Effect of Additives on Gamma Radiolysis of Methanol*  

by  
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메탄올의 감마선 분해에 대한 첨가물의 영향  

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(1970. 3. 6 접수)  

ABSTRACT  

Effect of added 1-hexene on the yield of hydrogen produced from Co-60 gamma radiolysis of methanol was investigated at room temperature. The results indicated that the yield of hydrogen decreased rapidly with increasing 1-hexene concentrations. Effect of added methyl borate on the radiolysis of methanol was also studied in the presence of oxygen. The results revealed that methyl borate acted as a less effective scavenger than oxygen towards the precursors of the radiolysis products. Experimental data previously obtained on the systems with oxygen added were treated more quantitatively to re-examine mechanism of the radiolysis of methanol in detail.

Introduction  

In the course of our studies on the radiolysis of liquid methanol by Co-60 gamma rays, we investigated the effect of oxygen on the radiolysis reaction. The results indicated that the yields for the major products of the radiolysis reactions were subject to rapid change with increasing oxygen concentrations, reaching the “plateau” values at the oxygen concentration of approximately $10^{-8}$ mole/l.

We also studied the effect of alkali halides added to methanol prior to the Co-60 gamma...
radiolysis. The results revealed that the presence of alkali iodides and bromides affected the yields for the major products to some extent, whereas alkali chlorides and fluorides had less pronounced effect. The effect of added methyl borate on the gamma radiolysis of methanol was also studied. The results indicated that methyl borate did not change greatly the yields of major products of the radiolysis.

Thus, methyl borate and alkali halides were found to act as much less effective scavengers than oxygen for the precursors of all the radiolysis products of methanol. It appeared then of interest to search other additives to affect yields for the major products of the gamma radiolysis of methanol. It was decided to examine the effect of olefins on the gamma radiolysis of methanol, in the hope of better understanding of both the roles of various additives on the radiolysis and the detailed mechanism of the radiolysis reactions. Thus, the present study concerned the effect of 1-hexene on the yields of major products of the gamma radiolysis of methanol, and the re-examination of the radiolysis mechanism by a more quantitative treatment of the data previously obtained.

Experimental Part

Materials

Methanol (A.R., Mallinckrodt) was purified by the method described in the previous papers. This involved the fractionation in a 100-cm. Todd column, and the treatment of the middle fraction with metallic magnesium followed by final fractionation in the vacuum line. Hexene-1 (C.P., Wako) was distilled through a 40-cm. fractionation column packed with glass helices, and introduced into the vacuum line.

Irradiation Cells.

The shape and size of the irradiation cells were described in the previous paper. After the irradiation cells were attached to the vacuum line and degassed, appropriate amounts of methanol and 1-hexene were transferred into the cells, which were then sealed off under vacuum. Vacuum line techniques, such as degassing, vacuum transfer and vacuum seal, used in the present study were similar to those described by Sanderson.

Gamma Irradiation.

Irradiation cells were placed around the Co-60 gamma source for irradiation. In order to determine dose rates of the samples, the dose rate to the Fricke dosimeter of the following compositions was measured:

\[
\begin{align*}
    \text{H}_2\text{SO}_4 & : 0.8\text{N} \\
    \text{Fe(NH}_4\text{)}_2\text{(SO}_4\text{)}_3 \cdot 6\text{H}_2\text{O} & : 0.1388\text{g./100ml.} \\
    \text{NaCl} & : 0.0295\text{g./100ml.}
\end{align*}
\]

Dose rates for methanol were calculated by multiplying the dose rates observed for Fricke dosimeter by the following factor, the ratio of electron density (electrons/cm\(^2\)) of methanol to water:

\[
\frac{18 \times (0.790/32)}{10 \times (1.02/18)}
\]

Analyses of Radiolysis Products.

Radiolysis products were identified and analyzed by the methods reported in previous papers. Gaseous products were transferred from the irradiation cells to the gas sample tube in the vacuum line with the aid of a Toepfer pump, and analyzed by gas chromatography. Liquid products were analyzed by the methods described in previous papers.

Results

Effect of 1-Hexene on Radiolysis of Methanol.
Effect of Additives on Gamma Radiolysis of Methanol

It was concluded from Table I that the G value for hydrogen decreased with increasing 1-hexene concentration in methanol, reaching the "plateau" value at the 1-hexene concentration of approximately 10^{-2} mole/l. This was fairly strong effect, comparable with that of added oxygen on the radiolysis reaction.\(^{(3)}\) It was therefore concluded that 1-hexene could be also an effective scavenger for precursors of hydrogen molecules produced from the gamma radiolysis of methanol.

**Effect of Methyl Borate on Radiolysis of Methanol.**

Effect of added methyl borate on the gamma radiolysis of methanol was previously studied in the absence of oxygen.\(^{(6)}\) In order to compare the behavior of methyl borate with that of oxygen towards the gamma radiolysis reaction, the studies were extended to similar system in the presence of oxygen. The results are summarized in Table II, where the data previously obtained in the absence of oxygen are also included.

