The Photosensitized Decomposition of Nitrous Oxide in Alkaline Methanolic Solution. A Chain Reaction Resulting in the Formation of Molecular Hydrogen

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IT was noted recently[1] that the yield of hydrogen in the radiolysis of alkaline methanolic solutions of nitrous oxide was significantly greater than that generally observed in the radiolysis of methanolic solutions or pure methanol. From these preliminary results it is not clear whether the increased yield is due to the presence of potassium hydroxide and nitrous oxide fundamentally modifying the nature or yield of the short-lived primary radiation products (electrons and excited molecules), or more simply due to reactions of longer-lived chemical intermediates, such as free radicals and ions, which are not unique to ionising-radiation chemistry. It was therefore thought pertinent to determine whether hydrogen is formed when an alternate method is used to generate radicals and ions in alkaline solutions of nitrous oxide.

Di-t-butyl peroxide (DTBP) undergoes homolytic scission when exposed to ultraviolet light to yield two t-butoxy-radicals per molecule.[2] Since the strength of the O–H bond in t-butyl alcohol is considerably greater than the C–H bond of methanol, reaction (1) is a thermodynamically favourable reaction for t-butoxy-radicals generated photochemically in methanol.

$$C_4H_9O\cdot + CH_3OH \rightarrow C_4H_9OH + \cdot CH_2OH \qquad (1)$$

Hydrogen, nitrogen, and methane were observed† as gaseous products in the photolysis, under aerobic conditions, of methanolic solutions containing DTBP, potassium hydroxide, and nitrous oxide. The light source was a high-pressure mercury lamp with a Pyrex filter to cut off light below 290 mμ. It was found that the rate of product formation was constant with time up to about 50% conversion of nitrous oxide into nitrogen. Product yields as a function of solute concentration for solutions initially containing 5×10^{-3}M-DTBP are plotted in Figures 1 and 2. A linear dependence of the yields of all three products on the nitrous oxide concentration may be noted, whilst the dependence on the potassium hydroxide concentration is somewhat complex.

It was not possible to observe any diminution in the concentration of DTBP in any of these experiments. Since the minimum decrease in concentration which could be experimentally detected (by gas chromatography) was one part in twenty, it would appear that the yield of t-butoxy-radicals was less than 5×10^{-4} M. This figure would put the minimum yields of hydrogen, nitrogen, and methane at 7·6, 30, and 1·1 molecules per t-butoxy-radical, respectively, in the experiment with 1×10^{-1}M-potassium hydroxide and 2×10^{-1}M-nitrous oxide (Figure 1). The high yields of hydrogen and nitrogen are consistent with a reaction mechanism which involves a chain reaction. Since in the absence of DTBP the solution was

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† Identified and analysed by gas chromatography using a column of molecular sieve 5A.

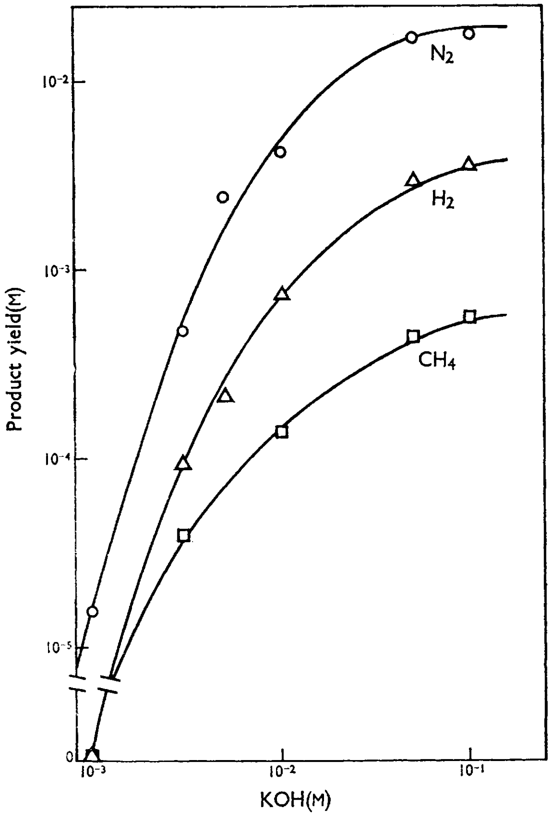

FIGURE 1. *Photolysis of alkaline methanolic solutions of nitrous oxide and DTBP* (5×10^{-3} M). *Product yields as a function of potassium hydroxide concentration. Photolysis time,* 60 *min.* △, H_2, ○, N_2, □ CH_4.

completely transparent, and no gaseous products were observable on irradiation, it is evident that DTBP photosensitizes this chain reaction.

