Action of γ-Rays on Aqueous Solutions of Carbon Monoxide

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Solutions of carbon monoxide ($4{\cdot}84\times10^{-4}$ M) in 0·1 N H_2SO_4 (oxygen-free) have been irradiated with γ-rays (~30,000 rad/h) and found to give hydrogen with $G = 0{\cdot}95$, carbon dioxide $G = 2{\cdot}6$, formaldehyde $G = 0{\cdot}5$, glyoxal $G = 0{\cdot}3$, and formic acid $G = 0{\cdot}4$. Hydrogen peroxide could not be detected. The results are interpreted in terms of a mechanism involving CHO and COOH radicals, some of the products being secondary. The effect of variations in acidity have been investigated, a striking observation being that formic acid is produced with $G = 44$ in alkaline solution. In the presence of ferrous ions (2×10^{-4}-2×10^{-3} M Fe^{2+}, 0·1 N H_2SO_4) no ferric was produced, but in the presence of ferric ions (2×10^{-4}-1×10^{-3} M Fe^{3+}, 0·1 N H_2SO_4) ferrous ions are produced with $G = 6{\cdot}3$-$6{\cdot}4$. The ratio of the rate constants for the reactions H+HCHO to H+CO (in 0·1 N H_2SO_4) is $14{\cdot}8\pm3$, of OH+CO to $OH+Fe^{2+}$ (in 0·1 N H_2SO_4) is $3{\cdot}6\pm0{\cdot}5$ and of H+CO to $H+H^++Fe^{2+}$ (in 0·1 N H_2SO_4) is $2{\cdot}2\pm0{\cdot}3$, all at 23°C.

Aqueous solutions of carbon monoxide were first irradiated by Fricke, Hart and Smith [1] in 1938 (X-rays) but apart from a brief mention by Johnson and Weiss,[2] no work on the X- or γ-irradiation of the system has been published, although carbon monoxide is simple, neutral, and industrially important. We have now examined the action of γ-rays on aqueous solutions of carbon monoxide (absence of oxygen) and have found evidence of reactions which are related to those occurring in the irradiation of aqueous solutions of formic acid and similar organic compounds.

EXPERIMENTAL

Distilled water was redistilled from alkaline potassium permanganate and then distilled again; its pH was about 5·6. Solutions of different pH were obtained by adding either sulphuric acid or sodium hydroxide. Water was freed from carbon dioxide by boiling before adding filtered concentrated sodium hydroxide solution.[3] Ferrous ammonium sulphate and iron alum in 0·1 N H_2SO_4 were used for experiments with ferrous and ferric ions respectively. All chemicals were of A.R. grade. Cylinder carbon monoxide, (stated to be 99 % pure) was passed through a liquid-oxygen trap and bubbled through an alkaline pyrogallol solution followed by an alkaline sodium hydrosulphite solution sensitized by the addition of sodium anthraquinone β sulphonate.[4] Analysis showed absence of carbon dioxide and oxygen, but presence of about 0·5 % of hydrogen. The reaction vessel was a 250 ml round-bottom flask which could be connected to a vacuum line and a gas storage flask through a ground joint and a tap. 100 ml of the solution were de-aerated by freezing in dry ice + acetone mixture, evacuating to less than 10^{-4} mm Hg using a mercury diffusion pump, then thawing while shaking and repeating the procedure. Carbon monoxide was then added, the vessel being shaken to equilibrate the solution with the gas phase at a final pressure of 400 mm Hg. The corresponding carbon monoxide concentration in 0·1 N H_2SO_4 at 23°C would be $4{\cdot}84\times10^{-4}$ M. The solutions were irradiated with γ-rays from a kilocurie cobalt 60 source.[5] Doses were determined with the Fricke dosimeter (in 0·1 N H_2SO_4), G being taken as 15·5.[6] Dose rates were 26,000-30,000 rad/h.

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Hydrogen was identified and determined by gas chromatography,[7] using charcoal columns; the carrier gas was N_2. The apparatus was the Griffin and George V.P.C., Mark II with a katharometer detector. The irradiated solutions were shaken, and a measured volume of gas collected in a gas burette and then injected into the column. The retention time of H_2 was 2 min in a 6 ft column at room temperature. A correction was always made for the hydrogen in the unirradiated carbon monoxide by running a blank.

