The Addition Reactions of Propanol-2 to Ethylene Induced by Gamma-ray Irradiation in the Gaseous Phase[*]

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It is known that the α-C-alkylation of primary and secondary alcohols results from their peroxide- and light-induced reactions with olefins.[1] Similar reactions are also induced by gamma-ray irradiation. The addition reactions of propanol-2 to ethylene in the liquid phase have been studied with gamma-rays by Hirota and Hatada.[2] It would be interesting to study if some differences are found between the liquid and gaseous phases. Therefore, in the present study, the samples were prepared with care so as to prevent them from condensing at the reaction temperatures.

Experimental

Materials.—Propanol-2 was purified by column distillation after refluxing it over calcium oxide. Ethylene (99.8%) was purified repeatedly by vacuum distillation at −196°C. No impurities were found by gas chromatography after these purifications. The samples were collected by vacuum distillation in a hard-glass tube (about 40 ml.).

Irradiation. — The samples were irradiated at 2.2×10^4 r./hr. of cobalt-60 gamma-rays while being kept within ±1°C of the given temperature in a controlled electric heater. The absorbed energy, E, is estimated by the equation:

$$E=87.7\times tD(\sum\rho_i m_i) \qquad \text{(erg.)} \qquad (1)$$

where t=irradiation time (hr.)
D=dose rate measured by the Fricke dosimeter (r./hr.)
ρ=relative electron density to air
m=mass of the reactant (g.)

The relative electron densities, ρ, are 1.11 and 1.13 for ethylene and propanol-2 respectively.

The experiments were carried out under the conditions listed in Table I.

Analytical.—After irradiation, the total amounts of the gases in the tube and of the non-condensable gases at −196°C were measured. The latter compositions were analyzed by the mass-spectrum method in order to determine the amounts of hydrogen and methane produced. Then the condensed liquids were analyzed immediately by gas chromatography, using a column of PEG 6000 at 70 and 150°C.

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[*] The Radiation Chemistry of Gaseous Alcohols at Elevated Temperatures. I.

[1] W. H. Urry, F. W. Stacey, E. S. Huyser and O. O. Juveland, *J. Am. Chem. Soc.*, **76**, 450 (1954).

[2] K. Hirota and M. Hatada, This Bulletin, **34**, 1644 (1961).

Results

Non-condensable Gases.—The results of experiments 1–5 (Table I) are shown in Fig. 1 against the irradiation time for the decrement of ethylene (◬) and the amount of the non-condensable gases produced (⊙). The G-values of hydrogen and methane, based on the total absorbed energy in the mixture, were found to be 4.2 and 3.8 from mass-spectrometric analysis. The corresponding values are 2.77 and 1.65 for the gamma-ray radiolysis of pure propanol-2 at room temperature,³⁾ and 1.28 and 0.21 for the 2 MeV. electron-radiolysis of ethylene of 150 mmHg at 25°C.⁴⁾ These facts suggest that the hydrogen abstraction reactions by hydrogen atoms and methyl radicals are of minor importance in the present chain process.

TABLE I. EXPERIMENTAL CONDITIONS

No.	Composition, 10^{-3} mol. Propanol-2	Ethylene	Temp. °C	Time hr.
1	3.5	2.1	175	4
2	3.5	2.1	175	8
3	3.5	2.1	175	20
4	3.5	2.1	175	40
5	3.5	2.1	175	65
6	3.5	2.1	100	20
7	3.5	2.1	125	20
8	3.5	2.1	150	20
9	3.5	2.1	200	20
10	3.5	0.0	175	20
11	3.5	0.42	175	20
12	3.5	0.80	175	20
13	3.5	1.1	175	20
14	3.5	1.5	175	20
15	3.5	1.8	175	20

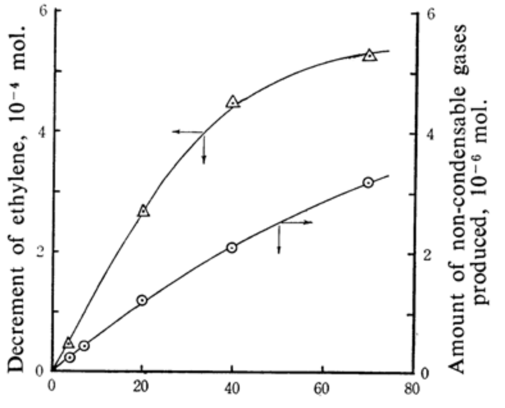

Fig. 1. The decrements of ethylene (◬) and the amounts of the non-condensable gases produced (⊙) as a function of irradiation time (experiments 1—5).

