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Radiation Chemistry of Aqueous Formic Acid Solutions. Effect of Concentration[1]

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The radiolysis of formic acid solutions by Co^{60} γ-rays at concentrations in the range 1.0 to 26.6 M, pure formic acid is reported. Carbon dioxide, carbon monoxide and hydrogen are the sole gaseous products and formaldehyde is a reactive intermediate. $G(CO_2)$ reaches values as high as 12, increases as $(HCOOH)^{1/2}$ at high dose rates, and as (dose rate)$^{-1/2}$ at constant concentration. These results indicate a chain reaction. The reaction sequence

$$COOH + HCOOH = CO_2 + HCO + H_2O$$
$$HCO + HCOOH = HCHO + COOH$$

explains the chain formation of carbon dioxide. $G(H_2)$ decreases from 3.2 in dilute solutions to 2.4 at 5–10 M formic acid and then remains unchanged with increasing concentration. $G(CO)$ rises from zero with increase of formic acid concentration, rapidly at first and then more gradually to 1.25 in pure formic acid. Direct excitation of formic acid by water sub-excitation electrons is suggested as the mechanism explaining the carbon monoxide yields at low concentrations. Some supporting photochemical studies at 1860, 2537 and 2669 Å. are also reported.

Introduction

Irradiation of dilute aqueous solutions of formic acid has been used to establish free radical and molecular product yields.[3] Even though formic acid is not a particularly efficient free radical scavenger,[4] the formic acid–water system has particular merit in the study of radiation effects in concentrated solutions since the components are miscible in all proportions.

In aqueous solutions of formic acid of concentration 10^{-4} to 10^{-2} M and at pH less than 4.0, carbon dioxide and hydrogen, the sole products of γ-radiolysis, are formed with equal yields. These yields are substantially independent of concentration and dose rate.[3,5] The mechanism consistent with these results is

$$H_2O \longrightarrow H, OH, H_2, H_2O_2 \quad (1)$$
$$OH + HCOOH \longrightarrow H_2O + COOH \quad (2)$$
$$H + HCOOH \longrightarrow H_2 + COOH \quad (3)$$
$$COOH + H_2O_2 \longrightarrow CO_2 + H_2O + OH \quad (4)$$
$$COOH + COOH \longrightarrow CO_2 + HCOOH \quad (5)$$

The over-all reaction is

$$HCOOH \longrightarrow H_2 + CO_2$$

The "molecular" hydrogen peroxide formed in (1) disappears *via* a chain mechanism involving steps (4) and (2).[3] The molecular hydrogen and hydrogen peroxide yields formed by pairwise recombination of hydrogen and hydroxyl radicals within the "spur" are represented by $g(H_2)$ and $g(H_2O_2)$, respectively. These yields are expected to decrease as the formic acid concentration is increased because of reactions 2 and 3. The above mechanism predicts that the carbon dioxide yield increases as $g(H_2)$ decreases but is independent of $g(H_2O_2)$.

In this paper $G(CO_2)$ is used as a measure of the efficiency of free radical formation in water—by excitation as well as ionization since it is known that water activated or dissociated by light of wave length 1849 or 1980 Å. decomposes formic acid.[6] Results are reported for formic acid radiolysis in the concentration range from 1.0 to 26.6 M, pure formic acid in order to determine primary yields for water decomposition and to investigate the effect of superimposing formic acid ionization and dissociation processes on water radiolysis.

Experimental

Formic acid (Matheson 98–100%) was distilled at 20 cm. pressure through a 30 plate fractionation column at 59° to give a product having $n^{20}D$ of 1.3715. The previously described techniques of irradiation, dosimetry, solution deaeration, cell filling and Van Slyke gas analysis were used.[3] The gaseous irradiation products were separated from the solution in the Van Slyke apparatus, collected in a storage tube and the contents analyzed by conventional techniques *viz.* absorption by 1 M KOH for CO_2 and mass spectrometer analysis for H_2 and CO.