Carbon dioxide was detected and determined using the method of Gregary and Mapper.[8] The irradiated solutions, after shaking, were connected to the vacuum line, and the reaction flask immersed in dry ice + acetone mixture. The gas mixture was introduced slowly to an evacuated trap immersed in liquid nitrogen, and the amount of carbon dioxide finally measured on a calibrated McLeod gauge. Peroxides were detected by the titanium sulphate method,[9] the iodide method,[10] and the ferrous thiocyanate method.[11]

Aldehydes were identified by paper chromatography of their 2,4-dinitrophenylhydrazones [12]; 20 ml of 0·25 % 2,4-dinitrophenylhydrazine in 30 % perchloric acid were added to the irradiated solutions and the hydrazones formed were extracted into CCl_4, concentrated under vacuum and then applied to the paper. Aldehydes were quantitatively determined by the method of Johnson and Scholes,[13] formaldehyde 2,4-dinitrophenylhydrazone being determined at 430 mμ and glyoxal, or glycolaldehyde, at 570 mμ, both in CCl_4 after the addition of alcoholic sodium hydroxide. For formaldehyde, this method was at least ten times as sensitive as the chromotropic acid method,[14] which could not be used at the low concentrations found in this work. Attempts were made to detect ethylene glycol by the periodic acid method [15] with separation of the formaldehyde produced by steam distillation, but other expected irradiation products such as glyoxal, glycolaldehyde, and formic acid, interfere with the test under these conditions. Organic acids were tested for by specific colour reactions. The irradiated solutions were neutralized with dilute sodium hydroxide, concentrated by evaporation. Then (i) glyoxalic acid was tested for by the method of Eegriwe,[16] (ii) oxalic acid by heating with thiobarbituric acid to give a brick-red condensation product [17]; (iii) formic acid by reaction with mercuric chloride which is reduced in presence of formic acid or formate to mercurous chloride which can be detected by reaction with ammonia to form mercury.[18] For quantitative determination, formic acid was reduced by magnesium powder to formaldehyde,[19] and the formaldehyde determined as above. (iv) Glycolic acid was tested for by the method of Calkins.[20] Formaldehyde and other aldehydes, which would interfere, were removed by forming 2,4-dinitrophenylhydrazones and extraction of both reagent and derivatives with ethyl acetate.[21]

Ferric ions were determined spectrophotometrically at 304 mμ. Ferrous ions produced in ferric solutions was estimated by difference. A Unicam SP500 spectrophotometer was used except for the studies of decay curves, when a Spectra-Cord model 4000 was employed.

RESULTS

The formation of hydrogen as a function of dose is shown in fig. 1. The limited accuracy at the lowest doses makes it difficult to assess the initial yields. G-values at the lowest dose, shown in table 1, are significantly higher than the molecular yield from water in several cases. For pH 3·5, Fricke, Hart and Smith found the rate of hydrogen formation to be 1·0 μM per 1000 r,[1] which corresponds to $G = 0{\cdot}9$.[22, 23] The chromatography experiments also show that if oxygen is a product it is formed with $G < 0{\cdot}1$.

The formation of carbon dioxide with increasing dose is shown in fig. 2. The yield varies little with acidity, being 2·6 in 0·1 N sulphuric acid and 2·75 in water (table 1). No attempt was made to determine carbon dioxide or carbonate in 0·1 N sodium hydroxide. The carbon dioxide yield was dependent on ferrous concentration, being $G = 2{\cdot}6$ in 2×10^{-4} M Fe^{2+}. In solutions containing ferric ions, G was 3·5 independent of concentration. For solutions of pH 3·5, Fricke, Hart and Smith found the initial yield to be 2·45 μM per 1000 r,[1] which corresponds to $G = 2{\cdot}2$.[22, 23] For 0·8 N sulphuric acid, Johnson and Weiss found $G = 2{\cdot}53 \pm 0{\cdot}11$.[2]

