CHAIN FORMATION OF FORMALDEHYDE DURING γ-RADIOLYSIS OF METHYL ALCOHOL IN THE PRESENCE OF ALKALI AND NITROUS OXIDE

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UDC 547.281.1+541.15+547.261

Continuing our work on the radiolysis of methyl alcohol [1] and its aqueous solutions [2], we found that high yields of formaldehyde are obtained in γ-radiolysis of methanol containing alkali and saturated with nitrous oxide. The present paper deals with a study of this effect.

EXPERIMENTAL

We used Co^{60} gamma radiation. The dose rate was measured by the ferrosulfate method. A correction was made to the dose for the difference in the electron densities of methanol and the dosimetric solution. Methyl alcohol of C.P. grade was purified by boiling with 2,4-dinitrophenylhydrazine in a flask with a reflux condenser for several hours, followed by distillation twice in a current of nitrogen. The caustic potash was of C.P. grade. Methanol was saturated with nitrous oxide by passign the gas for 30-40 min. Oxygen was removed from the N_2O by passing it through a solution of pyrogallol. In most experiments the KOH concentration in the methanol was 0.1 M. The formaldehyde content of the irradiated specimens was determined by the spectrophotometric method with chromotropic acid [3, 4].

DISCUSSION OF RESULTS

Figure 1 plots G(HCHO) (G is the yield) versus $I^{1/2}$ (I is the dose rate) for a 0.1 M KOH solution in methanol, saturated with nitrous oxide. The yields were obtained at doses of 10^{17}–$7\cdot 10^{18}$ eV/ml. In this dose range G (HCHO) is independent of the dose. It will be seen from Fig. 1 that in this system the formaldehyde yields are high; G (HCHO) is proportional to $I^{1/2}$. An attempt was made to find ethylene glycol in the irradiated solutions by the method in [4, 5]. However, it was unsuccessful because it is difficult to detect ethylene glycol against an intense HCHO background by this method. According to our data, in absence of N_2O the yield of formaldehyde for methanol containing 0.1 M KOH (saturation with N_2) is 1.9, i.e., close to the yield in the case of neutral deaerated CH_3OH. For N_2O-saturated neutral CH_3OH, G (HCHO) is 2.8 ± 0.3. We can thus infer that chain formation of formaldehyde takes place only in the simultaneous presence of alkali and nitrous oxide.

The most probable formation mechanism of HCHO is apparently as follows:

$$CH_3OH \rightsquigarrow e_s^- \; CH_2OH, \text{ other products} \quad (1)$$

$$e_s^- + N_2O \rightarrow N_2O^- \rightarrow N_2 + O^- \quad (2)$$

$$CH_2OH \rightleftarrows CH_2O^- + H^+ \quad (3)$$

$$CH_2O^- + N_2O \rightarrow HCHO + N_2O^- \, (N_2 + O^-) \quad (4)$$

$$CH_3OH + O^- \rightarrow CH_2OH + OH^- \quad (5)$$

$$CH_2O^- + CH_2O^- \rightarrow \text{Product} \quad (6)$$

It is not unlikely that N_2O^- reacts directly with the alcohol to give CH_2OH, N_2, and OH^-. Note that a similar mechanism was proposed in [6] for chain radiation decomposition of isopropanol, and, according to Asmus et al. [7], the pK of dissociation of the CH_2OH radical in an aqueous solution is 10.7. From (1-6), we readily obtain the following kinetic equation:

Institute of Physical Chemistry of the Academy of Sciences of the USSR. Translated from Izvestiya Akademii Nauk SSSR, Seriya Khimicheskaya, No. 10, pp. 2377-2379, October, 1968. Original article submitted April 5, 1968.

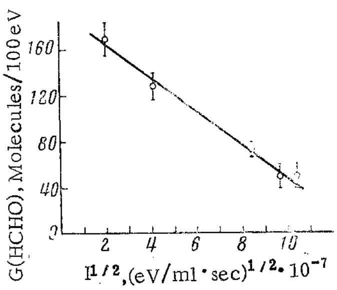

Fig. 1. Effect of dose rate on G (HCHO) during gamma radiolysis of CH_3OH saturated with N_2O and containing 0.1 M KOH.

$$G(\mathrm{HCHO}) = \frac{k_4[\mathrm{N_2O}]}{(2k_6)^{1/2}}[G(e_s^-) + G(\mathrm{CH_2OH})]^{1/2}\left(\frac{100\,N}{I}\right)^{1/2} \quad (7)$$

where k_4 and k_6 are the rate constants of the corresponding reactions in liter/M·sec; G (e_s^-) and G (HCHO) are the initial yields of e_s^- and CH_2OH, I is the dose rate in eV/liter·sec, and N is the Avogadro number.

The yield of radicals for radiolysis of liquid CH_3OH is 6.2–6.6 [8–10]. In this system virtually all the radicals are eventually transformed to CH_2OH. We can therefore assume that G (e_s^-) + G (CH_2OH) = 6.2–6.6. According to Hayon and Moreau [11], in the presence of relatively small amounts of electron acceptors G (e_s^-) increases when measured from the yields of their radiolytic conversion products. In the case of N_2O-saturated CH_3OH, this increase (measured from the increase in the yield of N_2) is ~1 [12, 13]. However, it is not unlikely that this increase of G (e_s^-) in the presence of N_2O is only an apparent one. According to Teply and Habersbergerova [13], when N_2O is added to methanol the yield of ethylene glycol, formed predominantly by recombination of CH_2OH, is virtually unchanged; but an increase is observed in the yield of formaldehyde, of which the formation is most probably due [1] to reactions in "branches." We also observed an increase in G (HCHO). We can therefore assume that the additional amount of N_2 in N_2O-saturated CH_3OH is due to the reaction with the "excited alcohol"

$$N_2O + CH_3OH^* \rightarrow N_2 + H_2O + HCHO \quad (8)$$

Thomas and Bensasson [14] showed recently by means of electron pulses of duration $1.2 \cdot 10^{-8}$ sec that an increase occurs in the concentration of e_s^-, which have escaped recombination in the "branches," when 0.1 M NaOH is added to ethanol. Their report [14] shows that this increase is ~100%. The effect is apparently due to suppression of the reaction:

$$e_s^- + C_2H_5OH_2^+ \rightarrow H + C_2H_5OH \quad (9)$$

However, exclusion of this process does not lead to a change in the overall yields of e_s^- and radicals from the alcohol.

It is thus quite probable that addition of N_2O and KOH to methanol has little effect on the sum G (e_s^-) + G (CH_2OH). It is therefore assumed that in the case of N_2O-saturated CH_3OH containing 0.1 M KOH this sum is ~6.4. Hence from the data in Fig. 1 we can calculate by (7) the relative constant † $k_4/k_6^{1/2}$. It is $(8.8 \pm 2.4) \cdot 10^{-2}$ (liter/M·sec)$^{1/2}$.

CONCLUSIONS

1. During gamma radiolysis of methanol containing alkali and nitrous oxide, formaldehyde is formed by a chain mechanism, the yields reaching 170 molecules/100 eV.

2. A mchenism is proposed for the formation of HCHO, the chain carrier being the CH_2O^- radical.

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† In accordance with [15] it is assumed that the N_2O concentration in CH_3OH, saturated at room temperature, is 0.13 M.

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