Condensable Products.—Compared with the retention time of propanol-2, the gas chromatography gave the twenty-one peaks of the shorter retention time at 70°C and the sixteen peaks of the longer one at 150°C. Among these the identified products are listed in the order of their retention times in Table II. Some results of experiments 1—5 (Table I) are shown in Fig. 2 against the irradiation time for the amounts of acetone (●), 2-methylbutanol-2 (⊙), 2-methylhexanol-2 (◬) and 2-methyloctanol-2 (⊡).

TABLE II. G-VALUE OF PRODUCTS*

Isopentane	26
Ethyl isopropyl ether	31
Acetaldehyde	35
Acetone	131
2-Methylbutanol-2 (1 : 1 telomer)	103
Pentanol-2	25
2-Methylhexanol-2 (1 : 2 telomer)	41
Hexanol-2	11
2-Methyloctanol-2 (1 : 3 telomer)	25.5

* From the results of the Experiment 3 (Table I).

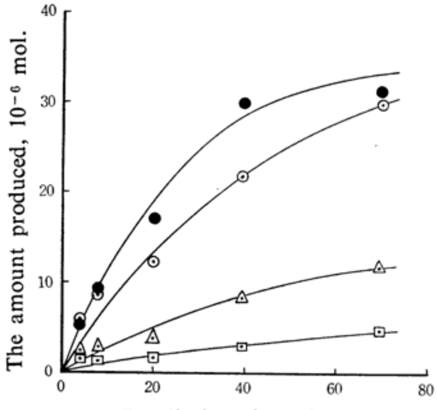

Fig. 2. The amounts of products as a function of irradiation time (experiments 1—5); acetone (●), 2-methylbutanol-2 (1 : 1 telomer) (⊙), 2-methylhexanol-2 (1 : 2 telomer) (◬), and 2-methyloctanol-2 (1 : 3 telomer) (⊡).

Although a large number of the products could not be identified, the peak area, A_i, is proportional to the mole concentration, M_i, independent of the materials of the related compounds, as is shown in Fig. 3. Therefore, even if there are some unknown products, the

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3) J. D. Strong and J. G. Burr, *J. Am. Chem. Soc.*, **81**, 776 (1959).

4) F. W. Lampe, *Radiation Research*, **10**, 619 (1959).

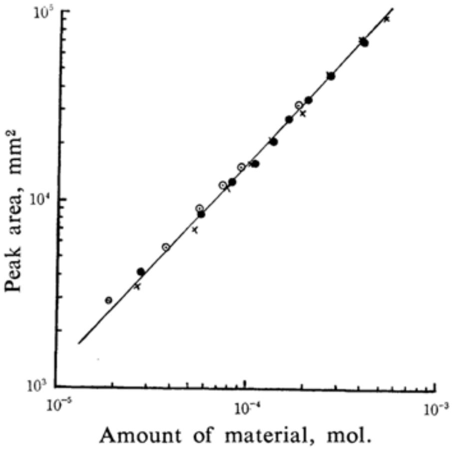

Fig. 3. Peak areas of various materials for gas chromatography at 100°C as a function of their mole concentration; acetone (●), propanol-2 (×) and 2-methylbutanol-2 (⊙).

mole concentration of the respective products, M_i, can be estimated from the gas chromatograph chart by the equation:

$$M_i = M_p \times \frac{A_i}{\sum A_i} \tag{2}$$

where M_p is the mole concentration of the parent reactant, propanol-2. The $\sum A_i$ is the sum of all the peak areas, including that of propanol-2. Therefore, the *G*-value is obtained by the equation:

$$G_i = 1.1 \times 10^{12} \times \frac{M_p A_i}{tD(\sum \rho_i)(\sum A_i)} \tag{3}$$

The *G*-values, estimated by Eq. 3 from the results of experiment 3 (Table I), are shown in Table II. For this case, the *G*-value of all the products is 815, judging from the sum of the peak areas, including those for the unidentified products. On the other hand, the *G*-value of the consumed ethylene is 1800 (cf. Fig. 1). This means that 2.2 ethylene molecules are apparently combined with a propanol-2 molecule.

Discussion

The Overall Reaction Scheme.—A part of the reaction scheme can be assumed to be as shown in Table III from the identified products in Table II, where PH is propanol-2, and, E, ethylene. This indicates that all the radicals which can be expected from propanol-2 are present as precursors. These precursor radicals, I—V (Table III), are formed not only by the reactions shown in Table III, but also by various reactions between propanol-2 and various radicals.