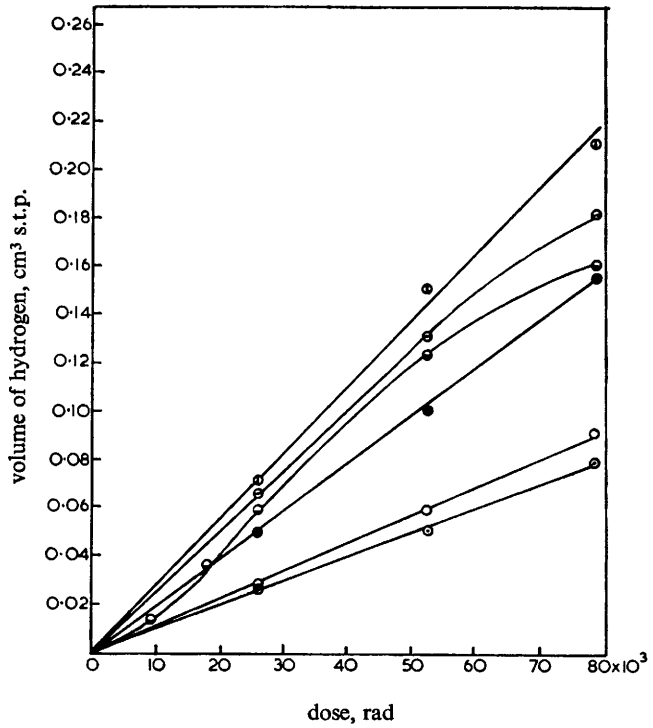

FIG. 1.—Formation of hydrogen in irradiated carbon monoxide solutions.
◒, 0·1 N H_2SO_4 (lowest two points are calculated, see text); ○, 10^{-4} N H_2SO_4; ⊙, neutral; ⦶, 0·1 N NaOH; ⊖, 0·1 N H_2SO_4, 2×10^{-4} M Fe^{2+}; ●, 0·1 N H_2SO_4, 2×10^{-4} M Fe^{3+}.

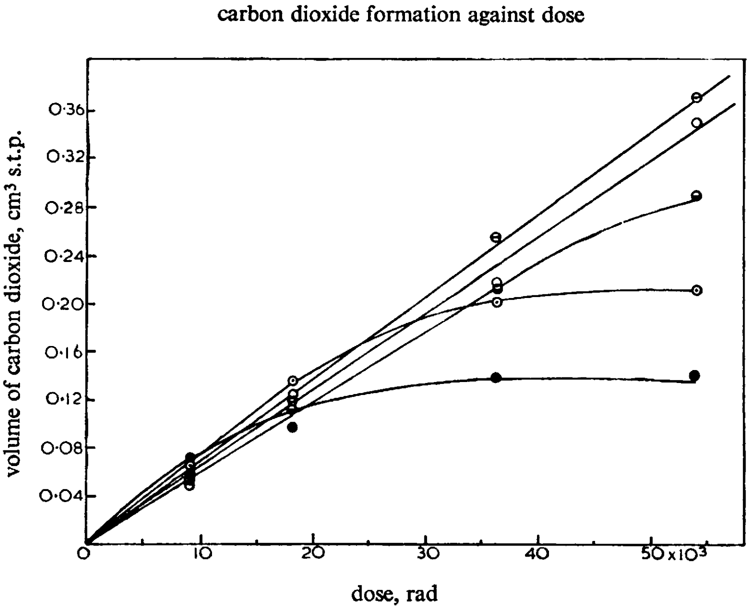

FIG. 2.—Formation of carbon dioxide in irradiated carbon monoxide solutions.
◒, 0·1 N H_2SO_4; ○, 10^{-4} N H_2SO_4; ⊙, neutral; ⊖, 0·1 N H_2SO_4, 2×10^{-4} M Fe^{2+}; ●, 0·1 N H_2SO_4, 2×10^{-4} M Fe^{3+}.

No hydrogen peroxide or other peroxides could be detected in the irradiated solutions, and therefore could not be formed with *G* greater than 0·05.

The 2,4-dinitrophenylhydrazone method showed formaldehyde to be the only monoaldehyde present. A further proof of formaldehyde was the decrease of optical density to about 50 % in 15 min,[24] at 430 mμ of the 2,4-dinitrophenylhydrazone in CCl_4 after the addition of alcoholic sodium hydroxide (0·1 N). For quantitative determination of formaldehyde, corrections were made using decay curves for the 2,4-dinitrophenylhydrazone in CCl_4 after the addition of alcoholic sodium hydroxide. The yield of formaldehyde as a function of dose is shown in fig. 3.

