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Radiolysis and Photolysis of Aqueous Formic Acid. Carbon Monoxide Formation[1a]

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Factors important in carbon monoxide formation in Co^{60} γ-ray and ultraviolet light irradiated aqueous formic acid solutions have been studied. G(CO) increases with increasing formic acid concentration, increasing temperature, with decreasing pH, and by added ferrous sulfate and hydrogen peroxide. The addition of formaldehyde and iodide ion decreases G(CO). In photolysis at 1849 and 2537 Å., ϕ(CO) increases with decreasing wave length, increasing temperature and by added hydrogen peroxide. Under conditions where hydrogen peroxide or iodide ion absorbs the light, little or no carbon monoxide is formed. Added oxygen eliminates all carbon monoxide in both radiolysis and photolysis. Two separate free radical mechanisms are postulated. The radical CHO, formed by excitation of formic acid, is one precursor of carbon monoxide; and the COOH radical, whose conversion to carbon monoxide is promoted in acid solutions, by hydrogen peroxide and by ferrous sulfate, is the other intermediate.

Recently, it has been suggested that the relatively high yields of carbon monoxide, observed in the radiolysis of dilute solutions of formic acid in water, might be due to the direct excitation of formic acid by sub-excitation electrons.[2,3] This suggestion was based on the observation that excitation of formic acid by light of 1849 Å. gave a relatively large yield of carbon monoxide, whereas absorption by water of light of this wave length yielded only hydrogen and carbon dioxide, the expected radiolysis products. In order to investigate this direct excitation idea more fully, a comparative study has been made of the γ-ray radiolysis and photolysis of formic acid solutions using light of wave lengths 1849 and 2537 Å. The effect of pH, added oxygen, hydrogen peroxide, formaldehyde and ferrous sulfate on G(CO) is also reported.

Experimental

Formic acid (Matheson 98-100%) was distilled under a nitrogen pressure of 20–25 cm. through a 30-plate fractionating column at 59°. It was found that, by irradiating a sample that had been allowed to stand for 2 or 3 weeks, carbon monoxide dosage curves did not give a linear extrapolation through the origin but indicated, rather, a rapid initial radiation induced production of carbon monoxide. The magnitude of this effect depended upon the age of the sample. It was found, however, that if freshly prepared formic acid was stored in dark bottles in the refrigerator, it could be used satisfactorily for several weeks.

The ultraviolet source was a low pressure mercury lamp made of high purity silica operated by a one kilovolt power supply. An intensity fluctuation of not more than ±2% was assured by manual monitoring of the primary current in the power transformer.

The high purity silica cells used in the photolyses were cylindrical in shape, having an internal diameter of 4 cm. and an internal thickness of 1 cm. The techniques of deaeration, filling of the cells, γ-ray dosimetry and irradiation have been described previously.[4] The intensity of the 2537 Å. component in the ultraviolet lamp was determined using the Parker ferrioxalate actinometer as modified by Baxendale and Bridge,[5] and the intensity of the 1849 Å. light was obtained using a deaerated solution of methanol (0.005 M) as an actinometer, in which the quantum yield for hydrogen is 0.6.[6]

The intensity of the 2537 Å. component of our lamp was a factor of 40 greater than that of the 1849 Å. component, and since monochromatic 1849 Å. light was not available, it was necessary to restrict the investigation at the shorter wave length to solutions containing less than 0.3 M formic acid. Under these conditions the rate of product formation by 2537 Å. light was small enough to enable one to determine the quantum yields at 1849 Å. The necessary corrections were made by determining the rate of product formation using filtered 2537 Å. light only, and after making suitable corrections for the partial transmission of the filter, subtracting this rate from that of the unfiltered lamp.

A rapid method of gas extraction and analysis was devised, using a modified Van Slyke apparatus, incorporated into the carrier gas circuit of a conventional Aerograph gas chromatograph. The gaseous irradiation products were separated from the irradiated solution in the Van Slyke pipet and were then transferred directly into a small gas chamber from which they could be rapidly injected into the carrier gas stream of the chromatograph. By using a subsidiary recorder amplifier, it was possible to make rapid and accurate analyses of small amounts of gas (10^{-8} mole). Since carbon monoxide is an efficient radical scavenger, it was necessary to limit the extent of reaction to a few micromoles of gas product per liter in order to obtain dosage curves.

Formaldehyde was measured by the chromotropic acid method[7] and hydrogen peroxide by the iodide method.[4a]

Results

The factors important in carbon monoxide formation have been studied in the radiolysis and photolysis of formic acid. The salient features involved may best be brought out by a comparison of the factors increasing and decreasing G(CO) and ϕ(CO).

