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7.37-6.95 (m, 6H, ArH), 4.00 (br, 8H, CH_2), 3.80-3.18 (m, 2H, CH) 1.18ppm (d, 12H, CH_3). Anal. C, 76.15; 6.52 (calcd for $C_{36}H_{36}O_6$. C, 76,56; H, 6.44). *p*-Benzoylcalix [4] arene 14. The crude product was purified by flash chromatography (eluent was 7:4 mixture of acetone to hexane). The residue obtained by evaporation of eluent was triturated with hexane to give the desired product in 76% yield as colorless crystalline solid; mp not melt or decompose until 400°C; IR(KBr) $3400cm^{-1}$ (OH stretching), 1640 (C=O stretching); ^1H=nmr ($CDCl_3$) δ 10.3 (s, 4H, OH), 7.75-6.93 (m, 28H, ArH), 3.90 ppm (b, 8H, CH_2). Anal. C, 79.69; H, 4.78 (calcd for $C_{56}H_{40}$ O_8. C, 79.98; H, 4.84).

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Gamma-Radiolysis of Carbon Dioxide (IV). Effect of the Addition of Alcohols on the Gamma-Radiolysis of Gaseous Carbon Dioxide[*]

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The gaseous carbon dioxide has been irradiated with Co-60 gamma-radiation in the presence and absence of various alcohols, and the radiolysis products analyzed by gas chromatography. Experimental results indicate that no detectable amount of carbon monoxide is formed when pure carbon dioxide is irradiated. By adding small quantities of alcohols to carbon dioxide, however, considerable amount of carbon monoxide, ketones, alcohols and other organic products have been detected. By adding 0.1% of methanol, ethanol, 1-propanol, 2-propanol, 1-butanol, 2-methyl-1-propanol, 2-butanol, and 2-methyl-2-propanol, G(CO) values obtained are 4.4, 4.5, 5.2, 4.4, 5.2, 5.0, 4.7 and 4.1, respectively. These high yields of carbon monoxide suggest that the oxidation reactions of carbon monoxide may be suppressed by scavenging oxygen atom with the alcohols. The main radiolytic decomposition reactions of the alcohols present in small quantity in carbon dioxide may be supposed to be the reactions with the oxygen atom produced by the radiolysis of carbon dioxide. The decomposition reactions seems to follow pseudo-first order kinetics with respect to the alcohols. The decomposition rate measured with 2-propanol is the fastest and that with 2-methyl-2-propanol the slowest. The mechanisms of the radiolytic decomposition reactions of the alcohols present in carbon dioxide are discussed on the basis of the experimental results of the present study.

Introduction

It was reported in the literature that the G(CO) value observed in the gammaradiolysis of pure carbon dioxide was practically negligible because of the rapid reoxidation of carbon monoxide.[1,2] By the radiolysis of carbon dioxide with various additives, however, considerable amount of carbon monoxide was found to be formed. A number of workers reported the effects of various additives on the yields of carbon

monoxide. Thus, some of inorganic gases,[3,4] such as nitrogen dioxide and sulfur dioxide, some organic gases,[5,6] such as methane and propane, and some solid materials,[7,8] such as graphite and glass beads, were proved to be effective additives to suppress the possible reoxidation reactions of carbon monoxide.

In a paper of this series, we reported the results of the studies on the effect of methanol, ethanol, formaldehyde, and acetaldehyde on the gamma-radiolysis of gaseous carbon dioxide.[9] It was found that the organic compounds mentioned above were effective additives to suppress the possible back reactions, or the reoxidation of carbon monoxide. Since the systematic investigations, however, were not yet carried out regarding the organic additives, more detailed studies were desirable.

In the present study, a series of alcohols such as

methanol, ethanol, 1-propanol, 2-propanol, 1-butanol, 2-methyl-1-propanol, 2-butanol, and 2-methyl-2-propanol were employed as the additives to carbon dioxide. After the mixtures were irradiated with Co-60 gamma-rays, the yields of both carbon monoxide and organic products were determined by gas chromatography. It was hoped that the role of the added alcohols on the production of carbon monoxide could be clarified, and the decomposition mechanisms of the alcohols in the mixtures could be rationalized.