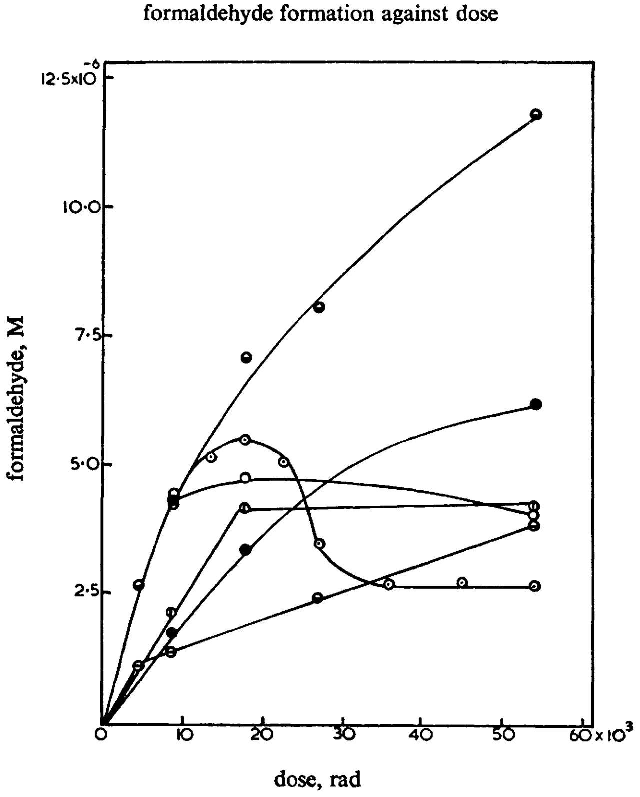

FIG. 3.—Formation of formaldehyde in irradiated carbon monoxide solutions.
◒, 0·1 N H_2SO_4; ○, 10^{-4} N H_2SO_4; ⊙, neutral; ⦶, 0·1 N NaOH; ⊖, 0·1 N H_2SO_4, 2×10^{-4} M Fe^{2+}; ●, 0·1 N H_2SO_4, 2×10^{-4} M Fe^{3+}.

The initial yield is $G = 0{\cdot}5$ for acid and neutral solutions, and less in the presence of ferrous or ferric ions or 0·1 N sodium hydroxide. Full *G* values for formaldehyde are shown in table 1. Fricke, Hart and Smith [1] found the initial yield at pH 3·5 to be 0·3 per 1000 r, i.e., $G = 0{\cdot}27$,[22, 23] in reasonable agreement with our result.

Paper chromatography showed the existence of one dialdehyde in the irradiated solutions which could be glyoxal or glycolaldehyde since both give the same 2,4-dinitrophenylhydrazone. The spot gave a bluish-purple colour when sprayed with alcoholic sodium hydroxide, a further proof of dialdehyde. The method of Dechary *et al.*[25] did not distinguish between glyoxal and glycolaldehyde because of the low concentrations formed. However, from the shape of the concentration against dose curve, fig. 4, it is likely that the dialdehyde is a primary product. This is consistent with the formation of glyoxal by dimerization of CHO radicals, whereas glycolaldehyde could only be a secondary product. Yields of glyoxal in the various solutions are given in table 1.

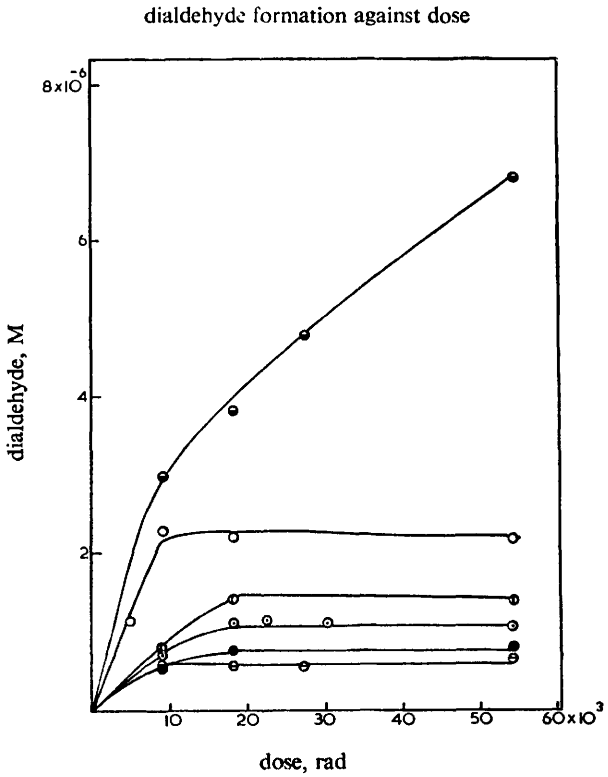

FIG. 4.—Formation of dialdehyde in irradiated carbon monoxide solutions. ◒, 0·1 N H_2SO_4; ○, 10^{-4} N H_2SO_4; ⊙, neutral; ⦶, 0·1 N NaOH; ⊖, 0·1 N H_2SO_4, 2×10^{-4} M Fe^{2+}; ●, 0·1 N H_2SO_4, 2×10^{-4} M Fe^{3+}.

