Radiation-induced Chain Reactions in Alkaline Solutions of Nitrous Oxide in Aliphatic Alcohols

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RECENT studies of the radiation-induced decomposition of nitrous oxide in alkaline aqueous solutions[1-3] have indicated that a chain mechanism is involved. The chain lengths are relatively short, the maximum 100 *e*v yield of molecular nitrogen being about 70. Work carried out in this laboratory on the radiation chemistry of acid and neutral alcoholic solutions of nitrous oxide has been reported elsewhere.[4] This Communication concerns an extension of this work to alkaline solutions.

The major gaseous products of the cobalt-60 γ-radiolysis of deaerated neutral or acid solutions of nitrous oxide in propan-2-ol are hydrogen, nitrogen, and methane.[4] The effect on these products of the variation of the concentration of potassium hydroxide in solutions initially containing 5×10^{-2} M-nitrous oxide are presented in Figure 1. In the concentration range 0—1×10^{-3} M the yields remained essentially unchanged from those observed in neutral solution. In the range 1×10^{-3}—*ca.* 1×10^{-2} M, $G(N_2)$ and $G(CH_4)$ increased rapidly, and attained limiting values at *ca.* 3×10^{-2} M-potassium hydroxide. The yields then became insensitive to further increases in potassium hydroxide concentration. There appeared to be a small increase in $G(H_2)$ with increasing alkalinity, from 3·2 for neutral solutions to about 4. However, in the presence of the largest yields of nitrogen and methane it was not possible to estimate $G(H_2)$ with an accuracy of greater than $\pm 20\%$.

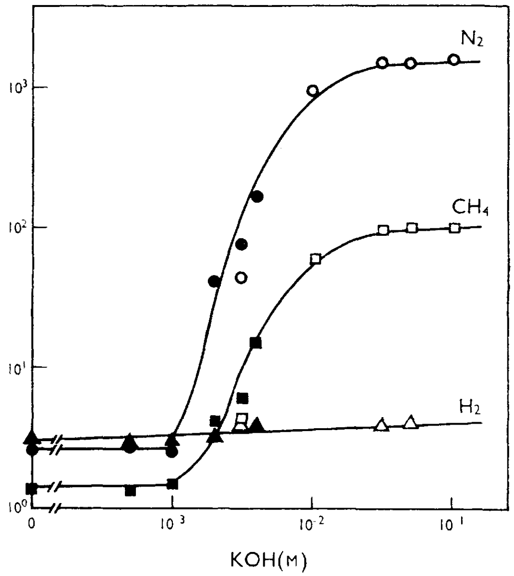

FIGURE 1

Yields of gaseous products as a function of potassium hydroxide concentration in the γ-radiolysis of deaerated solutions of 5×10^{-2} M*-nitrous oxide in propan-2-ol. Dose rate* $3{\cdot}6 \times 10^{17}$ ev *ml.*$^{-1}$ *min.*$^{-1}$ ○, N_2, □, CH_4, △, H_2; *total dose,* $1{\cdot}1 \times 10^{18}$ ev *ml.*$^{-1}$ ●, N_2, ■, CH_4, ▲, H_2; *total dose* $5{\cdot}4 \times 10^{18}$ ev *ml.*$^{-1}$

At low doses a dose effect was observed. In solutions containing equimolar 5×10^{-2} M-nitrous oxide and potassium hydroxide, $G(N_2)$ after doses of $1{\cdot}8 \times 10^{17}$, $3{\cdot}6 \times 10^{17}$, $7{\cdot}2 \times 10^{17}$, $1{\cdot}1 \times 10^{18}$, and $1{\cdot}4 \times 10^{18}$ *ev* ml.$^{-1}$ was 36, $2{\cdot}2 \times 10^2$, $1{\cdot}4 \times 10^3$, $1{\cdot}6 \times 10^3$, and $1{\cdot}4 \times 10^3$, respectively. This rapid attainment of the limiting value for $G(N_2)$ appears to indicate that the initial dose effect is not due to the presence of an impurity that initially inhibits the chain reaction and which is rapidly consumed, but rather a period during which the concentration of chain-carrying intermediate(s) is being build-up. In the radiolysis of aqueous solutions it was demonstrated[3] that molecular hydrogen was an important chain carrier. However, in the present work it was found that when the radiolysis at a dose of $1{\cdot}8 \times 10^{17}$ *ev* ml.$^{-1}$ was repeated under an atmosphere of hydrogen at a pressure of 50 mm. Hg no significant change in yields occurred. It would therefore appear that a build-up in the concentration of molecular hydrogen in the solution is not the cause of the dose effect at low doses.

