Cage Effects in the Photolysis of Hydrogen Peroxide in Alcohol–Water Mixtures

By JACK BARRETT*
(*Department of Chemistry, Chelsea College of Science and Technology, London, S.W.*3)
and A. L. MANSELL and R. J. M. RATCLIFFE
(*Department of Chemistry, Hatfield College of Technology, Hatfield, Herts.*)

IN dilute aqueous solution the effect of 2537 Å radiation upon hydrogen peroxide may be written as

$$H_2O_2 \xrightarrow{h\nu} (2\,OH)_{\text{solvent cage}} \rightarrow 2\,OH \qquad (1)$$

where the two hydroxyl radicals are initially produced in the original solvent cage of the hydrogen peroxide molecule. They may either recombine or diffuse from the cage into the bulk solution. The value of the quantum yield of reaction (1) has been reported[1] to be 0·5 in terms of the decomposition of hydrogen peroxide. The overall quantum yield is twice this value due to the subsequent reactions:

$$OH + H_2O_2 \rightarrow H_2O + HO_2 \qquad (2)$$

$$2HO_2 \rightarrow H_2O_2 + O_2 \qquad (3)$$

In the presence of alcohols a chain reaction is induced and from the reported values for the rate constants[2] of the reactions of hydroxyl radicals with alcohols and of that of reaction (2), it may be concluded that at alcohol concentrations greater than 10^{-3}M reaction (2), and consequently reaction (3), will be excluded from the reaction scheme.

In the case of ethanol, for example, the hydroxyl radicals in the bulk solution react entirely with the alcohol, *viz*:

$$OH + CH_3\cdot CH_2OH \rightarrow H_2O + CH_3\cdot CH\cdot OH \qquad (4)$$

as was initially suggested by Baxendale and Wilson[1] and which has received experimental (e.s.r.) verification.[3] The ensuing propagation reaction may be formulated as

$$CH_3{\cdot}CH{\cdot}OH + H_2O_2 \rightarrow CH_3{\cdot}CHO + H_2O + OH \quad (5)$$

acetaldehyde being the only solution product.

We have determined the values of the overall quantum yield, $\varnothing_{\mathrm{T}}$, in terms of the number of molecules of hydrogen peroxide decomposed for each **2537** Å quantum absorbed by the hydrogen peroxide. The primary yields ($\varnothing_{\mathrm{P}}$) were measured in the presence of allyl alcohol which competes with the alcohol present for the hydroxyl radicals. In this case only the primary photo-act causes decomposition of hydrogen peroxide.

The results for the ethanol–water system are shown in the Figure, and those for methanol–water and propan-2-ol–water mixtures are closely similar. The propagation steps, involving the CH_2OH and Me_2COH radicals produce formaldehyde and acetone, respectively, as solution products. These are the observed products in the two cases.

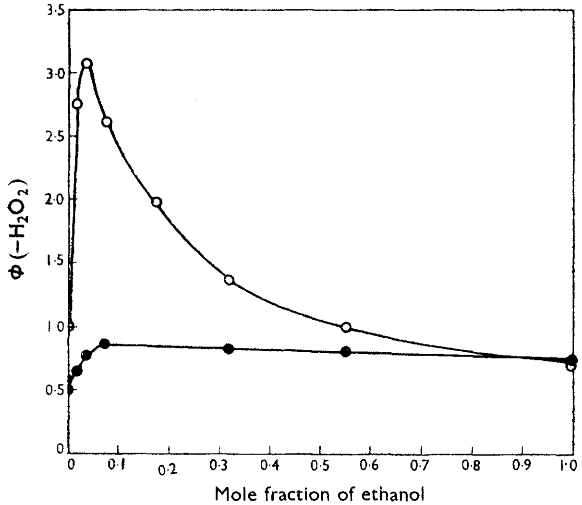

FIGURE. *The variation of* $\varnothing_{\mathrm{T}}$ *(open circles) and* $\varnothing_{\mathrm{P}}$ *(solid circles) with the mole fraction of ethanol*

With all three alcohols used, the increase in $\varnothing_{\mathrm{T}}$ is paralleled by an increase in $\varnothing_{\mathrm{P}}$. Presumably this is due to the presence of alcohol molecules in the solvent-cage region which prevents some of the hydroxyl radical-pairs from recombining. As the alcohol concentration increases, $\varnothing_{\mathrm{P}}$ increases, but at higher alcohol concentrations the values of $\varnothing_{\mathrm{P}}$ level off and those of $\varnothing_{\mathrm{T}}$ go through a maximum and finally (in the pure alcohols) have values equal to $\varnothing_{\mathrm{P}}$.

At these higher alcohol concentrations (> 2M) the chain decomposition is progressively replaced by a process which may be interpreted as a solvent-cage effect. The presence of more than one alcohol molecule in the solvent cage could lead to two alcohol radicals being produced in close proximity. These alcohol radicals may either diffuse from the cage and cause a chain decomposition of the hydrogen peroxide or they may interact within the original solvent cage.

This interaction may be either dimerization (to give a glycol) or disproportionation. In the case of ethanol and propan-2-ol the only solution products, respectively, were observed to be acetaldehyde and acetone. Their quantum yields were equal to $\varnothing_{\mathrm{T}}$ at all concentrations of the alcohols. The radicals $CH_3{\cdot}CH{\cdot}OH$ and Me_2COH are, therefore, presumed to be undergoing disproportionation reactions in the solvent cage at high alcohol concentrations.

In the case of the methanol–water system it was possible to distinguish between the two reaction paths. At low methanol concentrations formaldehyde (from the chain process) was the major product with ethylene glycol occurring to the extent of 15% of $\varnothing_{\mathrm{T}}$. Glycol would be formed in the termination step of the chain reaction by the dimerization of the hydroxymethyl radicals. At high concentrations of methanol the quantum yield of glycol increased and that of formaldehyde decreased such that in pure methanolic solution the quantum yield of formaldehyde dropped to only 5% $\varnothing_{\mathrm{T}}$. In all reactions $\varnothing_{\mathrm{T}}$ also represented the sum of the glycol and formaldehyde quantum yields. It is known that hydroxymethyl radicals dimerise in preference to disproportionation[4] and this being so our results for the methanol–water system at high methanol concentrations indicate that this dimerization is taking place within the solvent cage of the original hydrogen peroxide molecule. If any of the hydroxymethyl radicals did escape the original cage a chain decomposition would be initiated.

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