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# REDUCTION OF CARBON DIOXIDE IN AQUEOUS SOLUTIONS UNDER THE INFLUENCE OF RADIATION

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## $^{60}$Co-γ-Radiation

GARRISON et al.[1] have previously reported that carbon dioxide can be reduced to formic acid on irradiation of air-free $CO_2$ solutions with 40 MeV He ions, and in the presence of ferrous ions, small quantities of formaldehyde were also detected.

We have investigated in some detail the effect of $^{60}$Co-γ-rays on $CO_2$ in aqueous solutions under various conditions. It has been found that this can lead initially to the formation of formaldehyde, acetaldehyde and formic acid, whilst there are indications that oxalic and glycol are also formed, particularly after higher doses or radiation.

The yields of aldehyde and formic acid and their dependence on radiation dose and on pH have been determined. Solutions were made up in water which had been distilled at least three times. Pure carbon dioxide was prepared from sodium carbonate (A.R.) and sulphuric acid (A.R. and was

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[1] W. M. Garrison, D. C. Morrison, J. G. Hamilton, A. A. Benson and M. Calvin, Science 114, 416 (1951).

subsequently purified by several sublimations.

Experiments were carried out over a considerable pH range: to adjust the pH, sulphuric acid, sodium bicarbonate and sodium carbonate were used. Solutions were first evacuated and then saturated with carbon dioxide (1 atm).

The aldehydes formed were formaldehyde and acetaldehyde as shown by paper chromatography.[2] The total aldehydes were estimated as 2:4 dinitrophenylhydrazone[3] and evaluated as if only formaldehyde was present. Some typical yield-dose plots for the production of aldehydes at various pH's are shown in Fig. 1. It is interesting to note that at low pH's and in the

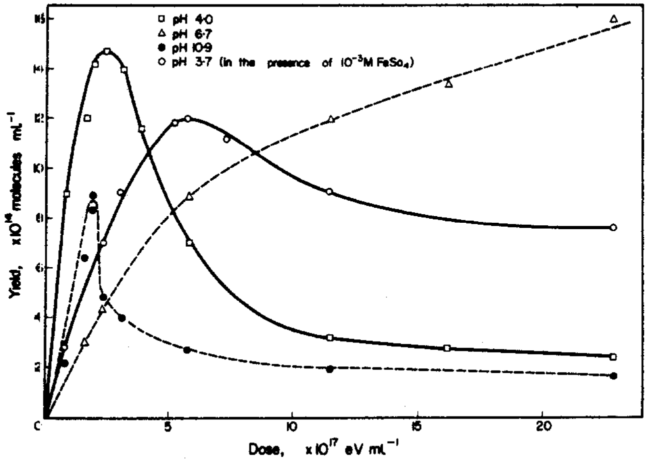


FIG. 1.

**Yields of aldehydes from the irradiation ($^{60}$Co-γ-rays) of aqueous solution of $CO_2$ at different pH values.**

more alkaline solutions the aldehyde yields go through a maximum after a fairly low radiation dose (1 to 6 x $10^{17}$ eV $ml^{-1}$). In the intermediate pH

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[2] J. Gasperic and M. Vecera, Coll. Czech. Chem. Comm. 22, 1426 (1957).
[3] G. R. A. Johnson and G. Scholes, Analyt. Chem. 79, 217 (1954).

range, on the other hand, no such maxima were observed. The nature of the yield-dose plots as well as the limited accuracy of the aldehyde determination at the lowest radiation doses makes it rather difficult to assess with any great certainty the values of the initial yields. It is obvious, however, that the formation of aldehyde is quite an important radiation-induced reaction; for example for the initial yield at pH 4.0 a G(HCHO) = 0.85 (G = molecule/100 eV) was found.

The presence of ferrous ions influence the yield of aldehyde, presumably by protecting the aldehyde from back reactions with the radiation-produced active species. This would account for the fact that Garrison et al.[1] could not tetect formaldehyde in solutions irradiated in the absence of ferrous salts.

Some data for the extent of formation of formic acid on irradiation are given in Table 1. The yields of formic acid, which were determined by the

TABLE 1

Irradiation of Aqueous Solutions of Carbon Dioxide with $^{60}$Co-γ-rays.

pH-Dependence of the Yields of Formic Acid as a Function of Radiation Dose

| Dose | G(Formic Acid) | | | |
|---|---|---|---|---|
| ($10^{16}$ eV $ml^{-1}$) | pH = 2.0 | pH = 4.0 | pH = 7.0 | pH = 3.8* |
| 57 | 0.25 | 0.17 | 0.04 | 0.21 |
| 228 | 0.08 | 0.06 | 0.05 | 0.11 |

* In the presence of $10^{-3}$ M $FeSO_4$.

method of Grant,[4] showed a strong pH-dependence. In the presence of ferrous ions, however, the yields were found to be greater; which is in agreement with Garrison's observations.