Experimental Section[10]

Materials. Carbon dioxide (Dongjin, Pure gas, 99.9%) was purified by repeated bulb-to-bulb distillation in vacuum. Methanol (Merck, GR), ethanol (Merck, GR), 1-propanol (Fisher), 2-propanol (Wako, 1st grade), 1-butanol (Merck, GR), 2-methyl-1-propanol (Merck, EP), 2-butanol (Merck, EP), and 2-methyl-2-propanol (Hayashi, EP) were dehydrated with Molecular Sieve 4A (Davison Chemicals, 8-12 mesh), and purified by repeated distillation under vacuo.

Gamma Irradiation. The 4 m*l* (I.D. 8 mm) and 80 m*l* (I.D. 30 mm) irradiation ampoules were made with Pyrex-glass tube. These ampoules were washed with distilled water, and baked at 550°C in a furnace for 8 hours before use. Both carbon dioxide and the alcohols were introduced by ordinary vacuum line technique into the ampoules which were connected to the vacuum line with ground joints. The pressures of the alcohols were measured with a Mercury-Oil manometer which was designed for the measurement of the pressures in the region of 1-10 torr.[10] This manometer was constructed by replacing one arm of a mercury manometer by an organic oil column so that the difference in height between the meniscuses of the two columns of the manometer could be magnified.

The samples were irradiated with 2,000 Ci Co-60 gamma-source at room temperature. The doses were measured by Fricke dosimeter[11] and the absorbed doses of carbon dioxide (D) were obtained from those of Fricke dosimeter (D_F) by considering relative electron densities of the two absorbers.[12] (A denotes the number of the electrons in the molecules, and M the molecular weight)

$$D = \frac{(A/M)_{carbon\ dioxide}}{(A/M)_{water}} D_F$$

Analysis of Products. The radiation products were analyzed by gas chromatography. In order to analyze the products more conveniently, two different columns were used, the column I (Molecular Sieve 5A, 60-80 mesh, 185 cm length, 3 mm diameter) being used for the analysis of the components which were not condensed at liquid nitrogen temperature, and the column II (Porapak Q, 100-120 mesh, 335 cm length, 3 mm diameter) for the condensable components. Helium was used as carrier gas and the column oven temperature was 180°C. Both the thermal conductivity detector and the flame ionization detector were used.

The G-values of the materials produced by radiolysis of carbon dioxide were calculated by the following equation.

$$G = \frac{6.02 \times 10^{23}\ (molecules/mol) \times Z/100 \times 1/44\ (mol/g)}{D \times 10^6\ (rad) \times 100\ (erg/g/rad) \times 6.25 \times 10^{11}\ (eV/erg)}$$
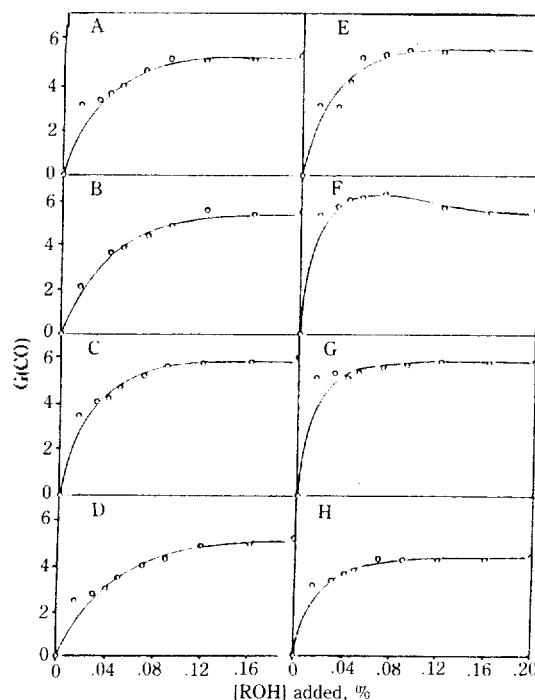
$$= 219 \times Z/D\ (molecules/100eV) \tag{1}$$

Figure 1. Effect of alcohol concentration on G(CO) at 5 Mrad. A: methanol, B: ethanol, C: 1-propanol, D: 2-propanol, E: 1-butanol, F: 2-methyl-1-propanol, G: 2-butanol, H: 2-methyl-2-propanol.