I. Radiolysis.—G(CO) increases with increasing formic acid concentration, increasing temperature, with decreasing pH, and by the addition of ferrous sulfate and hydrogen peroxide.

Previous work has shown that G(CO) increases with formic acid concentration, and with temperature of irradiation[3]. However, with gas chromotography much greater sensitivity and precision has been achieved for the analysis of carbon monoxide. Figure 1 shows carbon monoxide formation as a function of dosage. Steady state concentrations of carbon monoxide are found, which increase with increasing formic acid concentrations. Initial yields only are reported in this paper. Figure 2 shows that G(CO) increases from zero in 0.001 M acid to 0.94 in 10 M acid (see the lower curve of Fig. 2).

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[2] (a) E. J. Hart, *J. Am. Chem. Soc.*, **81**, 6085 (1959); (b) R. L. Platzman, *Radiation Research*, **1**, 558 (1954); **2**, 1 (1955).

[3] D. Smithies and E. J. Hart, *J. Am. Chem. Soc.*, **82**, 4775 (1960).

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

[5] J. H. Baxendale and N. K. Bridge, *J. Phys. Chem.*, **59**, 783 (1955).

[6] J. H. Baxendale and J. Barrett, *Trans. Faraday Soc.*, **56**, 37 (1960).

[7] C. E. Bricker and H. R. Johnson, *Ind. Eng. Chem.*, *Anal. Ed.*, **17**, 400 (1945).

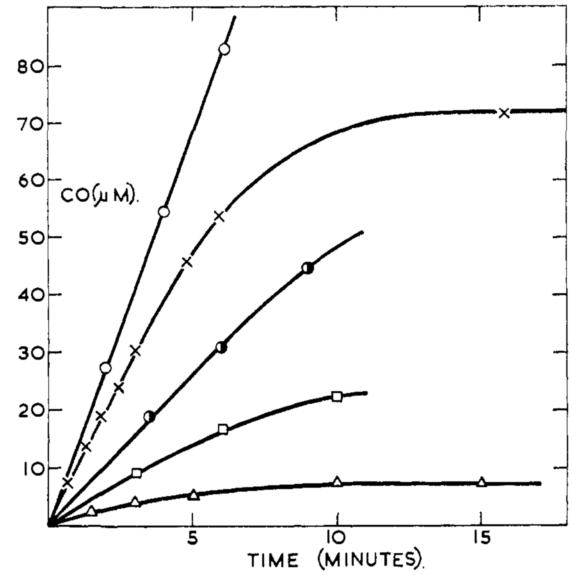

Fig. 1.—Effect of formic acid concentration on carbon monoxide formation. Using 2537 Å. light: Δ, 1 m*M* HCOOH; □, 3 m*M* HCOOH; ◑, 10 m*M* HCOOH; ○, 100 m*M* HCOOH; using Co^{60} γ-rays: ×, 100 m*M* HCOOH (time scale decreased by 50).

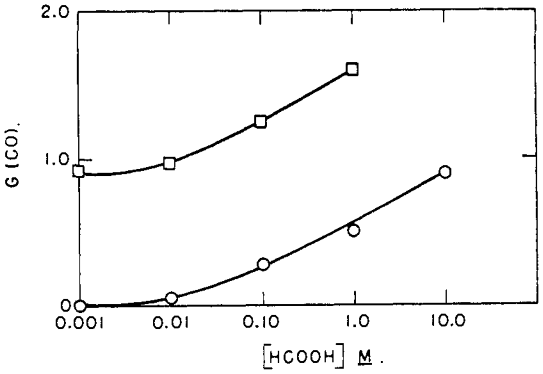

Fig. 2.—Effect of ferrous ion and formic acid concentration on *G*(CO): □, 0.001 *M* Fe^{++} + 0.001 *N* H_2SO_4; ○, no Fe^{++}.

TABLE I

EFFECT OF ADDITIVES ON *G*(CO) IN 0.1 *M* FORMIC ACID

Additive	*G*(CO)		Additive	*G*(CO)
None	0.28		1.0 m*M* KI	0.35
0.1 *N* H_2SO_4	2.06		3.2 m*M* KI	.35
.1 *N* $HClO_4$	1.67		5.0 m*M* KI	.21
.1 *N* HCl	1.30		10.0 m*M* KI	.097
1.0 m*M* O_2	0.00	*G*(−HCHO)	32 m*M* KI	.013
0.221 m*M* HCHO	0.15	4.71	100 m*M* KI	.008
.785 m*M* HCHO	..	5.22		
.933 m*M* HCHO	0.047	5.12		
2.2 m*M* HCHO	0.044	7.64		
3.31 m*M* HCHO	..	~9.2		
7.00 m*M* HCHO	0.04	...		
10.0 m*M* HCHO	0.035	...		