Formaldehyde was determined by a modification of the method of Laska.[7] This consisted of adding 10 ml. of a 45 μM solution of phenylhydrazine hydrochloride to 5 ml. of the solution being estimated and standing 5 minutes. Two ml. of 1.234% potassium ferricyanide were then added, stood 5 minutes, 5 ml. of 12 N H_2SO_4 added and the whole made up to 25 ml. The optical density at 5200 Å. was measured. Formaldehyde concentration was calculated from the equation

$$C = 41Dd$$

where C = formaldehyde concentration in μ M

D = optical density in 1 cm. cell

d = dilution

Carbon dioxide has appreciably greater solubility in formic acid solutions than in water. The Bunsen solubility coefficients (vol. CO_2/vol. sol.) measured by Adams and Anderson[8] in 5.0, 10.0, 15.0, 20.0 and 26.6 M formic acid are 1.03, 1.30, 1.67, 2.37 and 4.94, respectively. These coefficients were used in calculating the concentration of carbon dioxide in the irradiated solutions from equilibrium pressures existing above the solution in the Van Slyke pipet.

Results

Hydrogen, carbon dioxide and carbon monoxide plots of product formed *versus* absorbed dose are linear for a particular set of initial conditions. Even at the lowest dose rate used where carbon dioxide is formed mainly by a chain mechanism its formation is linear with dose. In contrast, the formaldehyde concentration rapidly reaches a low steady

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[1] Based on work performed under the auspices of the U. S. Atomic Energy Commission.

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[3] E. J. Hart, (a) THIS JOURNAL, **73**, 68 (1951); (b) *ibid.*, **76**, 4198 (1954); (c) *ibid.*, **76**, 4312 (1954); (d) *J. Phys. Chem.*, **56**, 594 (1952); (e) *Radiation Research*, 1, 53 (1954).

[4] (a) E. J. Hart, THIS JOURNAL, **74**, 4174 (1952); (b) J. L. Weeks and M. S. Matheson, *ibid.*, **78**, 1273 (1956); (c) J. H. Baxendale and D. Smithies, *Z. Phys. Chem.*, **7**, 242 (1956).

[5] H. Fricke, E. J. Hart and H. P. Smith, *J. Chem. Phys.*, **6**, 229 (1938).

[6] J. L. Weeks and M. S. Matheson, unpublished results.

[7] F. Laska, *Chem. Listy*, **33**, 375 (1939).

[8] G. E. Adams and A. R. Anderson, U. S. Atomic Energy Commission, Report ANL-5991, April, 1959.

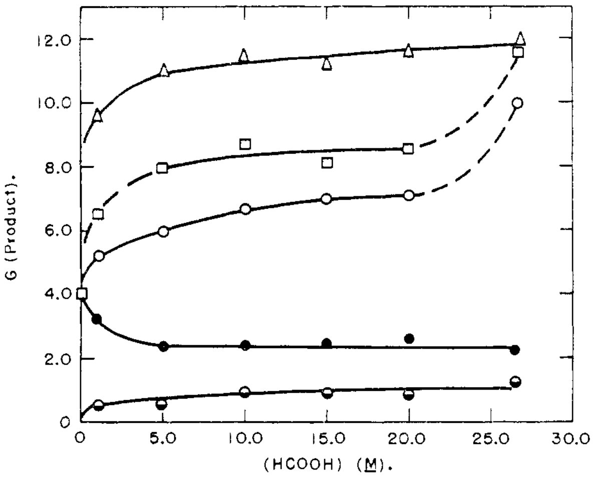

Fig. 1.—Effect of formic acid concentration and dose rate on $G(CO_2)$, $G(H_2)$ and $G(CO)$: ○, $G(CO_2)$ at 35 × 10^{19} ev./l. min.; □, $G(CO_2)$ at 2.2 × 10^{19} ev./l. min.; △, $G(CO_2)$ at 0.33 × 10^{19} ev./l. min.; ●, $G(H_2)$; ◒, $G(CO)$.

state level. Each of these four compounds is a primary product.