In equation (1), Z denotes the percent concentration of the material produced with the dose of D Mrad.

Results

Effects of Alcohol Concentrations on G(CO). The mixture samples of carbon dioxide with various alcohols were prepared in 4 m*l* Pyrex ampoules with total pressure of 1.5 atm., and irradiated at room temperature with Co-60 gamma-radiation at the constant dose rate of 1.9×10^5 rad/hr with total dose of 5 Mrad. The G(CO) values were measured at various concentrations of alcohols up to about 0.20%. The results obtained are shown graphically in Figure 1.

It was concluded from the data shown in Figure 1 that all the alcohols examined in this experiment were very effective for the production of carbon monoxide by the gamma-radiolysis of carbon dioxide. It could also be concluded that the shapes of the curves obtained were very similar among all the alcohols involved. In all cases the G(CO) values increased rapidly with increasing alcohol concentrations in the concentration range below 0.05 %. As the alcohol concentrations increase, the rates of the increase of G(CO) values became smaller, and constant G(CO) values were obtained at the alcohol concentrations higher than 0.1 %. The constant G(CO) values varied with the added alcohols, ranging from 4.4 for 2-methyl-2-propanol to 5.8 for 2-butanol.

Effect of Dose on CO Yields. The samples of ethanol-carbon dioxide with various alcohol concentrations were irradiated at three different doses, 5, 10 and 20 Mrad. The results obtained are shown in Figure 2. It was concluded from the data that the smaller G(CO) values were obtained with higher doses.

In order to examine the effect of the total doses on the CO yields in more detail, the mixture samples of carbon dioxide
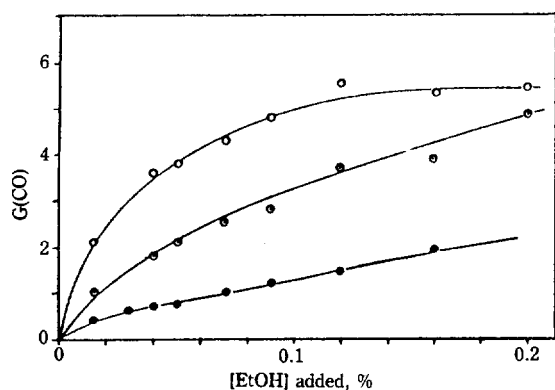
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Figure 2. Effect of ethanol concentration on G(CO) at various doses. o: 5 Mrad, ⊙: 10 Mrad, ●: 20 Mrad.
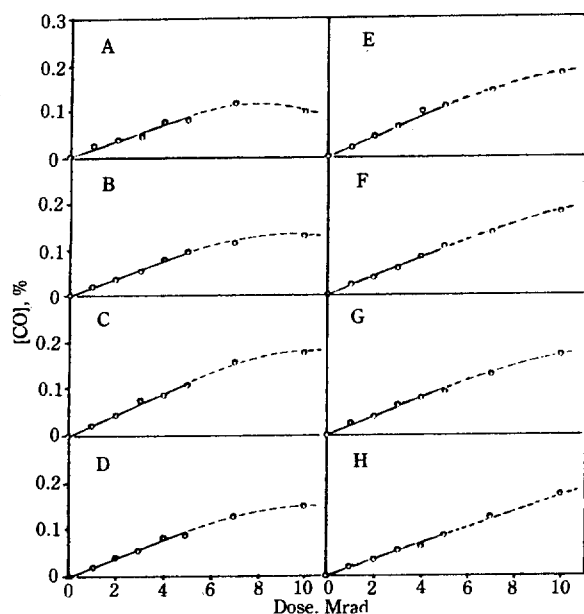

Figure 3. Carbon monoxide produced by radiolysis of 0.1% alcohol-carbon dioxide mixtures. A: methanol, B: ethanol, C: 1-propanol, D: 2-propanol, E: 1-butanol, F: 2-methyl-1-propanol, G: 2-butanol, H: 2-methyl-2-propanol.

