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Effect of Additives on Gamma Radiolysis of Methanol*

by

Sang Up Choi

Department of Chemistry, Sogang University, Seoul.

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메탄올의 감마선 분해에 대한 첨가물의 영향

서강대학교 이공대학 화학과

崔 相 業

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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 revealved 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. (1,3) 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^{-3} mole/l.

We also studied the effect of alkali halides added to methanol prior to the Co-60 gamma

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* The Radioation Chemistry of Organic Compounds. III.

radiolysis.[3] 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.[4] 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.[1]

Experimental Part

Materials

Methanol (A.R., Mallinckrodt) was purified by the method described in the previous papers.[1,3,4] 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.[1,3] After the irradiation cells were attached to the vacuum line and degassed, appropriate amounts of atmethanol 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.[5]

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:[3,6,7]

H_2SO_4 : 0.8N.
$Fe(NH_4)_2(SO_4)_2 \cdot 6H_2O$: 0.1388g./100ml.
NaCl : 0.0295g./100ml.

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.^{3}) of methanol to water:[3]

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

Analyses of Radiolysis Products.

Radiolysis products were identified and analyzed by the methods reported in previous papers.[1,3] Gaseous products were transferred from the irradiation cells to the gas sample tube in the vacuum line with the aid of a Toepler pump, and analyzed by gas chromatography. Liquid products were analyzed by the methods des-cribed in previous papers.[1,3]

Results

Effect of 1-Hexene on Radiolysis of Methanol.

Effect of added 1-hexene on the Co-60 gamma radiolysis of methanol was studied at room temperature. Since hydrogen, the major gaseous product, was subject to pronounced change due to the presence of oxygen as radical scavenger, it was decided that only hydrogen was analyzed in this case to compare behavior of olefin with that of oxygen for the yield of the major radiolysis product. The experimental results are summarized in Table I, where the yields of hydrogen produced from gamma radiolysis of methanol are expressed in terms of G values (molecules/100e.v.). For comparison, the data reported previously on the effect of added oxygen on the yield of hydrogen are included also in Table I.

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

Additive	Conc., 10^{-3}mole l^{-1}.	G value for H_2	Reference
1—Hexene	0	4.98	1
	0.084	3.03	Present study
	0.147	2.79	〃
	0.169	2.48	〃
	0.372	1.98	〃
	0.498	2.08	〃
	0.723	1.83	〃
Oxygen	0	4.98	1
	0.046	3.23	1
	0.093	2.69	1
	0.185	2.79	1
	0.380	1.99	1
	0.792	2.16	1
	1.63	1.77	1

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^{-3} mole/l. This was fairly strong effect, comparable with that of added oxygen on the radiolysis reaction.(1) 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.(4) 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

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

		With $B(OCH_3)_3$ of 0.22mole/l.,	
Product	G(no O_2 and no $B(OCH_3)_3$)*	G(no O_2)**	G(with O_2)***
H_2	4.98	4.81	1.83 (1.86, 1.80)
CH_4	0.43	0.41	0.13 (0.10, 0.16)
C_2H_6	0.006	0.005	0.004(0.004, 0.003)
CO	0.057	0.058	0.056(0.058, 0.054)
HCHO	2.20	2.11	8.74 (8.84, 8.64)
$(CH_2OH)_2$	3.23	2.29	0.02 (0.01, 0.02)
C_2H_4	0.004	0.003	0.002(0.002, 0.002)
Peroxide	0	0	3.04 (3.00, 3.07)
CO_2	0	0	0.098(0.095, 1.00)
HCO_2H	0	0	2 (2 , —)

* Ref. 1.

** Ref. 4.

*** The present study. Average value of two runs with added O_2 of 1.5 and $2.1\text{x}10^{-3}$ mole/l, respectively (shown in parenthesis).