Yields of hydrogen gas from aqueous $CO_2$ solutions irradiated at various pH's are shown in Table 2. The yield dose plots were non-linear falling

TABLE 2

Irradiation of Aqueous Solutions of Carbon Dioxide with $^{60}$Co-γ-rays. pH-Dependence of the Yields of Hydrogen as a Function of Radiation Dose

| Dose ($10^{16}$ x eV $ml^{-1}$) | G(Hydrogen) | | | | |
|---|---|---|---|---|---|
| | pH = 2 | pH = 4.0 | pH = 7.0 | pH = 10.5 | pH = 3.8* |
| 57 | 1.58 | 0.74 | 0.67 | 0.51 | 1.12 |
| 228 | 1.00 | 0.51 | 0.49 | 0.32 | 0.75 |

* In the presence of $10^{-3}$ M $FeSO_4$.

off with increasing dose. At the lowest doses used ($5.7 \times 10^{17}$ eV $ml^{-1}$) the yield for hydrogen was $G(H_2) = 1.58$ at pH 2, while at pH 10.5, it had decreased to $G(H_2) = 0.51$.

These results clearly indicate that the hydrogen atom procursor formed in the radiolysis of water can react with $CO_2$.

Carbon monoxide could not be detected in irradiated $CO_2$ solutions, over the range pH 2 to 10.9. However, small amounts of CO (G = 0.1) were found on irradiation ($5.7 \times 10^{17}$ eV $ml^{-1}$) in the presence of ferrous ion ($10^{-3}$ M, $FeSO_4$) saturated with $CO_2$ at pH 3.75. This would suggest the posibility

[4] W. M. Grant, Industr. Engng. Chem. (Analyt.) 19, 206 (1947).

that carbon monoxide can be an intermediate in the radiolysis of solutions of carbon dioxide, the ferrous ions, no doubt, preventing reactions between CO and radiation-produced radicals.

Preliminary experiments have been carried out with solutions saturated with mixtures of $CO_2$ and $O_2$ and it was found that yields of formaldehyde were much lower than obtained in the absence of oxygen. This effect of oxygen is in keeping with the fact that the radiation-produced hydrogen species are involved in the formation of the organic products.

The mechanism of these reactions is, as yet, far from clear. There are, however, a few points which can be stated with some certainty.

It appears that the radiation-induced process is the reduction of the carbon dioxide by the self-trapped electron (negative polaron)[5,6] and by hydrogen atom, leading to the formation of carbon monoxide which then could be further reduced either by polarons or hydrogen atoms to give the CHO radical. Once the latter radicals have been formed, the route to the aldehyde would be fairly obvious as the aldehyde could be formed by disproportionation of two CHO radicals or to further reduction of the CHO radical.

It appears, however, that there is also a second route for the formation of organic products, i.e. from the carbonate ion in alkaline solution, possibly by reaction with an OH radical.

The formation of the formic acid, on the other hand, is likely to proceed directly from the $CO_2^-$, the latter leading to the COOH radical which

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[5] J. Weiss, Nature, Lond. **186**, 751 (1960).

[6] J. T. Allan and G. Scholes, Nature, Lond. **187**, 218 (1960).

then would lead to formic acid and possibly also to oxalic acid.

Photochemical Experiments

As has been shown above carbon dioxide in aqueous solution can be reduced by electron transfer and by hydrogen atoms produced by ionizing radiations. It, therefore, seemed quite likely that this reduction could also be carried out by hydrogen atoms produced photochemically and/or by electronically excited species.[7] Solutions of ferrous sulphate ($10^{-2}$ M to $10^{-1}$ M) were saturated with carbon dioxide (1 atm) or irradiated with the unfiltered light from a low pressure mercury lamp and with the mercury resonance line (2537 Å) using a $CoSO_4$ - $NiSO_4$ solution as a filter. After irradiation the solutions were again analysed for formaldehyde in the manner described above. For example, $10^{-2}$ M $FeSO_4$ solution saturated with carbon dioxide (pH 3) was irradiated with the unfiltered u.v. light (approximately $5 \times 10^{-7}$ E $ml^{-1}$ $min^{-1}$.), after 10 min irradiation, $1.6 \times 10^{-4}$ moles aldehyde/l. were produced. Similar results were also obtained if the ferrous sulphate was replaced by potassium iodide solutions.[8] It is quite clear that the reduction of carbon dioxide by u.v. radiation can be brought about by any suitable substances which will produce hydrogen atoms or an excited species which can reduce $CO_2$ to $CO_2^-$ by an electron transfer process.

A full account of this work, together with a discussion of the mechanism of the reduction of carbon dioxide in solution, will be published elsewhere.

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[7] J. Weiss, Nature,Lond. **136**, 794 (1935); R. H. Potterill, J. O. Walker and J. Weiss, Proc.Roy.Soc. A **56**, 561 (1936); T. Rigg and J. Weiss, J.Chem.Phys. **20**, 1194 (1952).

[8] J. Franck and F. Haber, Sitzber.Preuss.Akad.Wiss. 250 (1931); T. Rigg and J. Weiss, J.Chem.Soc. 4198 (1952); F.H.C. Edgecombe and R.G.W. Norrish, Proc.Roy.Soc. A **253**, 154 (1959).

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