The API's mass-spectral data[5] show that almost all the propanol-2 molecules lose not a hydrogen atom but a methyl radical by ionization. On the other hand, the present findings indicate that the major precursor radical is 1-hydroxyisopropyl, as is to be expected from the radical mechanism. This indicates that the present processes are radical and not ionic, even if initiated by irradiation, namely, ionization and excitation.

The present finding in the gaseous phase is in contrast with the finding in the liquid phase, reported by Hirota and Hatada,[2] that almost all the products were from the 1-hydroxyisopropyl radical, although the mole fraction of ethylene in that experiment was different from that in the present experiments. This may show that the addition reaction is predominant in the liquid phase; it will be shown later that the chain transfer constant is smaller than that in the gaseous phase. In other words, the products produced only in the gaseous phase may perhaps be attributed to the radical transfer reaction of radicals with propanol-2 molecules.

Acetone and Acetaldehyde.—The *G*-values of acetone and acetaldehyde are nearly equal to those from the radiolysis of gaseous propanol-2 (experiment 10, Table I) and are independent of the mole fraction of ethylene (experiments 3, 11—15, Table I). Therefore, they are assumed to be formed independently of ethylene.

1-Hydroxyisopropyl Radical.—The 1-Hydroxyisopropyl radical (radical I, Table III) is the most important precursor radical formed from propanol-2, as is indicated by the *G*-value of the telomers in Table III. This radical might react variously with propanol-2 by means of radical transfer reactions as well as by the hydrogen transfer reaction.

It may not necessarily be concluded that acetone is formed through this radical, for the yield of acetone is independent of the ethylene content, which is indispensable for the formation of this radical. Although the molecular detachment of hydrogen from propanol-2 is sometimes assumed for the excited molecule of radiolysis or photolysis and for the thermal formation on the special solid catalysts, this may be supposed not to be the present case.

According to Mellow and Burton,[6] the addition reactions, started from this precursor radical, P, shown in Table III, are expressed by the following rate relations:

$$\frac{(\text{P–E–H})}{(\text{P–E–E–H})} = \frac{k_1(\text{PH})}{k_2(\text{E})} + \frac{k_1 k_4}{k_2 k_3} \tag{4}$$

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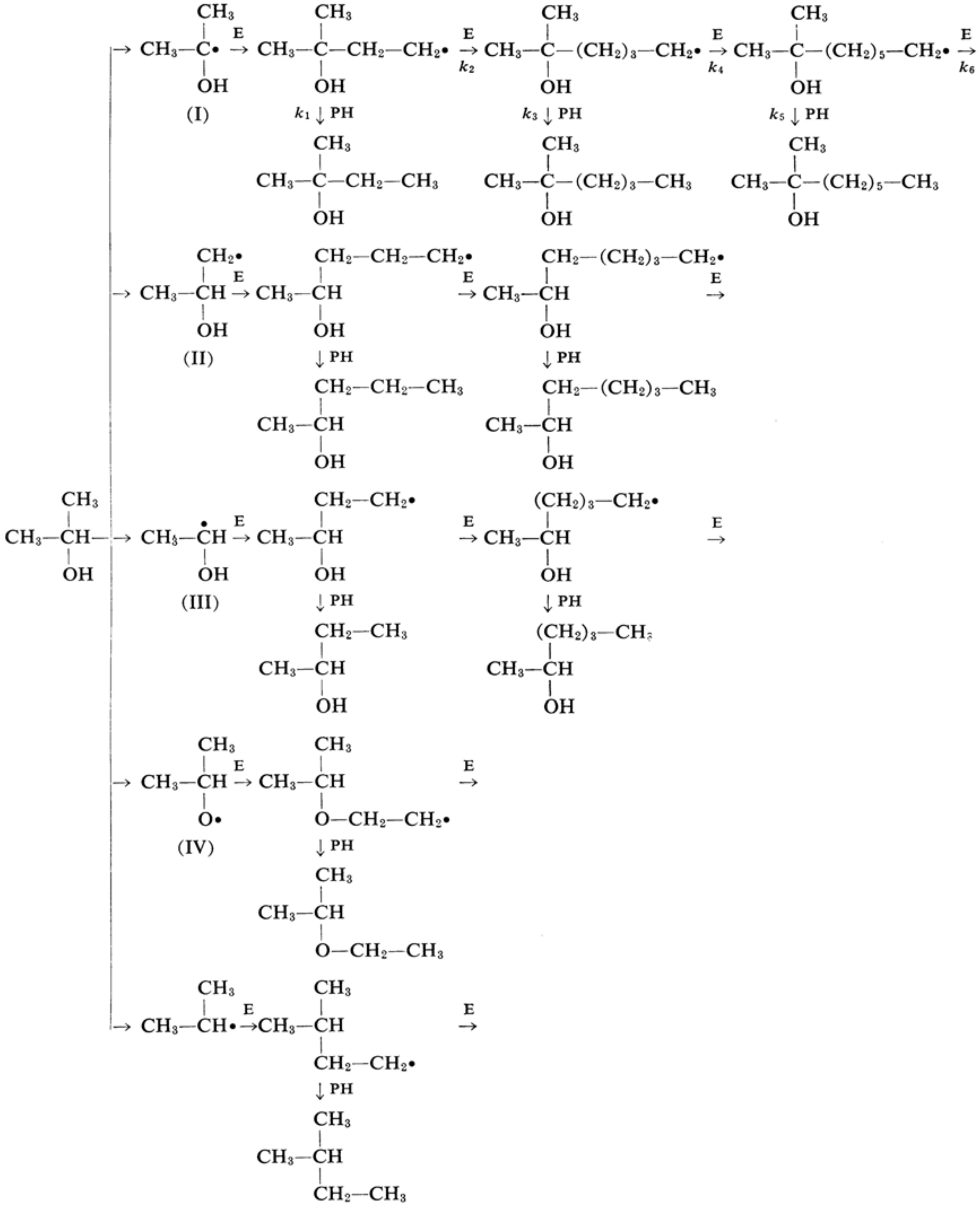
[5] Mass Spectral Data of American Petroleum Institute Research Project 44, Carnegie Inst. Techn., Pittsburgh (1957).