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

$$CH_3OH \longrightarrow H+CH_3O+CH_2OH+CH_3+OH +HCHO+H_2+CH_4+CO +C_2H_6+C_2H_4+(CH_2OH) \cdots (1)$$

(b) fairly rapid conversion of the free radicals listed in equation (1) into CH_2OH radicals in bulk solution (equation 2-5),

$$H+CH_3OH \longrightarrow H_2+CH_2OH \cdots\cdots (2)$$

$$CH_3O+CH_3OH \longrightarrow CH_3OH+CH_2OH \cdots\cdots (3)$$

$$CH_3+CH_3OH \longrightarrow CH_4+CH_2OH \cdots\cdots (4)$$

$$OH+CH_3OH \longrightarrow H_2O+CH_2OH \cdots\cdots (5)$$

and

(c) the combination of CH_2OH radicals to form ethylene glycol (equation 6),

$$2CH_2OH \longrightarrow (CH_2OH)_2 \cdots\cdots (6)$$

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

$$H+O_2 \longrightarrow HOO \cdots\cdots (7)$$

$$CH_3+O_2 \longrightarrow CH_3COO \cdots\cdots (8)$$

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.

$$H+CH_3OH \xrightarrow{k} H_2+CH_2OH \cdots\cdots (2)$$

$$H+O_2 \xrightarrow{k'} HOO \cdots\cdots (7)$$

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

$$G(H_2)=G_m(H_2)+\frac{k[CH_3OH]}{k[CH_3OH]+k'[O_2]} \times G(H) \cdots\cdots (9)$$

where $G_m(H_2)$ denotes the G-value for molecular hydrogen formed by hot processes in the "spurs", 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-value for hydrogen observed in the pure methanol system can be expressed by

$$G_{max}(H_2) = G_m(H_2) + G(H) \cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots (10)$$

From equations (9) and (10), the following relation is obtained between the value of $\triangle G(H_2)$, defined as $G_{max}(H_2) - G(H_2)$, and the O_2 concentration:

$$\frac{1}{\triangle G(H_2)} = \left\{1 + \frac{k[CH_3OH]}{k'[O_2]}\right\} \frac{1}{G(H)} \cdots (11)$$

The plots of $1/\triangle G(H_2)$ versus $1/[O_2]$, 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 1.8×10^{-6} for the k/k' ratio. Since the value of $G_{max}(H_2)$ observed is 5.0, the value of $G_m(H_2)$ must be 1.9.

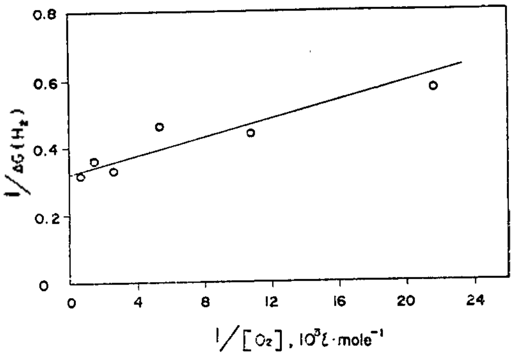

Fig. 1. Correlation of $\triangle G(H_2)$ with O_2 Concentration.

Effect of Added 1-Hexene on the Radiolysis Reaction.

As a result of the 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_2 added. The following reactions are assumed to be major competing reactions for H atoms:

$$H + CH_3OH \xrightarrow{k} H_2 + CH_2OH \cdots\cdots\cdots\cdots\cdots\cdots\cdots (2)$$

$$H + C_6H_{12} \xrightarrow{k''} C_6H_{13} \cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots (12)$$

In this case the following relation is obtained;

$$\frac{1}{\triangle G(H_2)} = \left\{1 + \frac{k[CH_3OH]}{k''[C_6H_{12}]}\right\} \cdot G(H) \cdots\cdots (13)$$

The plots of $1/\triangle G(H_2)$ 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 3.0×10^{-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_2 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.

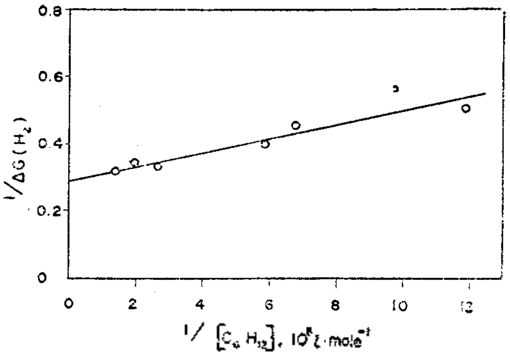

Fig. 2. Correlation of $\triangle G(H_2)$ with 1-hexene concentration.

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