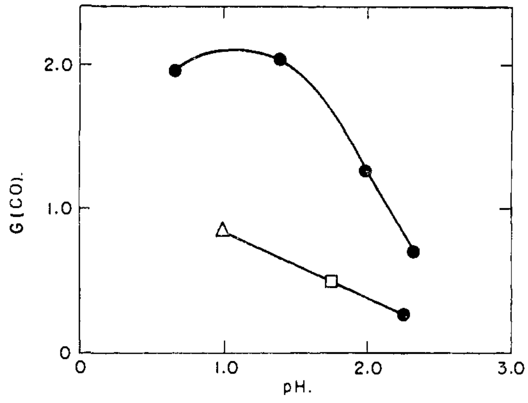

Fig. 3.—Effect of *p*H on *G*(CO) in irradiated formic acid: Δ, 5*M* HCOOH; □, 1.0 *M* HCOOH; ●, 0.1 *M* HCOOH.

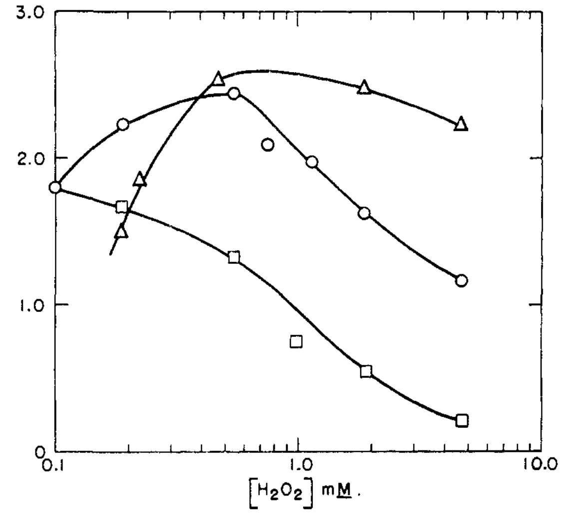

Fig. 4.—Radiolysis of formic acid-hydrogen peroxide solutions: Δ, 1.0 *M* HCOOH; ○, 0.1 *M* HCOOH; □, 0.01 *M* HCOOH.

G(CO) increases with decreasing *p*H (see Table I and Fig. 3). The lower curve shows the increase obtained as the natural *p*H of formic acid solutions decreases with increasing formic acid concentration. Much more pronounced, however, is the effect of decreasing *p*H at constant formic acid concentration. This is brought out by the upper curve of Fig. 3. Maximum effects are produced in 0.1 *M* formic acid containing 0.1 *N* sulfuric acid.

Ferrous ion catalyzes carbon monoxide development. In 0.1 *M* formic acid, 0.001 *N* ferrous sulfate increases *G*(CO) from 0.30 to 1.25 (see Table II and Fig. 2). Interestingly, the effect of ferrous ion increases *G*(CO) in an additive fashion as the formic acid concentration increases (note that the two curves of Fig. 2 are parallel).

TABLE II

EFFECT OF FERROUS SULFATE AND FORMIC ACID CONCENTRATION ON G(CO) IN 0.001 *N* SULFURIC ACID SOLUTION

Fe^{++}, m*M*	HCOOH, m*M*	*G*(CO)	*G*(CO_2)	*G*(H_2)
0.05	1.0	0.50		
.10	1.0	.78		
.28	1.0	.95		
.50	1.0	.98		
1.0	1.0	.93	2.73	3.12
1.0	10.0	.98	3.04	3.23
1.0	100.0	1.25	3.20	3.05
1.0	1000.0	1.61	3.0	3.26

The addition of hydrogen peroxide to formic acid increases not only *G*(CO_2), as has previously been reported,[4a] but it also increases *G*(CO)