Effect of Concentration.—$G(CO_2)$ increases from 4.08, the value in 0.1 *M* solutions (the first point in Fig. 1), with increasing formic acid concentration, rapidly at first and finally at each dose rate reaches concentration independent yields which increase as the dose rate decreases (see Fig. 1). $G(CO)$ abruptly rises from zero with increase of formic acid concentration and then more gradually. $G(H_2)$ however, decreases from 3.2 in dilute solution to about 2.4 at 5–10 *M* and then remains unchanged up to pure formic acid. $G(CO)$ and $G(H_2)$ are independent of dose rate and the yield of these shown in Fig. 1 are averages of the values obtained at dose rates of (35, 2.2 and 0.33) × 10^{19} ev./l.min. When the dose rate is 35 × 10^{19} ev./l.min., $G(CO_2)$ increases as $(HCO_2H)^{1/2}$ up to 15 *M* acid. At a dose rate of 2.2 × 10^{19} ev./l.min. this square root relation holds up to 10 *M* formic acid. (See Fig. 2.)

Effect of Dose Rate.—At constant formic acid concentration in the range from 5 to 20 *M*, $G(CO)_2$ increases from 5.76 at 120 × 10^{19} ev./l.min. to 21.3 at 0.05 × 10^{19} ev./*l*.min. In pure formic acid, $G(CO_2)$ is practically independent of dose rate, as also are $G(CO)$ and $G(H_2)$ over the whole range of concentration.

Effect of Temperature.—$G(CO_2)$, $G(CO)$ and $G(H_2)$ gradually increase in the temperature range from 6 to 78° for 5.0 *M* solutions (see Table I). $G(CO_2)$ increases more rapidly than $G(CO)$ or $G(H_2)$ both of which increase at about the same rate. This work was carried out using a high dose rate, 107 × 10^{19} ev./l.min., thereby minimizing the chain reactions. Plots of log Δ $G(CO_2)$, log $G(CO)$, and log $G(H_2)$ *vs.* $1/T$ give activation energies for the formation of these products falling in the range from 3.0 to 7.6 kcal./mole [$\Delta G(CO_2) = G(CO_2)(\text{obsd.}) - G(CO_2)(\text{infinite intensity})$]. $G(CO_2)$ at infinite intensity is obtained from the extrapolated points for plots of $G(CO_2)$ *vs.* $(I_a)^{1/2}$; see eq. 9 or 9'.

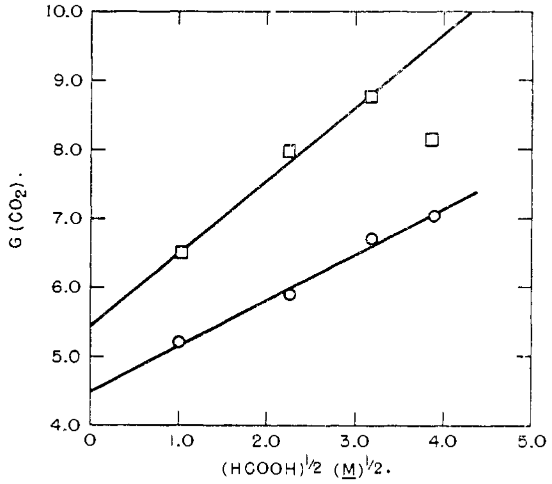

Fig. 2.—$G(CO_2)$ as a function of square root of formic acid concentration: ○, 35 × 10^{19} ev./l. min.; □, 2.2 × 10^{19} ev./l. min.

Effect of Ferric Sulfate, Benzoquinone and Formaldehyde.—Ferric sulfate and benzoquinone, free radical scavengers, reduce $G(CO_2)$, $G(H_2)$ and $G(CO)$ in 5 *M* formic acid (see Table II). In agreement with its greater efficiency as a hydrogen atom scavenger, benzoquinone reduces $G(H_2)$ more than ferric sulfate does. Relatively, $G(CO)$ is reduced more than $G(H_2)$. At low dose rates where $G(CO_2)$ becomes large, the effectiveness of ferric sulfate in reducing the yield increases (see Table II).

Initially added 0.001 *M* formaldehyde in 5.0 *M* formic acid causes little significant change in $G(CO_2)$ or $G(H_2)$ although $G(CO)$ is reduced. $G(-H{\cdot}CHO)$ is 6.15 showing that formaldehyde disappears with about the established radical yield.