TABLE 1.—YIELDS OF VARIOUS PRODUCTS IN IRRADIATION OF CARBON MONOXIDE SOLUTIONS

	G_{H_2}	G_{CO_2}	$G_{H_2O_2}$	G_{HCHO}	$G_{CHO\cdot CHO}$	G_{HCOOH}	$G_{Fe^{2+}}$	$G_{Fe^{3+}}$
	(26000 rad)	(9000 rad)	(9000 rad)	(9000 rad)	(9000 rad)	(9000 rad)	(5000 rad)	(5000 rad)
0·1 N H_2SO_4	0·95	2·6	0	0·5	0·3	0·4	—	—
10^{-4} N H_2SO_4	0·445	2·65	0	0·5	0·24	—	—	—
neutral	0·44	2·75	0	0·5	0·075	—	—	—
0·1 N NaOH	1·2	—	0	0·3	0·07	44	—	—
2×10^{-4} M Fe^{2+}, 0·1 N H_2SO_4	1·1	2·6	0	0·38	0·06	—	0	0
2×10^{-3} M Fe^{2+}, 0·1 N H_2SO_4	—	1·3	—	—	—	0·4	0	0
2×10^{-4} M Fe^{3+}, 0·1 N H_2SO_4	0·86	3·5	0	0·25	0·065	—	6·3	0
1×10^{-3} M Fe^{3+}, 0·1 N H_2SO_4	—	3·55	—	—	—	—	6·4	0

Examination of the irradiated 0·1 N sulphuric acid solutions for acids showed that, if glyoxalic, oxalic or glycolic acid were formed, the *G*-values must be less than 0·1. However, initial *G*-values for formic acid were determined in some of the solutions and are shown in table 1. Fig. 5 shows the formation of formic acid against dose in 0·1 N sodium hydroxide solution. Fricke, Hart and Smith give indirect evidence that formic acid is formed in high yield in alkaline solution.[1] Ethylene glycol a possible secondary irradiation product, was not definitely detected in the 0·1 N sulphuric acid solutions. However, from the material balance, glycol may be formed with $G = 0{\cdot}35$ in 0·1 N sulphuric acid.

In the experiments with ferrous ions present initially, ferric did not appear on irradiation but with added ferric ions, the yield of ferrous was $G = 6{\cdot}3$-$6{\cdot}4$.

formic acid formation in 0·1 N NaOH

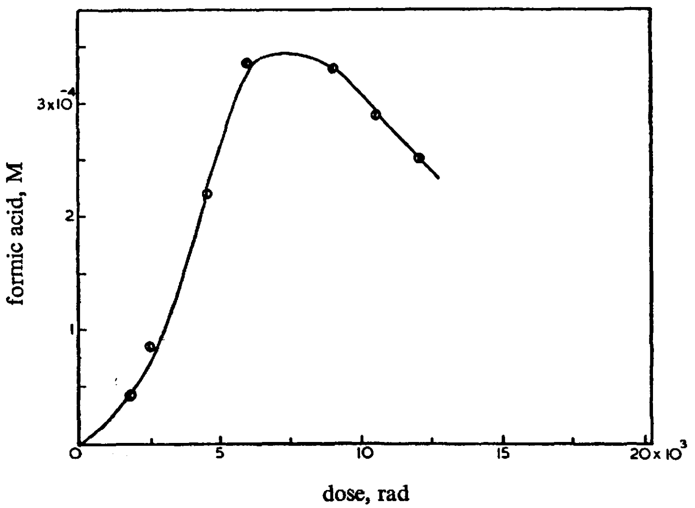

Fig. 5.—Formation of formate in a solution of carbon monoxide in 0·1 N sodium hydroxide.

DISCUSSION

In 0·1 N sulphuric acid, the following mechanism accounts for the results obtained (at 9000 rad).

$$H_2O \rightsquigarrow H, OH, H_2, H_2O_2 \qquad (0)$$

$$H + CO \rightarrow CHO \qquad (1)$$

$$OH + CO \rightarrow COOH \qquad (2)$$

$$CHO + CHO \rightarrow CO + HCHO \qquad (3)$$

$$CHO + CHO \rightarrow CHO\,.\,CHO \qquad (4)$$

$$COOH + COOH \rightarrow CO_2 + HCOOH \qquad (5)$$

$$CHO + COOH \rightarrow CO_2 + HCHO \qquad (6)$$

$$H + HCHO \rightarrow H_2 + CHO \qquad (7)$$

$$OH + HCHO \rightarrow H_2O + CHO \qquad (8)$$

$$COOH + HCHO \rightarrow CO_2 + CH_2OH \qquad (9)$$

$$CH_2OH + CH_2OH \rightarrow CH_2OH\,.\,CH_2OH \qquad (10)$$

$$COOH + H_2O_2 \rightarrow CO_2 + H_2O + OH \qquad (11)$$

Reaction (0) is the generally accepted mechanism for the decomposition of water by γ-rays, where the species H and OH may exist in any of several possible forms. The G-values for the formation of free radical and molecular products are taken as

$$G_{H}{}^{w} = 3\cdot65,\ G_{OH}{}^{w} = 2\cdot85,\ G_{H_2O_2}{}^{w} = 0\cdot8,\ G_{H_2}{}^{w} = 0\cdot4.^{26}$$