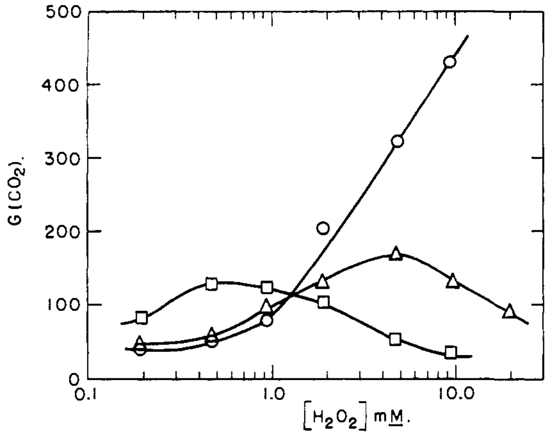

Fig. 5.—Radiolysis of formic acid-hydrogen peroxide solutions: ○, 1.0 *M* HCOOH; △, 0.1 *M* HCOOH; □, 0.01 *M* HCOOH.

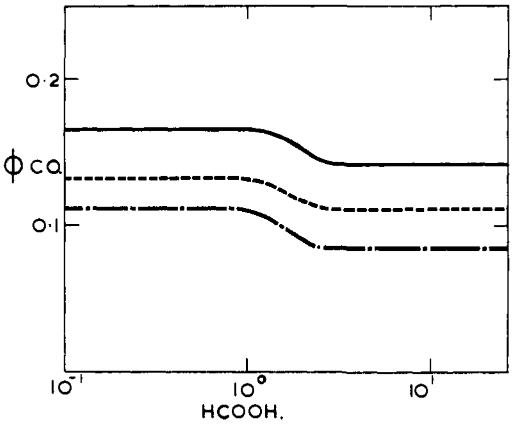

Fig. 6.—Effect of formic acid concentration and light intensity at 2537 Å. on carbon monoxide formation (quanta/ l. min. (× 10$^-$)^{20}: ———, 0.038; - - - -, 0.150; — - — 0.602.

(see Figs. 4 and 5). For example, in 0.01 *M* formic acid in which the yield is negligible, *G*(CO) increases to 1.80 upon the addition of 0.1 m*M* hydrogen peroxide. Maximum yields of about 2.5 are obtained in 1 *M* formic acid containing 1.0 m*M* hydrogen peroxide.

In 5 *M* formic acid both *G*(H$_2$) and *G*(CO) increase with increasing temperature. *G*(CO) rises from 0.34 at 6° to 1.45 at 78°.[8]

In contrast to the action of *p*H, hydrogen peroxide and ferrous sulfate, the addition of oxygen, formaldehyde or iodide decreases *G*(CO).

Carbon monoxide is not formed in irradiated 0.1 *M* formic acid containing 0.001 *M* oxygen (see Table I). Thus oxygen is extremely effective in reacting with the precursor of carbon monoxide. To a smaller extent formaldehyde acts in the same way. *G*(CO) decreases from 0.28 to 0.035 as the concentration of formaldehyde increases to 0.01 *M*. Table I also shows that formaldehyde is removed in yields up to 9.2.

In the radiolysis of 0.1 *M* formic acid, added potassium iodide has relatively little effect at concentrations below 0.005 *M*. Above this concentration iodide ion is only moderately effective in reducing *G*(CO) to 0.008 in 0.1 *M* potassium iodide (see Table I).

In the absence of formic acid, 0.001 *M* formaldehyde forms no carbon monoxide, although *G*(H) = 3.1, and *G*(CO$_2$) = 1.66. *G*(CO), with a yield of 0.09 is formed upon the addition of 0.001 *M* hydrogen peroxide. Under these conditions *G*(CO$_2$) increases to 2.60, and hydrogen decreases to 2.10. Therefore, hydrogen peroxide promotes carbon monoxide formation, not only in formic acid, but also in formaldehyde solutions. Although linear dosage curves were obtained for hydrogen, carbon dioxide was formed only after a short induction period. This indicates that carbon dioxide originates by a secondary reaction, probably involving formic acid.

II. Photolysis.—ϕ(CO) increases with decreasing wave length, increasing temperature and in the presence of hydrogen peroxide. Table III shows the effect of wave length, of formic acid concentration and of intensity on hydrogen, carbon monoxide and carbon dioxide quantum yields. Initially linear dosage curves were obtained in all cases. The quantum yield for 1849 Å. light is also expressed in terms of formic acid absorption only as ϕ'(CO) which is virtually independent of formic acid concentration over the range 0.001 to 2.3 *M*.