Table 1. The values of G(CO) and G° (−ROH) Obtained from 0.1% Alcohol-CO₂ Mixtures

Alcohol	G(CO)	G°(-ROH)
Methanol	4.4	8.6
Ethanol	4.5	9.1
1-Propanol	5.2	7.1
2-Propanol	4.5	12.1
1-Butanol	5.2	7.0
2-Methyl-1-propanol	5.0	6.2
2-Butanol	4.7	6.8
2-Methyl-2-propanol	4.1	4.2

with various alcohols (0.1 %) were prepared in 80 m*l* Pyrex ampoules with total pressure of 1 atm., and irradiated at room temperature with gamma-radiations at the dose rate of 3.4×10^5 rad/hr. The data (Figure 3) indicated that the yields of carbon monoxide increased linearly with the dose up to about 5-7 Mrad. The slopes of these plots (Figure 3)
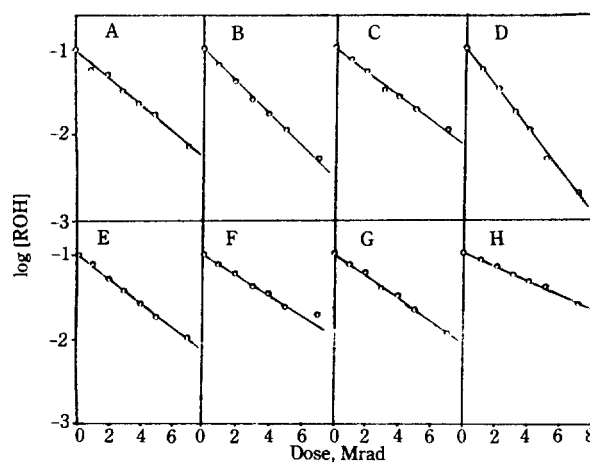

Figure 4. Residual alcohol concentration versus dose. A: methanol, B: ethanol, C: 1-propanol, D: 2-propanol, E: 1-butanol, F: 2-methyl-1-propanol, G: 2-butanol, H: 2-methyl-2-propanol.

varied with the alcohols added, ranging from 0.017 %/Mrad for 2-methyl-2-propanol to 0.0215 %/Mrad for 1-propanol.

The G(CO) values could be calculated from the slopes of the plots in Figure 3, using equation (1). The results of the calculation are summarized in Table I. The alcohols which gave the highest G(CO) value of 5.2 were 1-propanol and 1-butanol, and the lowest of 4.1 was 2-methyl-2-propanol.

Decomposition of Alcohols. When the mixtures of carbon dioxide with various alcohols were irradiated with gamma-radiation, it was observed that the added alcohols were also decomposed. The concentrations of residual alcohols were measured at various doses up to 14 Mrad. It was observed that the residual concentrations of the added alcohols seemed to decrease exponentially with the absorbed doses. Thus, the logarithms of the residual concentrations were plotted against the doses. The plots indicated good linear relationships between the two quantities, as shown in Figure 4. Hence, it could be concluded that the decompositions of the added alcohols followed the first-order kinetics, because the doses could be replaced by time under the condition of constant dose rate.

When the samples of 0.1 % alcohol-carbon dioxide mixtures were irradiated with gamma-rays, it was observed that some organic materials, such as hydrocarbons, ketones, and alcohols different from the added ones, were also produced. The major organic products observed are shown in Figure 5.