There has been doubt whether the COOH radical would rearrange to form $CO_2 + H$ or would react as such.[27] In the present work $G_{CO_2} = 2\cdot6$, consistent with the mechanism shown above, in which COOH does not rearrange. If COOH were to be slowly transformed to $CO_2 + H$, the G_{CO_2}, G_{HCHO}, and $G_{CHO.CHO}$ would have been much higher, and the G_{HCOOH} lower, than the experimental values. Furthermore, a chain reaction would have proceeded in the irradiation of de-aerated dilute formic acid solutions according to

$$H + HCOOH \rightarrow H_2 + COOH \tag{12}$$

$$COOH \rightarrow CO_2 + H \tag{13}$$

—but no chain reaction was found by Hart.[28]

By a similar argument, COOH does not react with CO to form the radical COOH . CO. According to Draganić this radical would decompose to $CO_2 + CHO$ and the reaction would explain the formation of formaldehyde and glyoxal in the irradiation of aqueous solutions of oxalic acid.[29] However, if COOH . CO was formed in the irradiation of aqueous solutions of carbon monoxide, and decomposed as suggested by Draganić, then the yield of most products would have been much higher than that obtained.

We have investigated the material balance of the 0·1 N sulphuric acid system at a dose of 9000 rad. From fig. 1 the hydrogen yield at 27,000 rad is $G_{H_2} = 0\cdot95$; since $G_{H_2}{}^{w} = 0\cdot4$, then the yield at 27,000 rad due to reaction (7) is $0\cdot95 - 0\cdot4 = 0\cdot55$. The concentration of formaldehyde increased non-linearly from zero at the beginning of the irradiation to $8\cdot1 \times 10^{-6}$ M at 27,000 rad (see fig. 3) and the carbon monoxide concentration decreased from $4\cdot84 \times 10^{-4}$ M to $3\cdot50 \times 10^{-4}$ M, (assuming G for loss of CO $= 4\cdot95$, which must be approximately true on any reasonable material balance). To estimate the ratio of the rate constants for reactions (7) and (1) we take the mean value of the formaldehyde concentration for the dose region up to 27,000 rad to be $5\cdot0 \times 10^{-6}$ M, and the corresponding carbon monoxide concentration to be $4\cdot17 \times 10^{-4}$ M. The average G-value for hydrogen atoms which react with formaldehyde, $g_{(7)}$, is then given by

$$g_{(7)} = g_{(1)}(k_{(7)} \times 5\cdot0 \times 10^{-6}/k_{(1)} \times 4\cdot17 \times 10^{-4}), \tag{14}$$

where $g_{(1)}$ is the G-value for hydrogen atoms which react with carbon monoxide. Since $g_{(7)} = 0\cdot55$ and $g_{(1)} + g_{(7)} = G_{H}{}^{w} = 3\cdot65$, then $k_{(7)}/k_{(1)} = 14\cdot8 \pm 3$. This value is of similar magnitude to the rough value of 6·1 estimated from the ratio $k_{(H+HCHO)}/k_{(H+H^{+}+Fe^{2+})} = 90 \times 10^{5}/6\cdot7 \times 10^{5} = 13\cdot4$ at pH = 2 obtained by Riesz and Hart using data in the gas phase [30] and the ratio $k_{(H+CO)}/k_{(H+H^{+}+Fe^{2+})} = 2\cdot2$ obtained in the present work. The ratio $k_{(7)}/k_{(1)}$ is now used to calculate the hydrogen yield due to reaction (7) at 9,000 rad, knowing that the arithmetic mean value of [HCHO] up to 9,000 rad is $2\cdot3 \times 10^{-6}$ M (from fig. 3) and of [CO] is $4\cdot62 \times 10^{-4}$ M. The yield due to reaction (7) is 0·25 so that the measured G_{H_2} at 9,000 rad should be 0·65. The following material balance equation, based on reaction (0)-(11), may now be given

$$\begin{aligned} 3\cdot65H + 2\cdot85OH + 0\cdot8H_2O_2 + 0\cdot4H_2 + 4\cdot95CO \rightarrow \underset{(0\cdot5)}{0\cdot55HCHO} + \underset{(0\cdot3)}{0\cdot3CHO\,.\,CHO} + \\ \underset{(0\cdot4)}{0\cdot45HCOOH} + 0\cdot35CH_2OH\,.\,CH_2OH + \underset{(0\cdot65)}{0\cdot75H_2} + \underset{(2\cdot6)}{2\cdot65CO_2} + 1\cdot35H_2O, \end{aligned} \tag{15}$$

where the G-values measured at 9,000 rad (or calculated for hydrogen) are shown in parenthesis. Several other ratios of rate constants could be calculated from eqn. (0)-(11) and (15). However this is not discussed further because these other ratios are not reliable without further work.

