Radical Yield of Propionaldehyde in the Radiolysis of n-Propanol

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IN a study of the formation of the major products in the radiolysis of n-propanol[1] we have suggested that propionaldehyde is formed by more than one process and that both radical and molecular yields of this product exist. This suggestion was based on the effect of scavengers on the hydrogen yield and considerations on the mechanism of the formation of molecular hydrogen. At that stage there was no definite experimental evidence of radical and molecular yields of aldehyde. Recently, however, we have obtained strong evidence in favour of a two-part yield in a study of the effect of ferric chloride on propionaldehyde production. In view of the support this lends to the mechanism suggested for the radiolysis of propanol we consider it of value to report our findings.

The purification of materials, handling of samples, and analytical methods were similar to those previously described. Ferric chloride concentration was varied from 10^{-5}—10^{-2}M and found to increase the yield of propionaldehyde from an initial value (*i.e.*, in the absence of solute) of 2·9 to a plateau value of 6·8 as shown in the Figure. The glycol yield was found to decrease rapidly from the initial value of 1·47 to 0 at 10^{-3}M-ferric ion.

These effects are essentially similar to those reported by Adams and Baxendale[2] who studied the effect of ferric chloride on the radiolysis products of methanol. These workers found that the increase in the aldehyde yield was roughly double the decrease in the glycol yield and equal to the yield

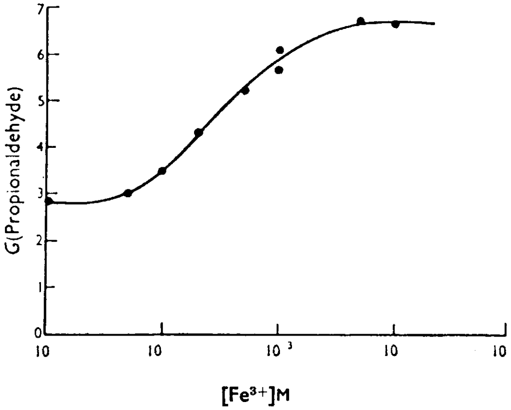

FIGURE. *Radical yield of propionaldehyde in the radiolysis of n-propanol.*

of $\cdot CH_2OH$ radicals, as measured by the decrease in solute concentration with dose, using ferric chloride and benzophenone as solutes. Their explanation of this effect was that hydroxymethyl radicals which dimerise in the absence of ferric chloride were now being oxidised to aldehyde.

$$2\ \cdot CH_2OH \rightarrow (CH_2OH)_2 \qquad (1)$$

$$Fe^{3+} + \cdot CH_2OH \rightarrow CH_2O + Fe^{2+} + H^+ \qquad (2)$$

This mechanism fits the experimental results well and strongly indicates that the formation of formaldehyde in pure methanol is an unscavengeable process.

The results in the case of propanol are somewhat different in that the increase in the aldehyde yield (3·9) is significantly greater than twice the decrease in the glycol yield (2·9). This immediately suggests that hydroxypropyl radicals may disproportionate as well dimerise. If this is so a radical yield of propionaldehyde must exist, the value of which may be deduced from the reaction scheme below.

Thus it seems in propanol, unlike in methanol, the hydroxyalkyl radicals disproportionate as well as dimerise with the ratio of the rate constants being $k(\text{disprop.})/k(\text{dimer.}) = 0{\cdot}6$. This presents strong support to our earlier contention[1] that a corresponding amount of molecular aldehyde is produced in those processes responsible for the molecular hydrogen yield. The close correspondence between $G(H_2)_M = 1{\cdot}8$ and $G(\text{Ald})_M = 2{\cdot}0$ is particularly pertinent to this conclusion.

$$2CH_3{\cdot}CH_2{\cdot}\dot{C}HOH \rightarrow (CH_3{\cdot}CH_2{\cdot}CH{\cdot}OH)_2 \qquad (3)$$

$$2CH_3{\cdot}CH_2{\cdot}\dot{C}HOH \rightarrow CH_3{\cdot}CH_2{\cdot}CHO + CH_3{\cdot}CH_2{\cdot}CH_2{\cdot}OH \qquad (4)$$

$$Fe^{3+} + CH_3{\cdot}CH_2{\cdot}\dot{C}HOH \rightarrow CH_3{\cdot}CH_2{\cdot}CHO + H^+ + Fe^{2+} \qquad (5)$$

$$\begin{aligned}
\text{Thus} \qquad G(\text{Ald}) &= G(\text{Ald})_{\text{pl}} - G(\text{Ald})_M \\
&= G(CH_3{\cdot}CH_2{\cdot}\dot{C}HOH) \\
&= 2G(CH_3{\cdot}CH_2{\cdot}CHOH)_2 + 2G(\text{Ald})_R \\
&= 2G(CH_3{\cdot}CH_2{\cdot}CHOH)_2 + 2G(\text{Ald})_0 - 2G(\text{Ald})_M \\
G(\text{Ald})_M &= 2{\cdot}0 \\
G(\text{Ald})_R &= 0{\cdot}9 \\
G(CH_3{\cdot}CH_2{\cdot}\dot{C}HOH) &= 4{\cdot}8
\end{aligned}$$

where $G(\text{Ald})_0 =$ yield in absence of Fe^{3+}; $G(\text{Ald})_R =$ yield due to radicals;

$G(\text{Ald})_M =$ molecular yield; $G(\text{Ald})_{\text{pl}} =$ maximum yield in presence of Fe^{3+}

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[1] R. A. Basson and H. J. van der Linde, *J. Chem. Soc.*, to be published.

[2] G. E. Adams and J. H. Baxendale, *J. Amer. Chem. Soc.*, 1958, **80**, 4215.