In the case of addition of the primary alcohols, such as ethanol, 1-propanol, 1-butanol or 2-methyl-1-propanol, the major organic products were the saturated hydrocarbons with the carbon number being one less than the added alcohols. In the case of the secondary and tertiary alcohols, very large amount of ketones were observed to be produced. The maximum concentrations of the ketones observed were 0.03-0.045 %, corresponding to 30-45 % of the added alcohol concentrations.

Discussion

Production of Carbon Monoxide. It is known that the stability of carbon dioxide to the low dose-rate radiations such as gamma-rays is ascribed to the back reactions, *i.e.* the reoxidation reactions of the produced carbon monoxide with oxygen atoms.[13] From the results of the present study, it is
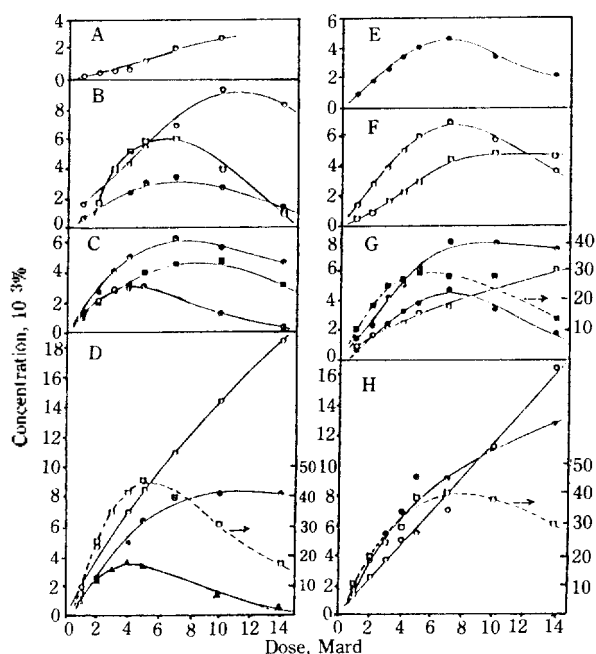
Figure 5. Major organic products obtained by radiolysis of 0.1% alcohol-carbon dioxide mixtures. A: methanol, B: ethanol, C: 1-propanol, D: 2-propanol, E: 1-butanol, F: 2-methyl-1-propanol, G: 2-butanol, H: 2-methyl-2-propanol. ○ : methane, ◎ : ethane, ● : propane, ◐ : n-butane, □ : acetone, ■ : methylethylketone, ▲ : 2-methyl-2-propanol.

concluded that all the alcohols used in this experiment seemed to be effective additives to suppress the reoxidations of carbon monoxide, and that the addition of alcohols in small quantities (0.1 %) is sufficient to suppress the back reactions at the radiation dose of up to 5 Mrad (Figure 1 and Figure 3). In the present study the G(CO) values are obtained in two different ways, one from the data observed at constant dose of 5 Mrad (Figure 1, in smaller ampoules) and the other from the slopes of the plots of CO yields versus doses at constant alcohol concentration of 0.1 % (Figure 3, in larger ampoules). These indicate good agreement, but the former values seem to be slightly higher than the latter. This may be regarded as experimental error, but it may also be speculated that larger wall effect anticipated in smaller ampoules may enhance the formation of carbon monoxide.

Decomposition of Alcohols. As shown in Figure 4, the logarithms of the residual alcohol concentrations seem to give good linear relationships with the doses. Thus, the experimental results can be expressed by the following equation:

$$- \frac{d[ROH]}{dD} = k' \ [ROH] \tag{2}$$

In equation (2), [ROH] and k' denote the residual concentrations of the added alcohols and a constant, respectively. The integration of equation (2) leads to the following equation ([ROH]$_0$ represents the initial concentrations of the alcohols):