ϕ(CO) appears to be intensity dependent at 2537 Å., lower intensities favoring higher yields. The apparent concentration dependence of ϕ(CO) is not realistic, however, since as the concentration increases the intensity of absorbed light increases for a given incident intensity. Quantum yields,

Table III

Quantum Yields from Formic Acid Solutions

HCOOH, *M*	% Light absorbed in HCOOH	ϕ(H$_2$)	ϕ(CO)	ϕ'(CO)	ϕ(CO$_2$)	Intensity quanta/ l. min. × 10^{-20}
			λ = 1849 Å.			
0.0003	4.4	0.49			0.31	0.57
.001	13.8	.47	0.14	0.30	.39	.64
.003	32.8	.39	.10	.31	.37	.82
.010	61.0	.31	.15	.26	.31	1.43
.030	83.0	.24	.25	.30	.25	3.25
.100	94.0	.13	.32	.33	.19	9.25
.300	98.0	..	.37	.37	..	27.4
			λ = 2537 Å.			
0.1	100	0.110	0.142		0.48	0.077
0.3	100	.093	.138		.46	.23
1.0	100	.061	.115		.53	.58
3.0	100	.042	.075		.64	1.35
10.0	100	.035	.047		1.01	5.53
26.6	100	...	.034		0.91	27.6
0.3	100		...		.475	0.024
1.0	100		0.154		.63	.060
3.0	100		.116		.99	.142
10.0	100		.087		2.06	.579
26.6	100		.066		1.44	2.89
0.3	100		...		0.55	0.0033
1.0	100		0.207		0.84	.0082
3.0	100		.152		1.52	.019
10.0	100		.120		2.92	.079
26.6	100		.121		2.27	.396
1.0	100	0.085	0.12(*T* 23°)			.103
1.0	100	.12	.. (*T* 40°)			.105
1.0	100	..	.17(*T* 55°)			.118
1.0	100	.15	.. (*T* 60°)			.120
1.0	100	..	.22(*T* 80°)			.138
1.0	100	.25	.. (*T* 90°)			.148

therefore, were interpolated from an empirical intensity curve. The variation of ϕ(CO) with concentration at three intensities is shown in Fig. 6. A region of concentration dependence is evident, ϕ(CO) being constant up to 1 *M*, then decreasing to a lower limiting value at concentrations greater than 3 *M*. For any concentration, ϕ(CO) is not proportional to (intensity)$^{1/2}$.

$\phi(H_2)$ parallels that of ϕ(CO). The concentration dependence, similar to that of carbon monoxide, is also evident. This effect, however, is complicated by the fact that the rate of light absorption increases with increased formic acid concentration. $\phi(CO_2)$ is independent of both intensity and formic acid concentration for solutions less than 0.2 *M*. Above this concentration, $\phi(CO_2)$ increases rapidly with increasing concentration, and also with decreasing intensity. In 10 *M* solutions $\phi(CO_2)$ as high as 3.46 is found. This high quantum yield indicates a chain reaction similar to that found in the radiolysis of concentrated formic acid solutions. For the lower concentration range, a linear relationship is observed, although some deviations are apparent at low intensities. However, all curves extrapolate to a value at infinite intensity of 0.46, *i.e.*, the yield obtained in very dilute solutions; this "non-chain" carbon dioxide is therefore independent of concentration.

Oxygen completely eliminates carbon monoxide formation in 1 *M* solutions photolyzed at 2537 Å. (see Table IV).

TABLE IV

ϕ(CO) IN FORMIC ACID PHOTOLYZED AT 2537 Å.

HCOOH, *M*	H_2O_2, m*M*	O_2, m*M*	2537 Å. absorption by HCOOH, %	ϕ(CO)
1.0	0.0	0.0	100	0.12
1.0	.0	.3	100	.00
3.0	.0	.0	100	.075
3.0	.28	.0	87	.52
0.001	5.0	.0	10	~ .005

Both $\phi(H_2)$ and ϕ(CO) increase with increasing temperature, although the over-all change in $\phi(H_2)$ for a given temperature range is somewhat greater than that of ϕ(CO). The apparent activation energies for hydrogen and carbon monoxide formation is about 3.5, and 2.3 kcal./g. mole, respectively.

Carbon monoxide is not produced from photolyzed mixtures where all or most of the available light is absorbed by the iodide ion (see Fig. 7). Under these conditions there is an equivalent formation of hydrogen and carbon dioxide. ϕ(CO) decreases with increasing iodide ion concentration, just as it does in the case of γ-rays.