In 10^{-4} M H_2SO_4 and neutral solutions the hydrogen yield is reduced almost to the molecular yield. This is consistent with the view that " solvated electrons " are the predominant reducing species in these solutions, since reaction (7) would not occur. The presence of solvated electrons can also explain why the dialdehyde, and to some extent the formaldehyde yields reach a steady level in these solutions, but not in 0·1 N H_2SO_4; we assume that solvated electrons readily remove dialdehyde and formaldehyde to form non-aldehydic species, whereas hydrogen atoms do not do so.

In 0·1 N sodium hydroxide, formic acid is produced with $G = 44$, presumably through a chain reaction:

$$(H_2O)^- + CO \rightarrow (HCOOH)^- \qquad (16)$$

$$(HCOOH)^- + OH^- \rightarrow HCOO^- + (H_2O)^- \qquad (17)$$

where $(H_2O)^-$ represents that form of the H atom which is present in alkaline solutions and $(HCOOH)^-$ is related to other possible reduced forms of CO as follows:

$$(HCOOH)^- \overset{-H_2O}{\rightleftharpoons} CO^- \overset{H^+}{\rightleftharpoons} CHO \overset{H_2O}{\rightleftharpoons} CH(OH)_2. \qquad (18)$$

To account for the aldehyde formed, we suggest that the CHO radical which exists in equilibrium with $(HCOOH)^-$ reacts according to (3) and (4), thereby breaking the chain. Now carbon monoxide can react with concentrated sodium hydroxide solution at about 100°C at a pressure of 40 atm;[31]

$$CO_{(g)} + OH^-_{(aq)} \rightarrow HCOO^-_{(aq)}. \qquad (19)$$

Reaction (19) has a decrease of free energy $-\Delta G^\circ = 9{\cdot}6$ kcal/mole at 25°C as calculated from the standard free energy of formation of $HCOO^-$ (*aq*), OH^- (*aq*) and CO (*g*), showing that the reaction is thermodynamically feasible. However, in the absence of the radiation, the rate must be low at room temperature since no formic acid was formed in a blank of carbon monoxide in 0·1 N sodium hydroxide solution at 400 mm pressure.

In ferrous solutions in 0·1 N sulphuric acid no oxidation to ferric occurs, whereas in these solutions in the absence of carbon monoxide and air, the initial $G^{3+}_{Fe} = 7{\cdot}8$.[32] This could be explained by the formation of the reducing CHO and COOH radicals in the irradiated carbon monoxide solutions which would reduce any ferric produced. These results also, and especially the formation of formic acid, are inconsistent with decomposition of the COOH radical into CO_2 and H. The following mechanism accounts for the results obtained at low doses where secondary reactions do not occur:

$$H + CO \rightarrow CHO \qquad (1)$$

$$OH + CO \rightarrow COOH \qquad (2)$$

$$OH + Fe^{2+} \rightarrow Fe^{3+} + OH^- \qquad (20)$$

$$H + H^+ + Fe^{2+} \rightarrow Fe^{3+} + H_2 \qquad (21)$$

$$CHO + H^+ + Fe^{2+} \rightarrow Fe^{3+} + HCHO \qquad (22)$$

$$COOH + H^+ + Fe^{2+} \rightarrow Fe^{3+} + HCOOH \qquad (23)$$

$$CHO + Fe^{3+} \rightarrow Fe^{2+} + CO + H^+ \qquad (24)$$

$$COOH + Fe^{3+} \rightarrow Fe^{2+} + CO_2 + H^+ \qquad (25)$$

$$H_2O_2 + Fe^{2+} \rightarrow Fe^{3+} + OH^- + OH. \qquad (26)$$

From this mechanism, $k_{(\mathrm{OH+CO})}/k_{(\mathrm{OH+Fe^{2+}})}$ can be calculated from

$$g_{(2)}/g_{(20)} = k_{(2)}[\mathrm{CO}]/k_{(20)}[\mathrm{Fe}^{2+}], \qquad (27)$$

where $g_{(2)}$ and $g_{(20)}$ are the G-values for OH radicals reacting according to reactions (2) and (20) respectively, $k_{(2)}$ and $k_{(20)}$ being the rate constants. [CO] and [Fe^{2+}] are the concentrations of carbon monoxide and ferrous ions in the solution. Furthermore,

$$g_{(2)} = G_{\mathrm{CO_2}} + G_{\mathrm{HCOOH}}, \qquad (28)$$

$$g_{(2)} + g_{(20)} = G_{\mathrm{OH}}{}^{\mathrm{w}} + G_{\mathrm{H_2O_2}}{}^{\mathrm{w}}. \qquad (29)$$