Table I

Effect of Temperature on the Radiolysis[a] of 5 *M* Formic Acid

Temp., °C.	$G(CO_2)$	$G(H_2)$	$G(CO)$
6	5.53	1.93	0.34
24	5.81	2.26	0.50
35	5.94	2.26	0.61
52–55	7.15	2.67	1.27
75–80	7.42	2.83	1.39
78	6.93	3.60	1.45

[a] Dose rate = 107 × 10^{19} ev./l. min.

Table II

Effect of Additives on $G(CO_2)$, $G(H_2)$ and $G(CO)$ in Irradiated 5 *M* Formic Acid

$I \times 10^{-19}$ ev./l. min.	Additive	$G(CO_2)$	$G(H_2)$	$G(CO)$
34.9	None	5.93	2.37	0.52
34.9	0.01 *M* Fe^{+++}	5.67	2.10	.16
0.33	None	12.48	2.62	.71
0.33	0.003 *M* Fe^{+++}	7.20	(2.71 CO + H_2)	
34.9	.001 *M* Q[a]	4.59	1.55	0.10
34.9	.001 *M* HCHO[b]	6.42	2.18	.22
34.9	.1 *N* H_2SO_4	6.63	2.78	.62
34.9	.1 *N* H_2SO_4 + 0.01 *M* Fe^{+++}	5.87	2.26	.10

[a] Q = benzoquinone. [b] $G(-HCHO) = 6.15$.

TABLE III

PHOTOCHEMICAL DECOMPOSITION OF FORMIC ACID

HCOOH, M	λ(Å.)	$\phi(CO_2)$	ϕ(CO)	$\phi(H_2)$	Quanta absorbd. / l. min. × 10^{20}
0.0002	1860	0.68	0	0.60	0.0041
0.012	1860	0.37	0.16	.27	.0042
			(.20)	(.36)	
5.0	2669	1.98	.26	.15	.0036
5.0	2537	1.66	.14	.04	.0268
5.0	2537	2.28	.14	.04	.0032
5.0	1860	1.03	.58	.076	17.0
26.6	2669	0.89	.13	.0066	0.0345
26.6	1860	0.96	.80	.048	100.0

Photochemical Decomposition of Formic Acid.—Aqueous formic acid solutions are decomposed by light of wave lengths 2669, 2537 and 1860 Å. Preliminary results are reported in Table III. Carbon dioxide is the major product, formed with a quantum yield, $\phi(CO_2)$, of about 1.0 at the shortest wave length and at high intensity. At λ = 2537 − 2669 Å. and at lower intensities, $\phi(CO_2)$ becomes greater than 2.0. Carbon monoxide yields are dependent on wave length and formic acid concentration, the shorter the wave length and the higher the formic acid concentration the higher are the yields. Hydrogen is a minor product in all cases reported in Table III, although its relative importance increases with decreasing formic acid concentration.

Discussion

The radiation chemistry of dilute aqueous solutions of formic acid is adequately explained by reactions 1–5, but at concentration above 0.01 M more complex reactions are involved and both ionization and excitation effects in water and formic acid must be considered. Another complicating factor is the changing ionic and molecular species of formic acid. In order to hold the discussion within reasonable limits, it will be confined to accounting for the products and the dependence of their yields on formic acid concentration.

Carbon Dioxide.—In concentrated formic acid solutions a new feature, the inception of a carbon dioxide producing chain reaction, appears; hence $G(CO_2)$ no longer provides a measure of the molecular product and free radical yields as it does in dilute solutions. This reaction increases $G(CO_2)$ but has little or no effect on G(CO) and $G(H_2)$.