$$[ROH] = [ROH]_0 e^{-k'D} \tag{3}$$

$$\log[ROH] = - \frac{k'}{2.303} D + \log[ROH]_0 \tag{4}$$

Since equation (4) represents the curves in Figure 4, the

slopes (S) of the curves are equal to -k'/2.303. Since the dose (D) is the product of the dose rate (DR) and the irradiation time (t),

$$dD = (DR) \ dt \tag{5}$$

Thus, the equation (2) can be expressed as follows:

$$- \frac{d[ROH]}{dt} = -2.303 \ S \ (DR) \ [ROH] \tag{6}$$

If it is presumed that the decomposition reactions of the alcohols follow the first-order reaction kinetics, the reaction rate equation is expressed by

$$- \frac{d[ROH]}{dt} = k_1 \ [ROH] \tag{7}$$

By comparing the equations (6) and (7), the first-order rate constant (k$_1$) can be expressed as follows:

$$k_1 = -2.303 \ S \ (DR) \tag{8}$$

Since 99.9% of the gas mixture is carbon dioxide, the major species to lead to the decomposition of alcohols may be the primary radiolysis products of carbon dioxide. The G-values of the species produced in the primary process of the radiolysis of carbon dioxide are known to be as follows:[14]

$$7.53CO_2 \longrightarrow 0.07C^+ + 0.21 \ O^+ + 0.51 \ CO^+ + 2.24 \ CO_2^+$$
$$+ 4.74CO + 5.16 \ O + 3.03 \ e^- \tag{9}$$
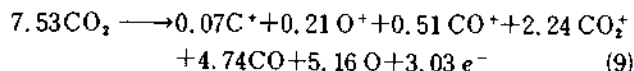
All the products except carbon monoxide in equation (9) could react with the alcohols. The G-values of the ionic species are much smaller than that of the oxygen atom, and furthermore, before the ionic species collide with the alcohol molecules, large portions of the ions are thought to be decayed by the reaction with carbon dioxide.[2,15] Thus, among the primary products, the oxygen atom is supposed to be the major species to decompose the alcohols.

If this supposition is valid, it can be said that the main decomposition reactions of the alcohols is the second-order reaction with the oxygen atom.

$$ROH + O \xrightarrow{k_2} products \tag{10}$$
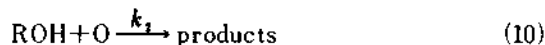
$$- \frac{d[ROH]}{dt} = k_2 \ [O] \ [ROH] \tag{11}$$

By comparing equation (11) with equation (6), the concentration of the oxygen atom can be expressed as follows:

$$[O] = - \frac{2.303 \ S}{k_2} \ (DR) \tag{12}$$

The concentrations of oxygen atom are maintained constant during the irradiation because the experiments are carried out at the constant dose rate. Thus, the decomposition reactions of the alcohols follow the pseudo-first order kinetics.

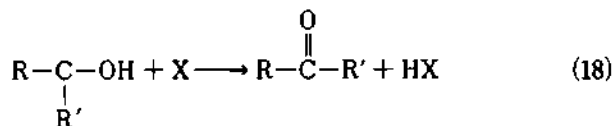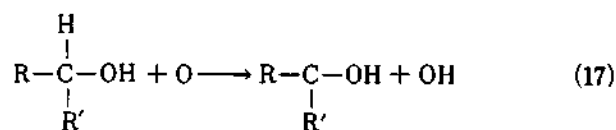**G(-ROH) Values.** Equation (6) can be rewritten as follows:

$$- \frac{d[ROH]}{dD} = -2.303 \ S \ [ROH] \tag{13}$$

The number of alcohol molecules decomposed by the absorbed radiation energy of 100 eV can be obtained by replacing Z/D in equation (1) with the right side of the equation (13).