[6] F. W. Mellow and M. Burton, *J. Phys. Chem.*, **66**, 2164 (1962).

TABLE III. REACTION SCHEME



and

$$\frac{(\text{P–E–E–H})}{(\text{P–E–E–E–H})}=\frac{k_3(\text{PH})}{k_4(\text{E})}+\frac{k_3k_6}{k_4k_5} \qquad (5)$$

where the symbols are as represented in Table III. The yields of these telomers depend on the ethylene content in the results of experiments 11—15 (Table I). The chain transfer constants, $c_1=k_1/k_2$, $c_2=k_3/k_4$, and $c_3=k_5/k_6$, are estimated by the use of Eqs. 4 and 5 to be 0.62, 0.55±0.05 and 0.50±0.05 from these results.

On the other hand, according to Walling,⁷⁾ the chain transfer constants, c_i, can be expressed by the equation:

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7) C. Walling, "Free Radicals in Solution," John Wiley and Sons, New York (1957), p. 246.

$$F_i=\frac{c_iR}{\Pi(c_iR+1)} \tag{6}$$

where F_i is the mole fraction of the i'th telomer to the whole telomers, and R, the mole ratio of the reactants, (PH)/(E). The mole fraction of the respective telomers, F, is plotted against the R in Fig. 4 on the basis of the results of experiments 11—15.

The chain transfer constants, obtained from the curves in Fig. 4 using Eq. 6, are plotted as the function of the R in Fig. 5. On the other hand, the constants in the liquid phase obtained by this method are $c_1=0.062$, $c_2=0.056$, and $c_3=0.073$ at $R=18$;[2)] these values are smaller than the present values in the gaseous phase.

The 1-Hydroxyethyl Radical.—The 1-Hydroxyethyl radical, (radical III, Table III) is considered to be one of the precursor on the basis of the presence of hexanol-2, as is shown in Table III. However, butanol-2 could not be identified by gas chromatography, for this peak was covered by the tail of 2-methylbutanol-2. Ethanol might be formed by the reaction with propanol-2, but this product could also not be identified because of the large peak of propanol-2. Therefore, the G-value of this precursor radical cannot be estimated quantitatively. However, this is not so important as in the mass-spectrum.

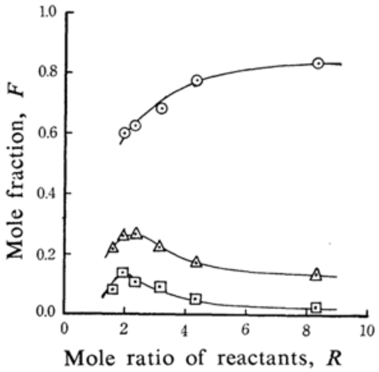

Fig. 4. The mole fractions of the telomers produced, F, as a function of the mole ratio, (propanol-2)/(ethylene), R (experiments 11—15). Marks are the same as in Fig. 2.