Significant features relating to the production of carbon dioxide are the high values for $G(\mathrm{CO})_2$, the proportionality of $G(CO_2)$ to (dose rate)$^{-1/2}$ in the concentration range 1 to 20 M (see Fig. 3) and the inhibitory effects of ferric sulfate and benzoquinone. In addition, $G(CO_2)$ increases as $[\mathrm{HCOOH}]^{1/2}$ at least at 35 × 10^{19} ev./l. min. (see Fig. 2). These results not only support the conclusion that a chain reaction producing carbon dioxide occurs but suggest that the mechanism parallels that for radiolysis of hydrogen peroxide.[9] The quantum yield, $\phi(CO_2)$ for photolysis of 5.0 M formic acid is also intensity dependent but the intensity exponent has not been established.

Possible propagation steps in the chain reaction are

$$\mathrm{COOH + HCOOH \longrightarrow CO_2 + H_2O + HCO} \quad (6)$$

$$\mathrm{HCO + HCOOH \longrightarrow HCHO + COOH} \quad (7)$$

A trimolecular termination step consistent with the observed dependence on formic acid concentration and similar to the one proposed for peroxide radiolysis is

$$\mathrm{2COOH + HCOOH \longrightarrow CO_2 + 2HCOOH} \quad (8)$$

Using a mechanism consisting of reactions 1, 2, 3, 4, 6, 7 and 8 and assuming steady state concentrations of intermediate free radicals, expression 9 for $G(CO_2)$ can be derived. This is in accord with the observed concentration and dose rate dependencies shown in Figs. 2 and 3.

$$G(\mathrm{CO_2}) = g(\mathrm{H_2O_2}) + \frac{g(\mathrm{H}) + g(\mathrm{OH})}{2} + k_6 \left\{\frac{g(\mathrm{H}) + g(\mathrm{OH})}{2k_8}\right\}^{1/2} \frac{(\mathrm{HCOOH})^{1/2}}{I_a^{1/2}} \quad (9)$$

where $g(H_2O_2)$, g(H) and g(OH) are the molecular product and free radical yields at formic acid concentration (HCOOH); k_6 and k_8 are the rate constants of reactions 6 and 8, respectively; I_a is the rate of energy input in ev./6.02 × 10^{25} l.sec. In this derivation the carboxyl radical is assumed to be much less reactive than the formyl radical. Reaction 6 is then the rate determining step and (8) becomes the effective termination step. The activation energy of 3.0 to 7.6 kcal./mole estimated above is ascribed to reaction 6 if one assumes zero activation energy for the radical–radical termination reaction 8.

While the $(\mathrm{HCOOH})^{1/2}$ relation seems definite in Fig. 2, the results shown in Fig. 3 indicate a zero order dependence on formic acid concentration. Note that the curves are nearly parallel and displaced to higher $G(CO_2)$ as the formic acid concentration increases. If the square root dependence held over the intensity range covered in Fig. 3, then $G(CO_2)$ should increase as $(\mathrm{HCOOH})^{1/2}$. Zero order kinetics can be derived by assuming that complex formation of the chain carrying COOH radical is followed by bimolecular termination

$$\mathrm{COOH + HCOOH \longrightarrow COOH{\cdot}HCOOH}$$

$$\mathrm{COOH{\cdot}HCOOH \longrightarrow CO_2 + HCO + H_2O} \quad (6')$$

$$\mathrm{2COOH{\cdot}HCOOH \longrightarrow CO_2 + 3HCOOH} \quad (8')$$

Now one obtains

$$G(\mathrm{CO_2}) = \frac{g(\mathrm{H}) + g(\mathrm{OH})}{2} + g(\mathrm{H_2O_2}) + k_6' \left[\frac{g(\mathrm{H}) + g(\mathrm{OH})}{2k_8' I_a}\right]^{1/2} \quad (9')$$

which is consistent with the data presented in Fig. 3. Further refinement of the data is necessary in order to explain the apparent anomaly between the $(\mathrm{HCOOH})^{1/2}$ dependence of Fig. 2 and the zero order dependence of Fig. 3. It may also be possible that the first two terms of equations 9 and 9′ depend on $(\mathrm{HCOOH})^{1/2}$.

Equations 9 or 9′ predict that $G(CO_2)$ extrapolated to infinite dose rate, $G(\mathrm{CO_2})_\infty$ provides a measure of $g(H_2O_2)$ + $\frac{1}{2}(g(\mathrm{H}) + g(\mathrm{OH}))$. Figure 4

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[9] E. J. Hart and M. S. Matheson, *Discussions Faraday Soc.*, **12**, 169 (1952).

