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# Radiation Synthesis of Methylal from Methanol Solution of Ferric Chloride

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**Synopsis.** The gamma radiolysis of $FeCl_3$–$CH_3OH$ solution was studied by measuring the $G$-values of the products. The mechanism of the selective formation of the main product methylal ($G$=8.3) was discussed.

The radiolysis of methanol has been studied by several workers.[1] In this paper, the $\gamma$-radiolysis of methanol solution of ferric chloride at high absorbed dose is described from the viewpoint of preparative radiation chemistry. The products of radiolysis, in the presence of ferric ion in high concentration known to act as a radical scavenger,[2–4] were analyzed in order to explain the main reaction scheme. The additive was found to act not only as a scavenger but also as a reactant.

## Experimental

*Preparation of Sample.* Reagent grade methanol was distilled twice, first with magnesium and then with tribromobenzoic acid on a 2 m column. Anhydrous ferric chloride (E.P. grade) was dissolved without further purification in methanol under dry nitrogen atmosphere. The irradiation sample (1 ml) was sealed in a 7 ml ampoule after evacuation at liquid nitrogen temperature.

*Irradiation.* Samples were irradiated by a 16 kCi $^{60}Co$ gamma source mostly at an exposure rate of $3.2\times10^5$ R/hr. Before and after irradiation, the samples were kept at Dry Ice temperature to suppress thermal reactions.

Dose rates were determined by Fricke dosimetry with correction for the difference in the electron densities of water and methanol, the energy absorbed by the additive being neglected.

*Analysis.* The evolved gas, consisting of hydrogen, methane and carbon monoxide, was analyzed by volumetry after being passed through a liquid nitrogen trap, and by mass spectrometry. Two $\mu$l of liquid condensed in the liquid nitrogen trap was sampled and injected into a capillary column gas chromatograph with a 60 m column of PEG-400 and a 30 m column of 3,3′-iminodipropionitrile in series connection for the determination of yields of dimethyl ether, methyl chloride, and methylal (dimethoxymethane). The remaining liquid was titrated for induced acidity with 1/10 M sodium hydroxide solution, using methyl red as an indicator. 20 ml of saturated dimedone solution, with pH adjusted to 4.5, was then added to determine formaldehyde yield by precipitation. The filtrate and residue of vacuum distillation were jointly dissolved in distilled water, and the yield of ferrous ion was determined by colorimetry at 552 m$\mu$, after the addition of $\alpha,\alpha'$-dipyridyl and sodium acetate solution for pH adjustment.

## Results and Discussions

The $G$-values of products from the methanol–ferric chloride system are shown in Table 1. The selective formation of methylal[5] at high ferric chloride concentration should be noted. The mechanism could be considered as follows.

$$CH_3OH \rightsquigarrow \cdot CH_2OH,\ H,\ CH_3O\cdot,\ e_s^-,\ etc. \qquad (1)$$

$$CH_3O\cdot + CH_3OH \longrightarrow \cdot CH_2OH + CH_3OH \qquad (2)$$

Hydroxymethyl radical $\cdot CH_2OH$ is produced directly and indirectly, and is oxidized by ferric ion producing formaldehyde:[4]

$$\cdot CH_2OH + Fe^{3+} \longrightarrow HCHO + Fe^{2+} + H^+ \qquad (3)$$

The hydroxymethyl radical, the precursor of ethylene glycol in the absence of ferric ion, is thus converted into formaldehyde, which subsequently reacts in acid solutions with methanol molecules to produce methylal. The thermal reaction between formaldehyde and methanol proceeds through hemiacetal as an intermediate:[7]

$$HCHO + CH_3OH \xrightarrow[acid]{} CH_2(OH)(OCH_3) \qquad (4)$$

$$CH_2(OH)(OCH_3) + CH_3OH \longrightarrow CH_2(OCH_3)_2 + H_2O \qquad (5)$$

Thus, formaldehyde and ethylene glycol are not formed in the presence of large quantities of ferric ions and methylal is obtained instead. If the above mechanism holds, $G$(methylal) should be equal to the sum of $G$(formaldehyde) and twice $G$(ethylene glycol) in the absence of the scavenger. $G$(methylal) in this experiment is 8.3, which is consistent with the sums calculated from literature values, 6.3—9.5.[1] The approximate agreement of the calculated and experimental $G$-values as well as the disappearance of formaldehyde caused

TABLE 1. EFFECT OF FERRIC CHLORIDE CONCENTRATION ON $G$-VALUES

| Concn. of $FeCl_3$(wt %) | 0 | 0.09 | 0.92 | 9.17 |
|---|---|---|---|---|
| $H_2$ | 5.0 | 6.3 | 6.0 | 1.7 |
| $CH_4$ | 0.5 | 0.7 | 0.5 | 0.2 |
| CO | 0.1 | 0.2 | 0.2 | 0.2 |
| $CH_3OCH_3$ | 0.1 | 0.1 | 0.2 | 0.3 |
| $CH_3Cl$ | 0.0 | 0.0 | 0.1 | 0.9 |
| $CH_2(OCH_3)_2$ | 0.0 | 3.3 | 6.7 | 8.3 |
| HCHO | 1.3 | 0.2 | 0.0 | 0.0 |
| $H^+$ | 0.1 | 0.2 | 1.5 | 6.5 |
| $Fe^{2+}$ | — | 0.2[a] | 1.6[a] | 7.9 |
| $(H_2O)$[b] | — | — | 7.5 | (9.7) |

Irradiation at room temperature, exposure rate $3.2\times10^5$ R/hr, exposure $3.0\times10^7$ R.

a) All ferric ions were converted into ferrous ions. b) Yields by mass balance calculation with regard to carbon and oxygen.

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by the increase in the amount of ferric chloride indicate that the above mechanism is satisfactory.

## References

1) B. Ya Ladygin and V. V. Saraeva, *Kinet. Katal.*, **6**, 221 (1965).

2) J. H. Baxendale and R. S. Dixon, *Z. Phys. Chem.*, **43**, 161 (1964).

3) J. Teply and A. Habersbergerova, *Collect. Czech. Chem. Commun.*, **30**, 785 (1965).

4) J. H. Baxendale and F. W. Mellows, *J. Amer. Chem. Soc.*, **83**, 4720 (1961).

5) At high ferric chloride concentration, an unidentified product was found to be present from the mass balance of yields by Teply and Habersbergerova.[3] The product was identified to be methylal.

6) S. F. Dainton, I. Janovsky, and G. A Salmon, *Proc. Roy. Soc., Ser. A*, **327**, 305 (1972).

7) Kirk-Othmer "Encyclopedia of Chemical Technology," Vol. 1, Interscience Encyclopedia, Inc., New York, (1947) p. 44.