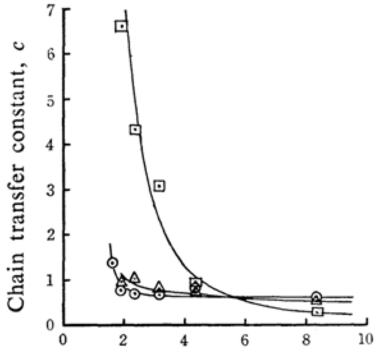

Fig. 5. The chain transfer constants, c, estimated by Eq. 6 as a function of mole ratio, (propanol-2)/(ethylene), R (experiments 11—15); c_1 (⊙), c_2 (△) and c_3 (⊡).

Other Precursor Radicals. — As Table III shows, the 2-hydroxypropyl, isopropoxyl and isopropyl radicals are also assumed to be precursors on the basis of the presence of the identified products. The G-value of heptanol-2, expected from the 2-hydroxypropyl radical, seems to be small.

The Temperature Dependence of the Yields.—The results of experiments 3, 6—9 (Table I) showed that the yields of the products, including the unidentified ones, decreased with a decrease in the temperature, except for the telomers of radical I in Table III, and that the twenty-two products could not be found by gas chromatography from the samples at 100 and 125°C. The amounts of some of the products produced are plotted in Fig. 6 against the reciprocal of the absolute reaction temperature. As is shown by the dotted lines in Fig. 6, the yield of telomers increased also at lower temperatures. This is either due to the condensation of some part of the propanol-2 on the wall of the tube, thus suppressing the radical transfer reactions or disproportionation reactions and promoting the addition reactions in the liquid phase, as has been discussed already, or to such conditions at a lower temperature, even if it is not condensed. This seems to support the latter assumption that a large number of the products are not

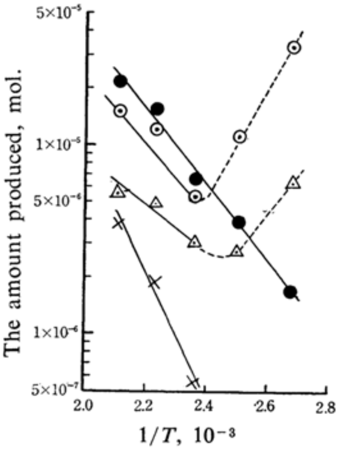

Fig. 6. The amounts of products as a function of the reciprocal of absolute reaction temperature (experiments 3, 6—9); acetone (●), 2-methylbutanol-2 (⊙), 2-methylhexanol-2 (△), and ethyl isopropyl ether (×).

formed at lower temperatures, as has been pointed out above.

The apparent activation energies of the formation of 2-methylbutanol-2, 2-methylhexanol-2, acetone and ethyl isopropyl ether are 8.40, 5.75, 9.19 and 15.7 kcal./mol. respectively, judging from the slope of the curves at higher temperatures in Fig. 6. The value of 2-methylbutanol-2 in the liquid phase is 6.3 kcal./mol. according to Hirota and Hatada.[2)] On the other hand, the activation energy of the hydrogen abstraction reaction from propanol-2 by the methyl radical is 7.3 kcal./mol. according to Trotman-Dickenson and Steacie.[8)]

Summary

When a mixture of propanol-2 and ethylene was irradiated in the gaseous phase by cobalt-60 gamma-rays at 100°C to 200°C, thirty-seven products were found by gas chromatography from the samples above 150°C in addition to the telomers already reported, while fifteen products were found at 100°C. While the yield of these products increased with an increase in the temperature, the yield of the telomers increased not only with an increase in the temperature but also with a decrease in the temperature below 125°C. The identified products show that all the kinds of radicals, which were expected from propanol-2 are present as the precursors of these products. It has been concluded from these facts that the various radical transfer reactions and disproportionation reactions occur in the gaseous phase, especially above 150°C, although the addition reactions are predominant in the liquid phase at lower temperatures. On the other hand, although 1-hydroxyethyl radical ions are predominant in the electron impact of propanol-2, the 1-hydroxyisopropyl radical is predominant among the precursor radicals. This shows that the present processes are radical and not ionic.

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8) A. F. Trotman-Dickenson and E. W. R. Steacie, *J. Chem. Phys.*, **19**, 329 (1951).