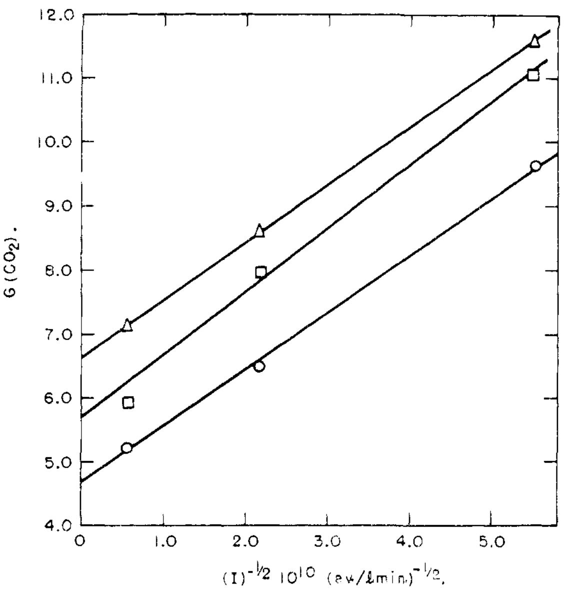


Fig. 3.—$G(CO_2)$ as a function of inverse square root of dose rate: O, 1 *M* HCOOH; □, 5 *M* HCOOH; △, 20 *M* HCOOH.

shows that $G(CO_2)_\infty$ rises rapidly at formic acid concentrations below 5 *M* to a constant value of about 6.5 at the intermediate concentrations and then rises again above 20 *M*. Since the chain reaction is eliminated at infinite dose rate, $G(CO_2)_\infty$ originates from primary nonchain processes occurring in the water and formic acid. At formic acid concentrations above 1 *M* the fraction of the energy absorbed by the formic acid is no longer negligible. Assuming (1) that the direct effect is independent of formic acid concentration, (2) that $G(CO_2) = 8.0$ for pure formic acid (later work at higher dose rates established that $G(CO_2)_\infty$ for pure formic acid is nearer 8.0 than the value of about 9.0 indicated by the results of Fig. 1), (3) that the energy absorbed by a component of a solution is proportional to the electron fraction of that component, $G(CO_2)_\infty$ from reactions originating in water radiolysis can be calculated. (Lower curve in Fig. 4.) This curve shows, as expected, that the yield of carbon dioxide from primary processes occurring in water increases with formic acid concentration. This increase is expected not only because of scavenging of the precursors of molecular hydrogen

$$H + H \longrightarrow H_2 \qquad (10)$$

but also because of interference with the radical recombination reaction

$$H + OH \longrightarrow H_2O \qquad (11)$$

Scavenging of the precursors of molecular hydrogen peroxide produces no increase in $G(CO_2)$ because of reaction 4. If reaction 11 is assumed to have twice the probability of reaction 10, then the expected increase in $G(CO_2)$ is given by $3g(H_2) = 3 \times 0.43 = 1.29$. $G(CO_2)$ increases from 4.1 in 0.1 *M* to a maximum of 5.3 in 10 *M* formic acid. This result indicates that scavenging of radicals is complete in 10 *M* formic acid and that 5.3 water molecules are dissociated by γ-rays per 100 ev. absorbed by the water.

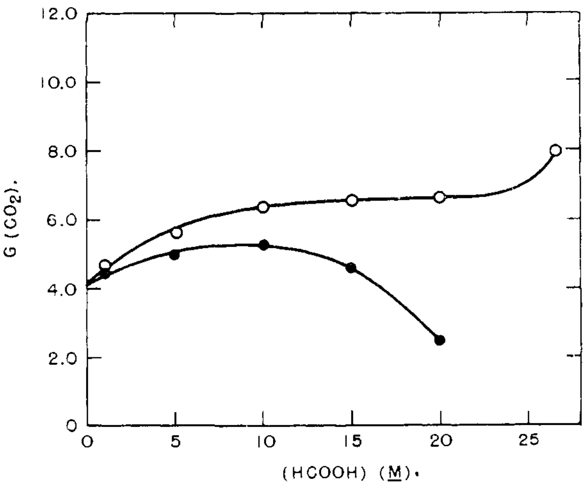
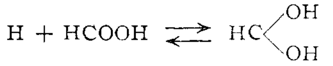
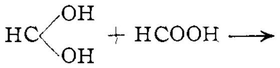


