentrations below 0.3 mM O$_2$, k_7/k_4 equals 540 ± 80. Experimental error is large in the estimation of k_7/k_4 at 0.1 mM formic acid since the change in hydrogen yield with oxygen is small even at very

low oxygen concentrations. Therefore appreciable deviations from the mechanism 1–8 may not be indicated by the values of k_7/k_4 obtained under these conditions. However, at 1000 mM formic acid conditions are favorable for a measurement of the ratio k_7/k_4. The exceedingly high value of 5200 is found for k_7/k_4. Here hydrogen evolution is far lower than would be predicted on the basis of the k_7/k_4 ratio of 540. (It would be still lower if the correction for carbon monoxide were made.)

Deviation from the above mechanism is indicated at 1000 mM formic acid by the large value calculated for k_7/k_4. At this concentration of formic acid primary electron recoils are predominantly from the water since formic acid contains but 4.7% of the electrons present in the solution. It is tentatively suggested that electron capture by formic acid is competing with electron capture by water. Under these conditions the following processes are postulated

$$\begin{align}
H_2O + \gamma\text{-rays} &= H_2O^+ + e & (13)\\
H_2O^+ &= H^+ + OH & (14)\\
H_2O + e &= H_2O^- & (15)\\
HCOOH + e &= HCOOH^- & (16)\\
H_2O^- &= H + OH^- & (17)\\
HCOOH^- &= HCO + OH^- & (18)
\end{align}$$

In view of the competition between reactions 15 and 16 for electrons, fewer hydrogen atoms are produced in reaction 17 thus leading to lower hydrogen produced *via* reaction 4. The formyl radical, HCO, must lead to a product other than hydrogen since hydrogen yields are lower than predicted from eq. 11. A possible reaction is

$$HCO + HCOOH = HCHO + HCOO$$
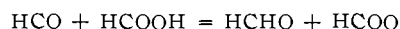
leading to formaldehyde, a product found in air-free 1000 mM formic acid solutions. Work is in progress to determine whether or not processes of types 16 or 18 are important in the radiation chemistry of aqueous formic acid solution.

Table III contains a summary of the average free radical and molecular product yields with the standard deviation estimated from the data of Table I. On the basis of the assumed mechanism, oxygen consumption is an exact measure of reaction 1 regardless of the appearance of secondary reactions involving hydrogen peroxide (see eq. 10). $G_{(1)}$ increases as formic acid concentration increases. Since γ-ray energy absorption is independent of formic acid concentration in this range, the extent of the initial ionization reaction 13 is not altered. The greater efficiency of radical capture by formic acid at higher concentrations probably corresponds to suppressing the radical recombination reaction

$$H + OH = H_2O$$

and making more hydrogen and hydroxyl radicals available for reactions 3, 4 and 7.

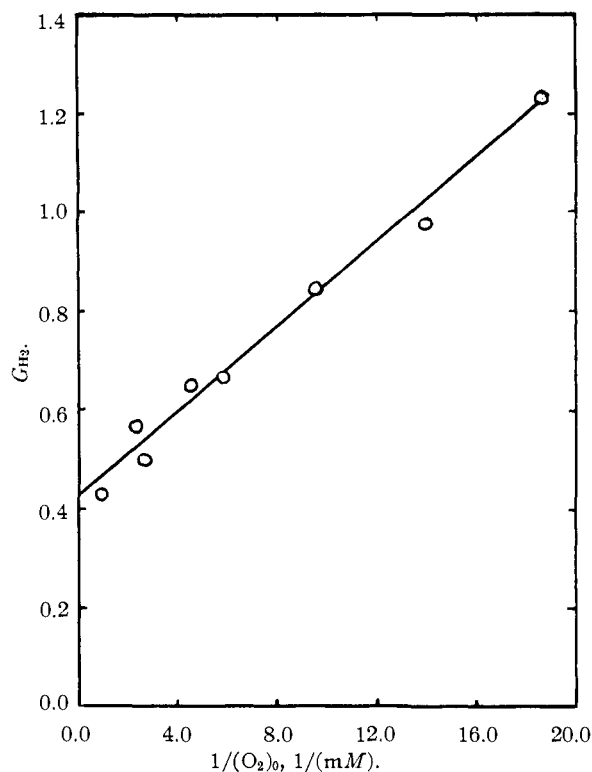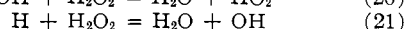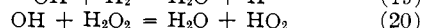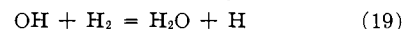$G_{(2)}$, the yield of eq. 2, also appears to be a function of formic acid concentration. The drop in yield

Fig. 2.—Effect of initial oxygen concentration on the γ-ray oxidation of 0.01 M formic acid.

at lower HCOOH concentrations probably rises from intratrack reactions of the type

$$\begin{align}
OH + H_2 &= H_2O + H & (19)\\
OH + H_2O_2 &= H_2O + HO_2 & (20)\\
H + H_2O_2 &= H_2O + OH & (21)
\end{align}$$

These reactions occur in the expanding track reducing the yield of reaction 2 and also of reaction 1 since radical–radical recombination also follows. (Compare yields of $G_{(1)}$ and $G_{(2)}$ appearing in Table III.) In 10 mM formic acid where $G_{(2)}$ equals 0.86, reaction of the free radicals with formic acid takes place in preference to reactions 19–21. In this manner, the reactive hydrogen and hydroxyl radicals are replaced by the relatively inert formate radical thus decreasing the probability of destruction of hydrogen and hydrogen peroxide formed in reaction 2. However, $G_{(2)}$ is 0.64 in 0.1 mM formic acid indicating that partial destruction of molecular products is caused by reactions of the type 19–21.

$G_{(1)}$ and $G_{(2)}$ are functions of formic acid concentration. The hydrogen peroxide yield increases with increasing formic acid concentration approximately in accord with eq. 12′ relating $G_{(H_2O_2)}$, $G_{(1)}$ and $G_{(2)}$. A comparison of the experimental and calculated hydrogen peroxide values is given in Table III.