It has been suggested[3] that the alkoxide radical anion is the chain carrier in the radiation-induced decomposition of nitrous oxide in alkaline aqueous solutions containing propan-2-ol. An analagous reaction sequence in the present system may be written (reactions 2—5).

$$\cdot CH_2OH + CH_3O^- \text{ (or } OH^-) \rightarrow \cdot CH_2O^- \text{ (I)} + CH_3OH \text{ (or } H_2O) \qquad (2)$$

$$\text{(I)} + N_2O \rightarrow N_2O^- + HCHO \qquad (3)$$

$$N_2O^- \rightarrow N_2 + O^- \qquad (4)$$

$$O^- \text{(or } N_2O^-) + CH_3OH \rightarrow OH^- \text{ (or } N_2 + OH^-) + \cdot CH_2OH \qquad (5)$$

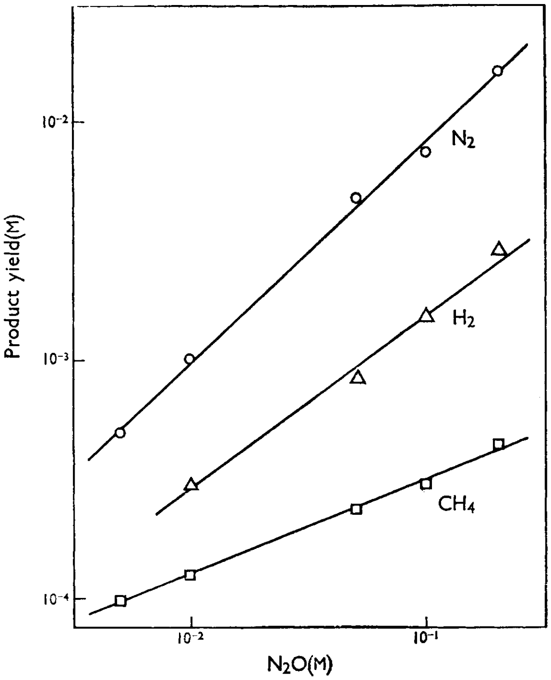

FIGURE 2. *Photolysis of alkaline methanolic solutions os nitrous oxide and DTBP* (5×10^{-3} M). *Product yieldf as a function of nitrous oxide concentration. Photolysis time,* 60 *min.* △, H_2, ○, N_2, □ CH_4.

The observed linear dependence of the reaction rate on the concentration of nitrous oxide is consistent with reaction (3) being a rate-determining step.

A chain mechanism for the formation of molecular hydrogen is not readily formulated in terms of thermodynamically favourable reactions. It is noteworthy that the maximum energy of the light absorbed by the solution is about 97 kcal./einstein. Since the chain reaction for hydrogen formation presumably involves the splitting off of hydrogen atoms from the solvent, at least one step in this chain must be highly exothermic to supply the driving force for the breaking of seven or more bonds each of which has a bond strength greater than 90 kcal./mole.[4]

No decrease in the yield of gaseous products was observed in the photolysis of a solution of DTBP (5×10^{-3} M), potassium hydroxide (5×10^{-2} M), and nitrous oxide (2×10^{-1} M) in the presence of benzene (1×10^{-2} M). However, the presence of carbon tetrachloride (5×10^{-3} M) was found to inhibit the reaction completely.‡ Carbon tetrachloride is completely transparent to light with a

‡ In a fuller study of the γ-radiolysis of alkaline methanolic solutions of nitrous oxide which will be published elsewhere, it was similarly found that carbon tetrachloride and nitrobenzene decreased the yields of chain products while benzene had little effect.

wavelength greater than 290 mμ; the observed inhibition is not therefore due to masking. While benzene and carbon tetrachloride are both reactive towards free radicals, the latter is a good electron acceptor while the former is not.[5] The observed solute effects are therefore consistent with an anionic species (*e.g.*, I) being an intermediate in the formation of all three gaseous products, and with carbon tetrachloride competing successfully for the charge of this intermediate (*e.g.*, reaction 6).

$$\mathrm{I} + \mathrm{CCl_4} \rightarrow \mathrm{HCHO} + \mathrm{CCl_4^-} \qquad (6)$$

Nitrobenzene also has a high electron affinity,[5] and the presence of 5×10^{-5} M of this compound was found to decrease the product yields. However, since this concentration of nitrobenzene has a significant optical density at the wavelengths of interest it was not possible to determine whether the effect was not due simply to masking.

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[4] T. L. Cottrell, "The Strengths of Chemical Bonds", Butterworths, London 1958, p. 270.
[5] W. V. Sherman, *J. Phys. Chem.*, 1966, **70**, 667.