The experimental results (Table II) indicated that the presence of methyl borate did not change greatly the yields of the radiolysis products whereas the presence of oxygen had pronounced effect to the yields of the radiolysis products. It appeared reasonable to conclude that methyl borate acted as a less effective scavenger than oxygen towards the precursors of the radiolysis products.

**Discussions**

**Mechanism of Gamma Radiolysis of Methanol.**

In the previous paper,\(^{(1)}\) it was assumed that the mechanism of the gamma radiolysis of pure methanol involved the followings:

(a) the diffusion of the molecular species

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**TABLE I. Effect of 1-Hexene and Oxygen on Yields of Hydrogen Produced from Gamma Radiolysis of Methanol (Room Temperature).**

<table>
<thead>
<tr>
<th>Additive 10^{-2}mole l^{-1}</th>
<th>G value for H(_2)</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>1-Hexene 0</td>
<td>4.98</td>
<td>1</td>
</tr>
<tr>
<td>0.084 3.03</td>
<td></td>
<td>Present study</td>
</tr>
<tr>
<td>0.147 2.79</td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.169 2.48</td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.372 1.98</td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.498 2.08</td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.723 1.83</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Oxygen 0</td>
<td>4.98</td>
<td>1</td>
</tr>
<tr>
<td>0.046 3.23</td>
<td></td>
<td>1</td>
</tr>
<tr>
<td>0.093 2.69</td>
<td></td>
<td>1</td>
</tr>
<tr>
<td>0.185 2.79</td>
<td></td>
<td>1</td>
</tr>
<tr>
<td>0.380 1.99</td>
<td></td>
<td>1</td>
</tr>
<tr>
<td>0.792 2.16</td>
<td></td>
<td>1</td>
</tr>
<tr>
<td>1.63 1.77</td>
<td></td>
<td>1</td>
</tr>
</tbody>
</table>

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TABLE II. Effect of Added Oxygen and Methyl Borate on G-values for Products from Gamma Radiolysis of Methanol (Room Temperature).

<table>
<thead>
<tr>
<th>Product</th>
<th>G(no O2 and no B(OCH3)2)*</th>
<th>G(no O2)***</th>
<th>G(with O2)***</th>
</tr>
</thead>
<tbody>
<tr>
<td>H2</td>
<td>4.93</td>
<td>4.81</td>
<td>1.83 (1.86, 1.80)</td>
</tr>
<tr>
<td>CH4</td>
<td>0.43</td>
<td>0.41</td>
<td>0.13 (0.10, 0.16)</td>
</tr>
<tr>
<td>C2H6</td>
<td>0.006</td>
<td>0.005</td>
<td>0.004 (0.003, 0.003)</td>
</tr>
<tr>
<td>CO</td>
<td>0.057</td>
<td>0.058</td>
<td>0.056 (0.058, 0.054)</td>
</tr>
<tr>
<td>HCHO</td>
<td>2.20</td>
<td>2.11</td>
<td>8.74 (8.84, 8.64)</td>
</tr>
<tr>
<td>(CH3OH)2</td>
<td>3.23</td>
<td>2.29</td>
<td>0.02 (0.01, 0.02)</td>
</tr>
<tr>
<td>C2H4</td>
<td>0.004</td>
<td>0.003</td>
<td>0.002 (0.002, 0.002)</td>
</tr>
<tr>
<td>Peroxide</td>
<td>0</td>
<td>0</td>
<td>3.04 (3.00, 3.07)</td>
</tr>
<tr>
<td>CO2</td>
<td>0</td>
<td>0</td>
<td>0.098 (0.095, 1.00)</td>
</tr>
<tr>
<td>HCO2H</td>
<td>0</td>
<td>0</td>
<td>2 (2 , —)</td>
</tr>
</tbody>
</table>

* Ref. 1.  
** Ref. 4.  
*** The present study. Average value of two runs with added O2 of 1.5 and 2.1x10^-8 mole/l, respectively (shown in parenthesis).

and free radicals listed below from spurs into bulk solution (equation 1).

\[
\text{CH}_3\text{OH} \rightarrow \text{H} + \text{CH}_2\text{O} + \text{H}_2\text{O} + \text{CH}_2 + \text{OH} + \text{HCHO} + \text{H}_2 + \text{CH}_4 + \text{CO} + \text{C}_2\text{H}_4 + \text{C}_2\text{H}_6 + (\text{CH}_3\text{OH}) \]  

