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Radiolysis of Methanol Containing Cyanogen Iodide

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The use of cyanogen iodide as a scavenger of some intermediates formed in the radiolysis of several organic solvents has been reported by Hughes *et al.*[1,2] The present paper, in addition to reporting on the formation of iodine, which has also been studied by previous investigators, reports on the effect of cyanogen iodide on the radiolytic yield of hydrogen and formaldehyde, which are known to be the main products from irradiated methanol. The reactivity of solvated electron towards cyanogen iodide has also been determined by using nitrous oxide as a competing solute.

Experimental

Methanol was purified according to the procedure proposed by Lichtin *et al.*[3] Cyanogen iodide was prepared by the method of Goy *et al.*[4] and sublimated in a vacuum several times before use. ^{60}Co γ-irradiation was carried out at a dose rate of 1.56×10^{18} eV·ml^{-1} hr^{-1}. A deaerated solution of 5 ml prepared by the conventional vacuum technique with freeze-and-thaw cycles was sealed in a cylindrical glass cell (20 ml). Nitous oxide was taken in a calibrated volume to a definite pressure and then transferred to the irradiation vessel by using liquid nitrogen. The concentration of the gas in the solution was calculated from the solubility data.[5] The iodine was determined spectrophotometrically at 450 mμ. The formaldehyde was determined by means of chromotropic acid; however, this method could not be applied to the solutions above 10 mM ICN because of the inhibition of iodine produced by the decomposition of ICN. The amounts of hydrogen and nitrogen were determined by gas chromatography using a molecular sieve 5A column and argon as the carrier gas.

Results

Figure 1 shows the yields of hydrogen and iodine as a function of the concentration of cyanogen iodide in deaerated methanol. The radiolytic yields of these products were obtained from the initial slopes of the product-dose plots and are expressed as G-values. $G(I_2)$ appears to increase with an increase in the concentration of cyanogen iodide, but it tends to reach a limiting value of 3.2 at 5 mM ICN. The value for $G(I_2)$ reported by Hughes was slightly higher than our result. The addition of cyanogen iodide decreases the $G(H_2)$ considerably. One can obtain 5.4 for $G(H_2)$ when the solute concentration is extrapolated to zero; this is the same value as the $G(H_2)$ value for pure methanol determined by several investigators.[6-8] The yield of formaldehyde is considerably

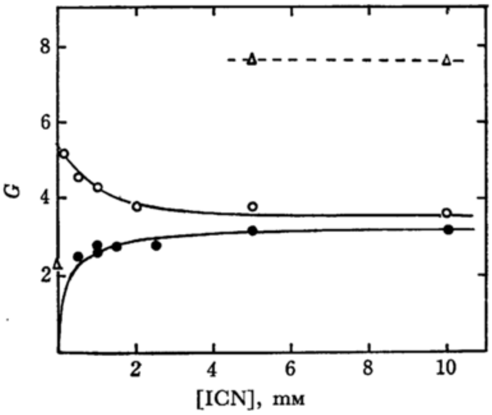

Fig. 1. The radiolytic yield as a function of ICN concentration in deaerated methanol.
●; $G(I_2)$, ○; $G(H_2)$, △; $G(CH_2O)$

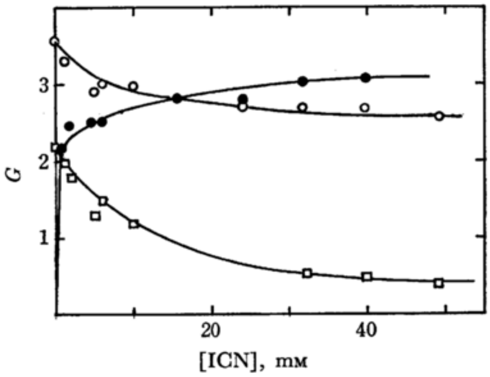

Fig. 2. The radiolytic yield as a function of ICN concentration in deaerated methanol containing 5 mM N_2O.
●, $G(I_2)$; ○, $G(H_2)$; □, $G(N_2)$

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[1] G. Hughes and W. M. Garisson, *J. Phys. Chem.*, **64**, 695 (1960).

[2] G. Hughes, *ibid.*, **65**, 2160 (1961).

[3] M. Imamura, S. U. Choi and N. N. Lichtin, *J. Am. Chem. Soc.*, **85**, 3565 (1963).

[4] C. A. Goy, D. H. Shaw and H. O. Pritchard, *J. Phys. Chem.*, **69**, 1504 (1965).

[5] Inetern. Critical Tables, **3**, 264 (1928).

[6] G. Meshitsuka and M. Burton, *Red. Res.*, **8**, 285 (1958).

[7] J. H. Baxendale and F. W. Mellows, *J. Am. Chem. Soc.*, **83**, 4720 (1961).

[8] K. N. Jha and G. R. Freeman, *J. Chem. Phys.*, **48**, 5480 (1968).

increased by the addition of cyanogen iodide, even at a low concentration; over the concentration range investigated the yield is seen to be almost steady at about 7.6, a value which is very high compared with the value (2.3) for pure methanol.

The radiolytic yield curves for hydrogen, nitrogen, and iodine as a function of the cyanogen iodide concentration in deaerated methanol containing 5 mM N_2O are presented in Fig. 2.

A competition between cyanogen iodide and nitrous oxide for solvated electrons in methanol is obvious in Fig. 3.