Hydrogen peroxide increases ϕ(CO) under conditions where formic acid absorbs most of the 2537 Å. light, but it decreases ϕ(CO) if hydrogen peroxide absorbs most of the light (see Table IV). In the first case, ϕ(CO) increases by a factor of four, whereas in the second case, ϕ(CO) is somewhat smaller than would be expected from the fraction of light absorbed in the formic acid component of the solution. Since hydrogen peroxide dissociates into hydroxyl radicals, these data show that carbon monoxide is not derived from a radical produced by a reaction of OH with formic acid.

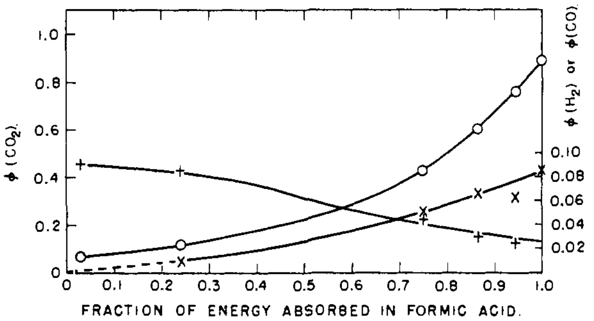

Fig. 7.--Photolysis of formic acid-iodide solutions at 2537 Å.: O, CO_2; +, H_2: ×, CO.

Discussion of Results

Carbon monoxide originates in irradiated formic acid by at least two separate mechanisms. The radical CHO, possibly produced from excitation of formic acid, is one precursor of carbon monoxide. An intermediate species, COOH, whose conversion to carbon monoxide is favored in acid solutions, by hydrogen peroxide and by ferrous sulfate, is proposed in the second mechanism.

The CHO Radical.—A general conclusion from our studies is that factors influencing carbon monoxide formation in the radiolysis of additive-free formic acid similarly affect the photolysis. We further postulate that in unbuffered formic acid radiolysis, the principal, if not the sole, precursor of carbon monoxide is the CHO radical. The evidence is as follows: 1. In the photolysis of aqueous solutions by 1849 and 2537 Å. light, ϕ(CO) is proportional to the light fraction absorbed by formic acid. When water is the sole absorber at 1849 Å., no carbon monoxide is observed, even though, at the relevant concentrations, formic acid is completely effective in scavenging all hydrogen and hydroxyl radicals produced from water dissociation (Table III).

The most probable primary dissociation process leading to carbon monoxide in the photolysis, as well as in the radiolysis, is

$$HCOOH + h\nu \longrightarrow HCO + OH \qquad (1)$$

similar to that recently proposed for the vapor phase photolysis.[8] The radical CHO then undergoes the unimolecular dissociation

$$CHO \longrightarrow CO + H \qquad (2)$$

The intensity dependence of both $\phi(H_2)$ and ϕ(CO) implies that CHO is also involved in one or more radical-radical reactions competing with 2. It is significant that the temperature coefficient of $\phi(H_2)$ is greater than that of ϕ(CO), thus indicating the existence of an additional source of carbon monoxide other than reaction 2.

Possible reactions are

$$CHO + CHO \longrightarrow HCHO + CO$$
$$CHO + COOH \longrightarrow HCOOH + CO$$

Since a region of dependence of *G*(CO) on formic acid concentration was observed, it is evident that

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[8] Ralph Gorden, Jr., and P. Ausloos, *J. Phys. Chem.*, **65**, 1033 (1961).

above a certain minimum concentration an additional reaction involving CHO becomes important, *i.e.*

$$\mathrm{CHO + HCOOH \longrightarrow products}$$
$$\mathrm{\longrightarrow CO + products}$$

2. In irradiated formic acid solutions, no carbon monoxide is observed below 0.01 *M*, although formic acid is an efficient scavenger for hydrogen and hydroxyl radicals at much lower concentrations (Fig. 3). This result proves that H and OH radicals generated in water do not produce carbon monoxide. Instead they produce the formate and carboxyl radicals. The reactions are

$$\mathrm{OH + HCOOH \longrightarrow HCOO + H_2O} \quad (3)$$
$$\mathrm{H + HCOOH \longrightarrow COOH + H_2} \quad (4)$$

The significance of the COOH radical will be discussed below.

3. At 2537 Å., where formic acid alone is the absorbing species, both ϕ(CO) and $\phi(H_2)$ are temperature and intensity dependent (Table III). There is a similar temperature effect on carbon monoxide formation in irradiated 5 *M* formic acid.[8] These results are accounted for by the dissociation reaction 2, followed by 4.