Fig. 4.—Non-chain $G(CO_2)_\infty$ and $G(CO_2)_{H_2O}$ as a function of formic acid concentration: O, $G(CO_2)_\infty$; ●, $G(CO_2)_{H_2O}$.

Hydrogen.—$G(H_2)$ decreases as the formic acid concentration is increased up to 10 *M* and then remains substantially unchanged to 26.6 *M*, pure formic acid. It is pertinent to ask why a change in the slope of the $G(H_2)$ *vs.* concentration curve occurs. The initial decrease in $G(H_2)$ can be explained by reactions 12 and 13 competing with (3) as suggested by Garrison and co-workers[10] or by electrons captured by formic acid.[3c]


(12)

$$H + HCOOH \rightleftarrows HC\begin{smallmatrix}OH\\OH\end{smallmatrix} \qquad (12)$$



$$HC\begin{smallmatrix}OH\\OH\end{smallmatrix} + HCOOH \longrightarrow HCO + H_2O + HCOOH \qquad (13)$$

Hydrogen is formed in reaction 3, whereas (12) and (13) yield a formyl radical which is normally removed *via* reaction 7. According to this scheme $G(H_2)$ tends to zero at high formic acid concentrations and is replaced by formaldehyde. This conclusion is supported by the photochemical data showing that $\phi(H_2)$ is substantially zero (Table III). However, in 26.6 *M* formic acid $G(H_2) = 2.2$ which indicates that the ionization processes operating are more complex. The following reasonable processes producing H atoms are revealed by electron impact studies on formic acid and its deuterated species[11,12]

$$HCOOH + e^- \longrightarrow CHO_2^+ + H + 2e^- \qquad (14)$$

$$HCOOH^+ + (M) \longrightarrow CHO_2^+ + H \qquad (15)$$

$$HCOOH^- \longrightarrow HCOO^- + H \qquad (16)$$

In view of the appreciable excess energy available or possible in these hydrogen atom producing reactions, we suggest that reaction 3 is favored relative to (12) by "hot" hydrogen atoms. In concentrated formic acid solutions moderation of the excess energy is by formic acid from which hydrogen atoms can be extracted. With increasing water content formic acid moderation is replaced by

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(10) W. M. Garrison, W. Bennett and M. Jayko, *J. Chem. Phys.*, **24**, 631 (1956).

(11) C. E. Melton and G. A. Ropp, *ibid.*, **29**, 400 (1958).

(12) G. A. Ropp and C. E. Melton, THIS JOURNAL, **80**, 3509 (1958).

water moderation which does not lead to hydrogen production and consequently $G(H_2)$ decreases.

We believe that hydrogen atoms are formed in 5.0 *M* formic acid. If all these react according to (3) then

$$G(H_2) = g(H) + g(H_2)$$

Even if $g(H_2)$ is assumed to have been reduced to zero, $g(H)$ cannot be greater than 2.38, the value of $G(H_2)$, which represents an appreciable decrease from 2.82 reported in 0.01 *M* solutions.[3c] The studies using benzoquinone as a radical scavenger support this conclusion. The ratio of rate constants $k(H + Q)/k(H + HCOOH)$ may be calculated from the data of Table II and the equation

$$\frac{k(H + Q)}{k(H + HCOOH)} = \frac{[HCOOH]}{[Q]}\left\{\frac{g(H)}{G(H_2)_Q - g(H_2)}\right\}^{-1}$$

The figures in Table II give a value of 3200 ± 500 for the ratio in agreement with the 3000 reported by Baxendale and Smithies.[4c]

Carbon Monoxide.—$G(CO)$ rises rapidly in the concentration range from 0.01 to 1.0 *M* and then more gradually until a yield of 1.25 is reached in 26.6 *M* formic acid. Since carbon monoxide is produced in the radiolysis of pure formic acid, it must be formed as a result of direct ionization and/or dissociation processes. However, direct ionization or dissociation cannot account for the unexpectedly high yields of 0.25 and 0.50 in 0.1 and 1.0 *M* formic acid, respectively. The yields from direct action at these concentrations are less than 0.005 and 0.05, respectively.