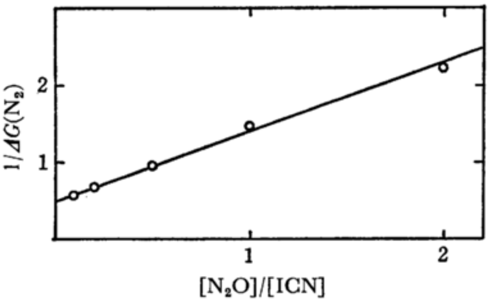

Fig. 3. $1/\Delta G(N_2)$ *vs.* $[N_2O]/[ICN]$ plotted according to Eq. (III).

Discussion

The chemical species initially produced during the absorption of ionizing radiation in methanol are usually represented as follows:

$$CH_3OH \rightsquigarrow e^-{}_{sol},\ H,\ CH_2OH,\ CH_3OH_2{}^+ \text{ and molecular products} \qquad (0)$$

According to the well-established mechanism for hydrogen formation from methanol radiolysis, the following reactions are taken into consideration:

$$e^-{}_{sol} + CH_3OH_2{}^+ \rightarrow H_2 + CH_2OH \qquad (1)$$

$$H + CH_3OH \rightarrow H_2 + CH_2OH \qquad (2)$$

The solvated electron can react with cyanogen iodide as follows:

$$e^-{}_{sol} + ICN \rightarrow I + CN^- \qquad (3)$$

Hughes *et al.*[1] have proposed the following reactions:

$$H + ICN \rightarrow I + HCN \qquad (4)$$

$$CH_2OH + ICN \rightarrow I + HCHO + HCN \qquad (5)$$

$$2I \rightarrow I_2 \qquad (6)$$

The addition of cyanogen iodide decreases $G(H_2)$ effectively, as is shown in Fig. 1; this indicates that the precursor of hydrogen will react with the solute as in reactions (3) and (4). The observed increase in the yield of formaldehyde upon the addition of cyanogen iodide may be attributed to reaction (5). This reaction scheme, together with what is presented by Hughes *et al.*,[1] can afford the following meterial balance:

$$2G(I_2) = G_{e^-sol} + G_H + G_{CH_2OH} = G(R) \qquad (I)$$

where $G(R)$ denotes the total radical yield from methanol.*[1] One can obtain 6.4 for $G(R)$ from the observed $G(I_2)$ value; this is in good agreement with the values reported by Baxendale[9] and by Lichtin.[10] As to the yield of formaldehyde, the following expression can be derived from our present reaction scheme:

$$G(CH_2O) = G_0(CH_2O) + G(R) - \Delta G(H_2) \qquad (II)$$

where $G_0(CH_2O)$ denotes the molecular yield of formaldehyde and where $\Delta G(H_2)$ is the decrease in hydrogen yield due to the addition of cyanogen iodide in methanol. Taking $G_0(CH_2O)$, $G(R)$, and $\Delta G(H_2)$ to be 2.05,[9] 6.4, and 1.6—1.8 respectively, one can obtain the $G(CH_2O)$ value from (II) to be 6.7—6.9 over the concentration range of 5 to 10 mM ICN; this is nearly the same as our present data, as is shown in Fig. 1.

As may be seen in Fig. 2, $G(H_2)$ decreases gradually with an increase in the concentration of cyanogen iodide in methanol containing nitrous oxide at 5 mM. Since all the solvated electrons are scavenged by nitrous oxide at this concentration or by cyanogen iodide, the observed decrease in $G(H_2)$ may be attributed to reaction (4). It may be seen that $G(H_2)$ continues to decrease very gradually with an increase in the concentration of cyanogen iodide. This finding suggests that reaction (4) proceeds very slowly as compared with reaction (3) and that it is not so important to reduce $G(H_2)$ at the concentration of cyanogen iodide below 10 mM. When nitrous oxide is present in the system, reaction (7) will compete with reaction (3):

$$e^-{}_{sol} + N_2O \rightarrow N_2 + O^- \qquad (7)$$

Based on simple competition kinetics, one can formulate:

$$\frac{1}{\Delta G(N_2)} = \frac{1}{G_{e^-sol}}\left\{1 + \frac{k_7[N_2O]}{k_6[ICN]}\right\} \qquad (III)$$

where $\Delta G(N_2)$ denotes the decrease in nitrogen yield due to the added cyanogen iodide in the presence of nitrous oxide. A plot of $1/\Delta G(N_2)$ *vs.* $[N_2O]/[ICN]$ is seen to give a straight line, as in Fig. 3. From the intercept in the ordinate, one can obtain 2.2 for $Ge^-{}_{sol}$, and from the slope

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*[1] In addition to these major radical products, CH_3 and OH radicals are considered to be present in very low yields, but these may be converted to CH_2OH radicals by the reaction with methanol. Therefore, these are equivalent to other radicals with regard to the formation of iodine.

9) G. E. Adams and J. H. Baxendale, *J. Am. Chem. Soc.*, **80**, 4215 (1958).

10) S. V. Choi and N. N. Lichtin, *ibid.*, **86**, 3948 (1964).

of line, one can obtain k_7/k_3 for 1.9. Taking $1.3\times 10^{10}\ \text{M}^{-1}\text{sec}^{-1}$ for k_7,11) k_3 is estimated to be $6.8\times 10^{9}\ \text{M}^{-1}\text{sec}^{-1}$. Reactions (4) and (5) indicate that hydrogen cyanide should be produced. However, it is detected only qualitatively at the present stage because of the interference of cyanogen iodide.

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11) H. Seki and M. Imamura, *J. Phys. Chem.*, **71**, 870 (1967).