4. At 2537 Å., in mixtures of formic acid and iodide ion, no carbon monoxide is observed when iodide is the absorber even though the significant $\phi(H_2)$ and $\phi(CO_2)$ indicate appreciable free radical reaction with formic acid (Fig. 7). Under these conditions hydrogen and iodine atoms are the effective species found.

$$\mathrm{I^-(H_2O)} + h\nu \longrightarrow \mathrm{I + H + OH^-}$$

5. No carbon monoxide is observed from 2537 Å. photolyzed mixtures of formic acid and hydrogen peroxide where hydrogen peroxide is the principal absorber, and where decomposition of formic acid is initiated by hydroxyl radicals (Table IV).

6. At 2537 Å., as in radiolysis, oxygen eliminates carbon monoxide. Under these conditions the CHO radical probably disappears by reaction

$$\mathrm{HCO + O_2 \longrightarrow HCOO_2}$$

with oxygen resulting ultimately in formic acid plus hydrogen peroxide. Direct molecular detachment of carbon monoxide from formic acid is also ruled out by this oxygen-quenching reaction.

7. In formic acid radiolysis, *G*(CO) increases with formic acid concentration, but in the photolysis ϕ(CO) decreases with the increasing concentration (Table III). This result demonstrates that the increase in *G*(CO) with increasing concentration cannot possibly be due to a different formic acid species, such as formate ion or dimers. Instead, increasing formic acid concentration decreases *G*(CO). We postulate that in the radiolysis, the dissociation reaction 1 increases with increasing formic acid concentration, leading to appreciable net increases in carbon monoxide[1] (see Fig. 2).

Electron capture may be a source of the CHO radical and of carbon monoxide. Evidence is accumulating[9-11] in support of the idea that two transitory reducing species exist in the radiolysis of water, namely, the hydrogen atom and the hydrated electron. At low *p*H, the electron is rapidly converted to a hydrogen atom by the process

$$e_{aq}^- + \mathrm{H_3O^+ \longrightarrow H + H_2O}$$

However, as the *p*H increases, a sufficiently reactive solute may compete for the electron. In alcohols where similar phenomena have been opserved,[12,13] it has been shown that, for many simple organic solutes, this electron capture process is extremely efficient, in some cases, being observed at relatively low *p*H.

It is possible, therefore, that in γ-ray irradiated formic acid, CHO could arise from the reaction

$$\mathrm{HCOOH} + e_{aq}^- \longrightarrow \mathrm{HCO + OH^-}$$

as has previously been postulated.[4c]

On the basis of such a mechanism, it would be expected that carbon monoxide would decrease with decreasing *p*H, whereas the reverse trend has been observed.[14] However, in view of the complex radical mechanisms discussed below, the increase in *G*(CO) in the presence of mineral acids may not be a true *p*H effect.

Until further information is obtained on the variation of carbon monoxide yields in mixtures of formic acid and formate ion at natural *p*H, the origin of the CHO radical must remain in some doubt. However, in consequence of the marked similarities between the photolysis and γ-ray radiolysis of aqueous formic acid, the direct excitation mechanism remains a likely possibility in formic acid radiolysis.

The COOH Radical.—Although formic acid excitation may be a source of carbon monoxide, it is also produced from H atom attack on formic acid. *G*(CO) is increased by addition of ferrous sulfate (Fig. 2), acid (Table II and Fig. 3) and by hydrogen peroxide (Fig. 4).

Hydrogen atoms react with deuterioformic acid according to the reaction

$$\mathrm{H + DCOOH \longrightarrow HD + COOH}$$

It would appear, therefore, that this COOH radical is a precursor of carbon monoxide in formic acid containing ferrous sulfate and hydrogen peroxide.

Table II and Fig. 2 show the effect of solute concentration on *G*(CO) from γ-ray irradiated mixtures of formic acid and ferrous ion in the presence of 0.001 *N* sulfuric acid. In 0.001 *M* formic acid, *G*(CO) increases with increasing ferrous ion concentration up to a limiting value of about 1.0, and it is then independent of further increase in ferrous ion. At constant ferrous concentration of 0.001 *M*, *G*(CO) is independent of formic acid below 0.01 *M* but, at higher concentrations, increases with increasing formic acid (Fig. 2).

Carbon monoxide is not produced in the absence of any reducing additive, yet *G*(CO) approaches 1.0 in the presence of ferrous ion. Furthermore,

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[9] A. R. Anderson and E. J. Hart, *J. Phys. Chem.*, **66**, 70 (1962).