In irradiated dilute aqueous solutions dissociation and ionization of water occur. While the formation of H and OH radicals from ions formed in water is usually emphasized, an important contribution also comes from dissociation.

$$H_2O \longrightarrow H + OH$$

With light of wave length 1860 Å., Weeks and Matheson[6] show that the quantum yield for liquid water dissociation is 0.6 when 0.0002 *M* formic acid is used as the radical scavenger. Under these conditions carbon dioxide and hydrogen are the only products. As the formic acid concentration is increased, light absorption is mainly by formic acid and $\phi(CO_2)$ and $\phi(H_2)$ decrease (Table III). Carbon monoxide appears in significant yield in 0.012 *M* formic acid. Equations 17 and 18 represent the two over-all reactions and have been postulated to occur in the photolysis of formic acid vapor,[13] liquid[14] and solutions.[15,16]

$$HCOOH + h\nu \longrightarrow H_2 + CO_2 \qquad (17)$$

$$HCOOH + h\nu \longrightarrow H_2O + CO \qquad (18)$$

At higher concentrations $\phi(CO_2) >> \phi(H_2)$ or $\phi(CO)$ at wave lengths of 2537 and 2669 Å. but not at 1860 Å. (see Table III). In view of the photolytic formation of carbon monoxide, its absence in the radiolysis of dilute solutions and the negligible direct action expected in 0.1 *M* formic acid solutions, direct dissociation of excited formic acid molecules is concluded to take place during radiolysis. The water subexcitation electron has been suggested as the most likely excited species.[17] We suggest that as the formic acid concentration increases, water excitation processes normally occurring in irradiated water may be replaced by excitation of formic acid and that the excited formic acid leads to carbon monoxide production possibly through intermediate free radical reactions. The reduction in $G(CO)$ by ferric sulfate and benzoquinone is in accord with the formation of carbon-monoxide from free radical precursors.

The mechanism of CO formation must be consistent with a nondependence of $G(CO)$ on dose rate, with a free radical precursor and with an efficient scavenger action. We propose tentatively that carbon monoxide arises by radical–radical action within the expanding spherical spur. This insures the absence of an intensity dependence. If we assume further that the radical–radical reactions of the type occur only in the spur

$$CHO + CHO = CO + HCHO$$

$$\text{or } CHO + COOH = CO + HCOOH$$

Since these reacting radicals form by secondary reactions of the hydrogen and hydroxyl radicals as in reaction 2, 3, 12 and 13, we conclude that the free radical "spur" will expand beyond its original dimensions by the time it becomes populated with CHO and COOH radicals. Therefore lower concentrations of scavenger will be effective in reducing $G(CO)$ than is found in lowering the molecular hydrogen and hydrogen peroxide yields.

Mechanism of Formaldehyde Reactions.—Formaldehyde builds up to very low steady state concentrations in irradiated formic acid solutions. When initially added to 5.0 *M* formic acid formaldehyde is removed with a yield of 6.15. Neither $G(CO_2)$ nor $G(H_2)$ are altered to any appreciable extent under these conditions. $G(CO)$, however, is reduced (Table III). Without supporting evidence we postulate the reactions

$$COOH + HCHO = CO_2 + CH_2OH$$

$$CH_2OH + HCOOH = CH_3OH + COOH$$

This pair of reactions affects neither $G(CO_2)$ nor $G(H_2)$. If the formyl radical is a precursor of carbon monoxide, a reaction consuming these radicals such as

$$HCO + HCHO = CHO\text{-}OCH_2$$

would explain the decrease in $G(CO)$.

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