The Effect of Nitrous Oxide on the γ-Radiolysis of Liquid Methanol

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The formation of a solvated electron in irradiated liquid methanol has been generally assumed.[1,2] Evidence has also been given for methanol as well as for other alcohols.[3-5] Nitrous oxide has frequently been employed in determining the yield of the hydrated electron in aqueous solutions, for hydrated electrons react rapidly with nitrous oxide to produce nitrogen;

$$N_2O + e_{aq}^- \rightarrow N_2 + O^- \qquad (1)$$

while hydrogen atoms react relatively slowly. This communication will report our preliminary findings regarding the effect of nitrous oxide on the γ-radiolysis of liquid methanol.

Extra-pure methanol (Wako Pure Chemicals) was rectified after it had been refluxed with sodium borohydride. The middle third of the distillate was dried over magnesium turnings by refluxing. Pure nitrous oxide (Takachiho Chemicals, 99.9%) was further purified by distillation. The solutions were irradiated with ^{60}Co-γ rays at a dose rate of $(1.4-1.5)\times10^{17}$ eV./ml./min. for about 150 min. The determination of the products was carried out by methods similar to those described elsewhere.[6]

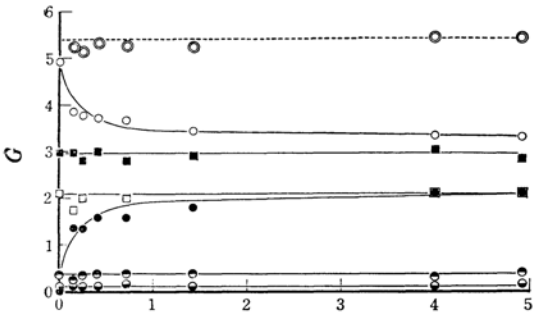

Fig. 1. Effect of N_2O on the product yields of methanol.
○, H_2; ●, N_2; ■, $(CH_2OH)_2$; □, CH_2O; ◓, CH_4; ◒, CO; ◎, H_2+N_2

The results are shown in Fig. 1. The addition of nitrous oxide decreases the $G(H_2)$ and leads to the formation of nitrogen. It should be noted, however, that, in spite of the considerable effect of nitrous oxide on $G(H_2)$, the yields of all the other products remain unaffected, and that the limiting $G(H_2)+G(N_2)$ value is 5.4, which is the same as the $G(H_2)$ values for pure methanol ascertained by Meshitsuka and Burton,[7] and by Baxendale and Mellows.[2] It would appear, therefore, that no nitrogen-formation reactions other than reaction 1 take place. It is also reasonable to assume that the reaction of nitrous oxide with hydrogen atoms is negligible under the present experimental conditions.*

Thus, insofar as nitrous oxide is assumed to react solely with the solvated electrons in the irradiated methanol, the yield of the solvated electron should be equal to the limiting $G(N_2)=2.1$. This value is substantially higher than those obtained from kinetic study (1.2)[2] and from pulse radiolysis study (1.1).[5] The reason for this disagreement is not obvious at present. Further studies are therefore in progress into the effects of the pH value and of higher nitrous oxide concentrations; our results will be published in the future.

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* The fact that the $G(N_2)$ value at a low pH value is negligibly small (unpublished results) would support this assumption.