The Hydroxy-radical-induced Oxidation of Ethylene in Aqueous Solutions

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AQUEOUS solutions of ethylene–oxygen mixtures, on γ-irradiation, give acetaldehyde, hydroxyacetaldehyde, formaldehyde, and β-hydroxyethyl hydroperoxide as the principal organic products.[1–4]

These presumably arise *via* the addition of the intermediates H, HO_2, and OH to the double bond of ethylene (e^-_{aq} reacts preferentially with O_2 in neutral solution and H^+ in acid solution). However, there seems to be little agreement as to which of these species is responsible for the formation of any particular product. We have therefore attempted to identify the products arising from OH addition to ethylene by photolysing hydrogen peroxide solutions ($\sim 10^{-4}$M) containing dissolved ethylene and oxygen ($[C_2H_4] = 3{\cdot}7 \times 10^{-3}$M; $[O_2] = 1{\cdot}0 \times 10^{-3}$M). Under these conditions the only reactive intermediates are OH radicals, produced by the photolysis of hydrogen peroxide:

$$H_2O_2 \xrightarrow[2537\,\text{Å}]{h\nu} 2\cdot OH$$

The products detected were formaldehyde, formic acid, hydroxyacetaldehyde and an organic hydroperoxide, shown to be β-hydroxyethyl hydroperoxide by measuring its rate of reaction with iodide ions: the first-order rate constant was found to be $1{\cdot}4 \times 10^4$ sec.$^{-1}$ at 25°, *cf.* $1{\cdot}28 \times 10^4$ sec.$^{-1}$ found for β-hydroxyethyl hydroperoxide.[3]

The yields of the products for various overall decompositions of hydrogen peroxide are shown in the Table. The decomposition of each hydrogen peroxide molecule leads to the formation of 2·81 and 3·82 molecules of organic products at pH 5·5 and 2·0 respectively. (Formaldehyde and formic acid are assumed to have a common C_2 precursor of yield $\frac{1}{2}([HCHO] + [HCO_2H]$.)

If each molecule of organic product requires one OH radical for its formation the actual amount of H_2O_2 required for the observed product yields is given by:

$$-[H_2O_2]_{calc.} = \tfrac{1}{2}\{[HO{\cdot}CH_2{\cdot}CHO] + HO{\cdot}CH_2{\cdot}CH_2{\cdot}O{\cdot}OH] + \tfrac{1}{2}([HCHO] + [HCO_2H])\}$$

The total product yield is thus a measure of the H_2O_2 decomposed by the light. The Table shows that $[-[H_2O_2]_{calc}/-[H_2O_2]_{obs}] = 1{\cdot}40$ (pH 5·5) and 1·66 (pH 2·0), indicating that hydrogen peroxide must be reformed during the reactions following the addition of the OH radicals to the ethylene.

The extent of the hydrogen peroxide decomposition was confirmed by photolysing deaerated solutions of hydrogen peroxide ($\sim 10^{-4}$M) containing allyl alcohol (10^{-2}M). Under these circumstances, where no hydrogen peroxide reformation is possible, the rate of hydrogen peroxide decomposition was faster than in solutions containing ethylene–oxygen by a factor of 1·3 at pH 5·5 and 1·7 at pH 2·0. The good agreement between the hydrogen peroxide decomposition calculated from the organic product yields and that measured by use of allyl alcohol indicates that all the products of the ethylene oxidation were being measured.

With the results at present available a detailed reaction scheme for the measured products cannot be written. However, we presume that they have as a common precursor, the peroxy-radical $HO{\cdot}CH_2{\cdot}CH_2{\cdot}O_2$:

$$OH + CH_2{=}CH_2 \xrightarrow{O_2} HO{\cdot}CH_2{\cdot}CH_2O_2{\cdot}$$

Interaction of pairs of these radicals can give hydroxyacetaldehyde and reform hydrogen peroxide:

$$2\,HO{\cdot}CH_2{\cdot}CH_2{\cdot}O_2{\cdot} \rightarrow 2\,HO{\cdot}CH_2{\cdot}CH_2{\cdot}CHO + H_2O_2$$

This stoicheiometry is similar to that of the formation of acetaldehyde and hydrogen peroxide from ethylperoxy-radicals.[5] However, the relative yields of hydroxyacetaldehyde and hydrogen peroxide show that hydroxy acetaldehyde formation must also take place by routes not producing hydrogen peroxide.

Formaldehyde and formic acid could be formed *via* an alternative route involving the intermediate formation of alkoxy-radicals:

$$2HO{\cdot}CH_2{\cdot}CH_2{\cdot}O{\cdot}O{\cdot} \rightarrow 2HO{\cdot}CH_2{\cdot}CH_2{\cdot}O{\cdot} + O_2$$

$$HO{\cdot}CH_2{\cdot}CH_2{\cdot}O{\cdot} \xrightarrow{O_2} HO{\cdot}CH_2{\cdot}O{\cdot}O{\cdot} + HCHO$$

The radical $HO{\cdot}CH_2{\cdot}O{\cdot}O{\cdot}$ has been proposed as an intermediate in the radiolysis of oxygenated aqueous methanol solutions where formic acid and methanol are products.[6]

Photolysis of hydrogen peroxide solutions [(1·5—2·5) × 10^{-4}M] *containing dissolved ethylene* [3 7 × 10^{-3}M]–*oxygen* [10^{-3}M] *mixtures*

	[H_2O_2] Decomposed M × 10^5	Y* (HO·CH_2·CHO·)	Y (HCHO)	Y(HCO_2H)	Y (organic hydroperoxide)
pH 5·5					
	8·95	1·43	1·28	0·88	0·42
	8·17	1·53	1·48	0·78	0·51
	12·00	1·40	1·37		0·37
	10·30	1·35	1 28	0·60	0·42
	12·00	1·21	2·00	0·40	0·45
	11·65	1·40	1·73	0·76	0·42
	14·50	1·32	1·27	0·64	0·41
	14·65	1·39	1·57	0·64	0·29
	17·20	1·13	1·40	0·84	0·11
	14·70	1·35	1·36	0·66	0·37
	Average	1·35 ± 0·2	1·47 ± 0·3	0·69 ± 0·2	0·38 ± 0·1
pH 2·0					
	9·96	1·80	1·75	0·18	0·33
	10·10	2·10	2·10	0·43	0·21
	10·05	1·92	1·92	0·27	0·30
	Average	1·94 ± 0·1	1·92 ± 0·1	0·29 ± 0·1	0·28 ± 0·1

* Y(X) = number of molecules of X formed for 1 molecule of H_2O_2 destroyed.

That no acetaldehyde was formed in these experiments suggests strongly that its formation in irradiated aqueous solutions of ethylene–oxygen results from the attack of either H atoms or HO_2 radicals at the double bond.

The photolysis was carried out with light from an Hanovia UVS medium-pressure mercury vapour lamp, filtered through 0·1M aqueous sodium chloride to remove water-decomposing radiations. The ethylene (British Oxygen Co. Ltd.) was 99·8% pure and contained roughly equal amounts (~0·05%) of methane, ethane, and butanes. It was used without further purification as was medical grade oxygen obtained from the same source.

Hydrogen peroxide was measured with the titanium sulphate reagent[7] and total peroxide (hydrogen peroxide + organic hydroperoxide) by iodimetry.[8] Formaldehyde was estimated by use of chromotropic acid[9] and formic acid estimated as formaldehyde after reduction with magnesium.[10] The 2,4-dinitrophenylhydrazone method of Johnson *et al.* was used to estimate hydroxyacetaldehyde.[11]

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