Substituting $g_{(2)}$ and $g_{(20)}$ in eqn. (27):

$$\frac{G_{\mathrm{CO_2}} + G_{\mathrm{HCOOH}}}{G_{\mathrm{OH}}{}^{\mathrm{w}} + G_{\mathrm{H_2O_2}}{}^{\mathrm{w}} - (G_{\mathrm{CO_2}} + G_{\mathrm{HCOOH}})} = \frac{k_{(2)}[\mathrm{CO}]}{k_{(20)}[\mathrm{Fe}^{2+}]}. \qquad (30)$$

Taking $G_{\mathrm{OH}}{}^{\mathrm{w}} = 2{\cdot}85$ and $G_{\mathrm{H_2O_2}}{}^{\mathrm{w}} = 0{\cdot}8$, $[\mathrm{CO}] = 4{\cdot}84 \times 10^{-4}$ M and $[\mathrm{Fe}^{2+}] = 2 \times 10^{-3}$ M, and substituting for $G_{\mathrm{CO_2}} = 1{\cdot}3$ and $G_{\mathrm{HCOOH}} = 0{\cdot}4$, then

$$k_{(2)}/k_{(20)} = k_{(\mathrm{OH+CO})}/k_{(\mathrm{OH+Fe^{2+}})} = 3{\cdot}6 \pm 0{\cdot}5 \text{ at } 23^{\circ}\mathrm{C},$$

compared with 3·79 obtained by Hardwick[33] for the same ratio using OH radicals from Fenton's reagent in 0·1 N perchloric acid.

$k_{(\mathrm{H+CO})}/k_{(\mathrm{H+H^{+}+Fe^{2+}})}$ can be calculated similarly, taking into account reaction (7); the ratio is 2·2±0·3.

In ferric solutions in 0·1 N sulphuric acid, ferrous ions are produced with $G = 6{\cdot}4$ in the range 2×10^{-4}-1×10^{-3} M Fe^{3+}; in ferric solutions in the absence of carbon monoxide and of air, no reduction occurs.[34] The following mechanism is in accord with the results obtained in these solutions under conditions where secondary reactions do not interfere:

$$\mathrm{H + CO \rightarrow CHO} \qquad (1)$$

$$\mathrm{OH + CO \rightarrow COOH} \qquad (2)$$

$$\mathrm{H + Fe^{3+} \rightarrow Fe^{2+} + H^{+}} \qquad (31)$$

$$\mathrm{CHO + Fe^{3+} \rightarrow Fe^{2+} + CO + H^{+}} \qquad (24)$$

$$\mathrm{COOH + Fe^{3+} \rightarrow Fe^{2+} + CO_2 + H^{+}} \qquad (25)$$

$$\mathrm{H_2O_2 + Fe^{2+} \rightarrow Fe^{3+} + OH^{-} + OH} \qquad (26)$$

From the above, the yield of ferrous is given by

$$G_{\mathrm{Fe^{2+}}} = G_{\mathrm{H}}{}^{\mathrm{w}} + (G_{\mathrm{OH}}{}^{\mathrm{w}} + G_{\mathrm{H_2O_2}}{}^{\mathrm{w}}) - G_{\mathrm{H_2O_2}}{}^{\mathrm{w}} = G_{\mathrm{H}}{}^{\mathrm{w}} + G_{\mathrm{OH}}{}^{\mathrm{w}} = 6{\cdot}50. \qquad (32)$$

$G_{\mathrm{Fe^{2+}}}$ gives the sum of the radical yields of water radiolysis. $G_{\mathrm{CO_2}}$ should be given by

$$G_{\mathrm{CO_2}} = G_{\mathrm{COOH}} = G_{\mathrm{OH}}{}^{\mathrm{w}} + G_{\mathrm{H_2O_2}}{}^{\mathrm{w}} = 3{\cdot}65. \qquad (33)$$

The values found (see table 1) are in reasonable agreement with the theoretical values.

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