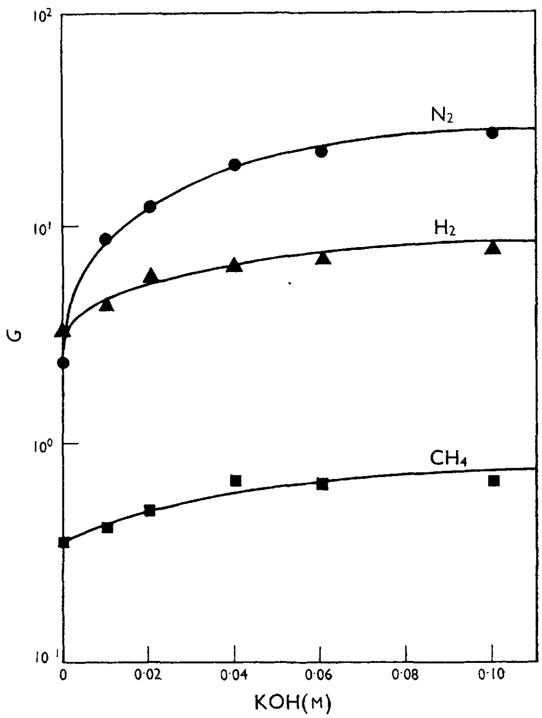

FIGURE 2

Yields of gaseous products as a function of potassium hydroxide concentration in the γ-radiolysis of deaerated solutions of 5×10^{-2} M *nitrous oxide in methanol. Dose rate* $3{\cdot}7 \times 10^{17}$ ev *ml.*$^{-1}$ *min.*$^{-1}$; *total dose* $1{\cdot}1 \times 10^{19}$ ev *ml.*$^{-1}$ ●, N_2, ■, CH_4, ▲, H_2.

It was previously shown that the solvated electron is a precursor of molecular nitrogen in the radiolysis of nitrous oxide in propan-2-ol at natural pH.[4] The addition of nitrobenzene and benzophenone, which are known to be very reactive towards the hydrated electron,[5,6] decreased $G(N_2)$, and it was concluded that these aromatic compounds compete favourably with nitrous oxide for solvated electrons. The presence of 5×10^{-2} M of each of these compounds in a solution of 5×10^{-2} M-potassium hydroxide and 5×10^{-2} M-nitrous oxide was found completely to inhibit the chain reaction leading to nitrogen and methane; the yields being approximately those found previously[4] when potassium hydroxide was absent. However, benzene, a poor electron-scavenger,[4,5] present at the same concentration did not significantly diminish $G(N_2)$ and $G(CH_4)$. These results are in accord with the solvated electron being an important intermediate in the initiation or propagation steps of the chain reaction leading to both nitrogen and methane.

It was also found that at a given potassium hydroxide concentration $G(N_2)$ and $G(CH_4)$ were dependent on the concentration of nitrous oxide. Thus with $[KOH] = 5 \times 10^{-2}$ M and $[N_2O] = 2 \times 10^{-2}$ M and 2×10^{-1} M, $G(N_2)$ was $8{\cdot}2 \times 10^2$ and $4{\cdot}4 \times 10^3$, while $G(CH_4)$ was $5{\cdot}3 \times 10^1$ and $2{\cdot}7 \times 10^2$. These results and the foregoing are in accord with Reaction 1 being a rate-determining step for the formation of molecular nitrogen.

$$e^-_{solv} + N_2O \rightarrow N_2 + O^- \qquad (1)$$

The most significant feature of the results presented above is that, apart from the striking nitrogen yields, the large yields of methane indicate that the solvent itself is greatly sensitized to radiation damage by the presence of the two solutes, nitrous oxide and potassium hydroxide.

A preliminary study has also been carried out on the radiolysis of methanol solutions of nitrous oxide and potassium hydroxide (see Figure 2). As with propan-2-ol both $G(N_2)$ and $G(CH_4)$ increase with increasing potassium hydroxide concentration, though the magnitude of the effect is smaller. Another notable difference is that with methanol there is a significant increase in $G(H_2)$, from 5·0 in neutral solution to 8·0 in a solution containing 0·1 M-potassium hydroxide.

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