(b) fairly rapid conversion of the free radicals listed in equation (1) into CH3OH radicals in bulk solution (equation 2-5),

\[
\text{H} + \text{CH}_2\text{O} \rightarrow \text{H}_2 + \text{CH}_2\text{OH} \]  
\[
\text{CH}_3\text{O} + \text{CH}_2\text{OH} \rightarrow \text{CH}_3\text{OH} + \text{CH}_2\text{OH} \]  
\[
\text{CH}_3 + \text{CH}_2\text{OH} \rightarrow \text{CH}_4 + \text{CH}_2\text{OH} \]  
\[
\text{OH} + \text{CH}_2\text{OH} \rightarrow \text{H}_2\text{O} + \text{CH}_2\text{OH} \]  

and

(c) the combination of CH3OH radicals to form ethylene glycol (equation 6),

\[
2\text{CH}_3\text{OH} \rightarrow (\text{CH}_3\text{OH})_2 \]  

It was also assumed that reactions (2) and (4) were suppressed by the following equations, if oxygen molecules were present:

\[
\text{H} + \text{O}_2 \rightarrow \text{HO}_2 \]  
\[
\text{CH}_3 + \text{O}_2 \rightarrow \text{CH}_3\text{COO} \]  

Experimental data obtained in the previous study (Table I) are now analyzed in more detail by assuming reactions (2) and (7) to be the major competing reactions for H atoms.

\[
\text{H} + \text{CH}_2\text{OH} \rightarrow \text{H}_2 + \text{CH}_3\text{OH} \]  
\[
\text{H} + \text{O}_2 \rightarrow \text{HO}_2 \]  

The G-values for hydrogen can be then expressed by the following equation:

\[
\text{G(H)} = \text{G}_n(\text{H}_2) + \frac{k[\text{CH}_3\text{OH}]}{k[\text{CH}_3\text{OH}] + k'\text{[O}_2]} \times \text{G(\text{H})} \]  

where \( \text{G}_n(\text{H}_2) \) denotes the G-value for molecular hydrogen formed by hot processes in the "spurs", \( \text{G(H)} \) the value for hydrogen atoms diffused out of the "spurs," and \( k \) and \( k' \) the rate constants for reactions (2) and (7), respectively. From equation (9), the maximum G-

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value for hydrogen observed in the pure methanol system can be expressed by

\[ G_{\text{max}}(H_2) = G_{\text{max}}(H) + G(H) \] .......................... (10)

From equations (9) and (10), the following relation is obtained between the value of \( \Delta G(H_2) \), defined as \( G_{\text{max}}(H_2) - G(H_2) \), and the \( O_3 \) concentration:

\[ \frac{1}{\Delta G(H_2)} = \left\{ 1 + \frac{k[CH_2OH]}{k'[O_3]} \right\} \frac{1}{G(H)} \] .................. (11)

The plots of \( 1/\Delta G(H_2) \) versus \( 1/[O_3] \), shown in Fig. 1, indicate fair linearity between the two quantities. The value of \( G(H) \) is obtained from the intercept of the plots, and the value of \( k/k' \) from both intercept and slope of the plots. A value of 3.1 is obtained for \( G(H) \), and a value of about \( 1.8 \times 10^{-6} \) for the \( k/k' \) ratio. Since the value of \( G_{\text{max}}(H_2) \) observed is 5.0, the value of \( G_{\text{max}}(H_3) \) must be 1.9.

![Fig. 1. Correlation of \( \Delta G(H_2) \) with \( O_3 \) Concentration.](image)

**Effect of Added 1-Hexene on the Radiolysis Reaction.**

As a result of the present study, it was observed that addition of 1-hexene to methanol prior to gamma irradiation reduced appreciably the yield of hydrogen, the major gaseous product of the radiolysis. Experimental data (Table I) are now analyzed in more detail by considering similar assumption to those for the system with \( O_3 \) added. The following reactions are assumed to be major competing reactions for \( H \) atoms:

\[ \begin{align*}
    H + CH_3OH & \rightarrow H_2 + CH_3OH \quad \text{(2)} \\
    H + C_6H_{14} & \rightarrow C_6H_{12} \quad \text{(12)}
\end{align*} \]

In this case the following relation is obtained:

\[ \frac{1}{\Delta G(H_2)} = \left\{ 1 + \frac{k[CH_2OH]}{k''[C_6H_{12}]} \right\} \cdot G(H) \] .......................... (13)

The plots of \( 1/\Delta G(H_2) \) versus \( 1/[C_6H_{12}] \) are shown in Fig. 2. From the intercept and slope of the straight line, a value of 3.5 is obtained for \( G(H) \), and a value of \( 3.0 \times 10^{-6} \) for the \( k/k'' \) ratio. Thus, it can be said that \( k'' \) must be much greater than \( k \), as was observed on the system with \( O_3 \) added. It is concluded therefore that 1-hexene is also an effective scavenger for precursors of hydrogen molecules produced from the gamma radiolysis of methanol.

![Fig. 2. Correlation of \( \Delta G(H_2) \) with 1-hexene concentration.](image)

**Acknowledgment.**

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References


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