[10] D. Armstrong, E. Collinson, F. S. Dainton, D. M. Donaldson, E. Hayon, N. Miller and J. Weiss, *2nd. U. N. Conf. on the Peaceful Uses of Atomic Energy*, P/1517, **29**, 80 (1958).

[11] A. O. Allen and H. Schwarz, *ibid.*, P/1403, **29**, 30 (1958).

[12] J. H. Baxendale and F. W. Mellows, private communication.

[13] G. E. Adams and R. D. Sedgwick, to be published.

[14] G. E. Adams and J. Sutton, private communication.

it can be seen from Fig. 2 that above 0.01 *M* formic acid the increase in *G*(CO) in the presence of ferrous sulfate parallels the increase produced in the absence of ferrous ion. These data clearly demonstrate the two quite independent modes of carbon monoxide formation in γ-ray irradiated formic acid, namely, carbon monoxide arising from the suggested direct dissociation mechanism discussed above and carbon monoxide from a reaction of ferrous ion with some form of the formate radical. We suggest that the latter reaction is

$$COOH + Fe^{++} \longrightarrow CO + OH^- + Fe^{3+} \quad (5)$$

The analogous reaction of the alternative form of the HCOO radical is probably a simple electron transfer

$$HCOO + Fe^{++} \longrightarrow HCOO^- + Fe^{3+}$$

Ferric ion was not found in irradiated mixtures; however, this is not surprising, since ferric ion is itself an efficient scavenger of formate radicals. This was indicated by the shape of the carbon monoxide dosage curves which were linear in the initial stages only. The reaction is

$$HCOO + Fe^{3+} \longrightarrow Fe^{2+} + H^+ + CO_2$$

The over-all effect of hydrogen peroxide concentration on *G*(CO) and *G*(CO_2) shows some qualitative similarities. For each formic acid concentration, *G*(CO) and *G*(CO_2) each increase with increasing peroxide concentration, reach a maximum and then decrease (Figs. 4 and 5). However, the maxima of the carbon monoxide curves do not appear to be related to those of the carbon dioxide curves. If the precursor of carbon monoxide observed under these conditions is CHO, it is difficult to understand the dependence of *G*(CO) on peroxide at high concentration. By analogy with the carbon dioxide data, the effect could be explained by removal of a possible precursor of CHO, namely, the hydroxyl radical, since this radical is involved in the alternating chain sequence forming carbon dioxide:

$$HCOO + H_2O_2 \longrightarrow CO_2 + H_2O + OH$$
$$OH + HCOOH \longrightarrow H_2O + HCOO$$

However, abundant evidence is presented in this paper against a reaction in which the hydroxyl radical is a precursor of CHO. An alternative explanation is that carbon monoxide is a product of a subsidiary reaction between formyl, COOH (or HCOO) radicals and hydrogen peroxide which leads to *reduction* rather than oxidation.

$$COOH + H_2O_2 \longrightarrow CO + H_2O + HO_2$$

Since the hydroxyl radicals formed from the photodissociation of hydrogen peroxide in the presence of formic acid do not produce carbon monoxide, we suggest that the principal reaction of this radical is

$$OH + HCOOH \longrightarrow H_2O + HCOO$$

The significant difference between photolysis and radiolysis is that in the latter both H and OH are radical precursors. We conclude, therefore, that the hydrogen atom generates a carboxyl radical, which can be reduced to CO by hydrogen peroxide.

Using the very high dose rates of the linear accelerator (LINAC), a carbon monoxide yield of 0.34 was found from 0.1 *M* formic acid containing 1 m*M* ferrous ion and 1 m*N* sulfuric acid. Under these conditions, radical–radical reactions are enhanced at the expense of radical solute reactions. The large decrease in *G*(CO) is in accord with the suggestion that reaction 5 is the major source of carbon monoxide in this system.

One must consider also the influence of *p*H and formic acid concentration on the possible equilibrium

$$HCOOH + HCOO \rightleftarrows HCOOH + COOH$$

If the reaction

$$COOH + COOH = CO + CO_2 + H_2O \quad (6)$$

occurs instead of

$$COOH + COOH = CO_2 + HCOOH$$

as normally postulated, then 6 is a source of carbon monoxide. Now if the following radical-radical reaction does not produce carbon monoxide

$$HCOO + HCOO = HCOOH + CO_2$$

carbon monoxide production will be enhanced by the stabilization of the radical COOH.

However, if this hypothesis is correct, it is difficult to account for the large increase in *G*(CO) in the presence of small amounts of the acid under conditions where the *p*H of the solution shows little change