$$G(-ROH) = 219 \times (-2.303 \ S \ [ROH]) = -504 \ S \ [ROH] \tag{14}$$

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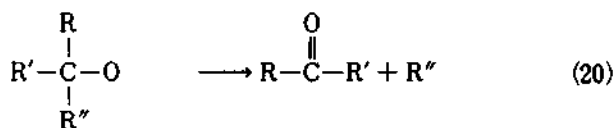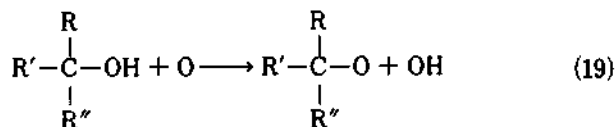
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This equation suggests that G(-ROH) values are linearly proportional to the residual alcohol concentrations. The G^o (-ROH) values obtained by equation(14) at zero dose (i.e., [ROH] = 0.1 %) are shown in Table 1. The G^o(-ROH) values may be regarded as the relative reactivities of the alcohols for the reaction with oxygen atom and/or other reactive primary products. Thus, it can be said that 2-propanol is the most reactive and 2-methyl-2-propanol is the most stable to the radiolysis of the alcohols in the carbon dioxide mixtures.

Production of Ketones. Extremely large amount of ketones are produced in the mixtures of carbon dioxide with secondary or tertiary alcohols. Acetone is produced from 2-propanol and 2-methyl-2-propanol, and methylethylketone from 2-butanol. Since the rate of the alpha-hydrogen abstraction reaction of oxygen atom is about 100 times faster than that of beta-hydrogen abstraction,[16] the mechanisms of the ketone formations from the secondary alcohols may be proposed as follows:

$$R-\underset{\underset{R'}{|}}{\overset{\overset{H}{|}}{C}}-OH + O \longrightarrow R-\underset{\underset{R'}{|}}{C}-OH + OH \qquad (17)$$

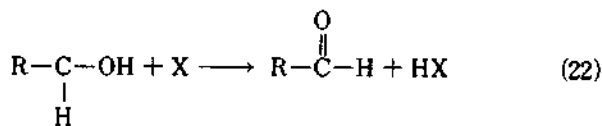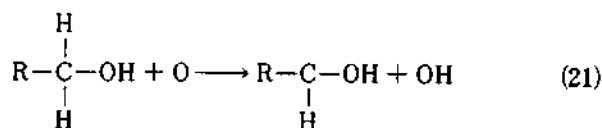$$R-\underset{\underset{R'}{|}}{C}-OH + X \longrightarrow R-\overset{\overset{O}{||}}{C}-R' + HX \qquad (18)$$

(X : O, OH, H, R, R', RR′COH, etc.)

Since there is no alpha-hydrogen in the tertiary alcohol molecules, the mechanisms of ketone formations from the tertiary alcohol may be different from those of the secondary alcohols. The abstraction reactions of the beta-hydrogens or the hydroxyl hydrogens could take place in this case. The experimental results support the speculation that the hydroxyl hydrogens may be abstracted more readily than the beta-hydrogens.

$$R'-\underset{\underset{R''}{|}}{\overset{\overset{R}{|}}{C}}-OH + O \longrightarrow R'-\underset{\underset{R''}{|}}{\overset{\overset{R}{|}}{C}}-O + OH \qquad (19)$$

$$R'-\underset{\underset{R''}{|}}{\overset{\overset{R}{|}}{C}}-O \longrightarrow R-\overset{\overset{O}{||}}{C}-R' + R'' \qquad (20)$$

It is presumed that aldehydes may be produced in the radiolysis of the primary alcohols, by analogy with the formation of ketone in the radiolysis of the secondary or tertiary alcohols.

$$R-\underset{\underset{H}{|}}{\overset{\overset{H}{|}}{C}}-OH + O \longrightarrow R-\underset{\underset{H}{|}}{C}-OH + OH \qquad (21)$$

$$R-\underset{\underset{H}{|}}{C}-OH + X \longrightarrow R-\overset{\overset{O}{||}}{C}-H + HX \qquad (22)$$

Experimentally, however, aldehydes are not detected. The aldehydes are relatively unstable compounds and known to be decomposed very easily by radiations.[17] This could be the reason why the aldehydes were not detected.

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