Synthesis of Several Tertiary Alcohols from Propanol-2 and Ethylene by Gamma-ray Irradiation[*]

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In previous reports[1,2], it was found that several higher ketones can be synthesized by a chain telomerization from acetaldehyde and terminal olefins by γ-ray irradiation with high G values. Similar telomerization may also occur with a high yield in the system of propanol-2 and ethylene, considering Urry's research[3] on the peroxide- and light-induced additions of several alcohols to olefins. The chain-carrying radical of this system, however, is $(CH_3)_2\dot{C}OH$ instead of $CH_3\dot{C}O$ in the systems of acetaldehyde and olefins, as will be shown as follows:

Initiating step:

$$(CH_3)_2CHOH \rightsquigarrow (CH_3)_2\dot{C}OH + H$$

Propagating step:

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[*] Chain Telomerization Induced by Gamma-rays. II.

[1] K. Hirota and M. Hatada, This Bulletin, 33, 1682 (1960).

[2] K. Hirota, S. Iizuka and M. Hatada, Abstract Papers of the 13th Annual Meeting of the Chemical Society of Japan (1960).

[3] W. H. Urry et al., *J. Am. Chem. Soc.*, 76, 450 (1954).

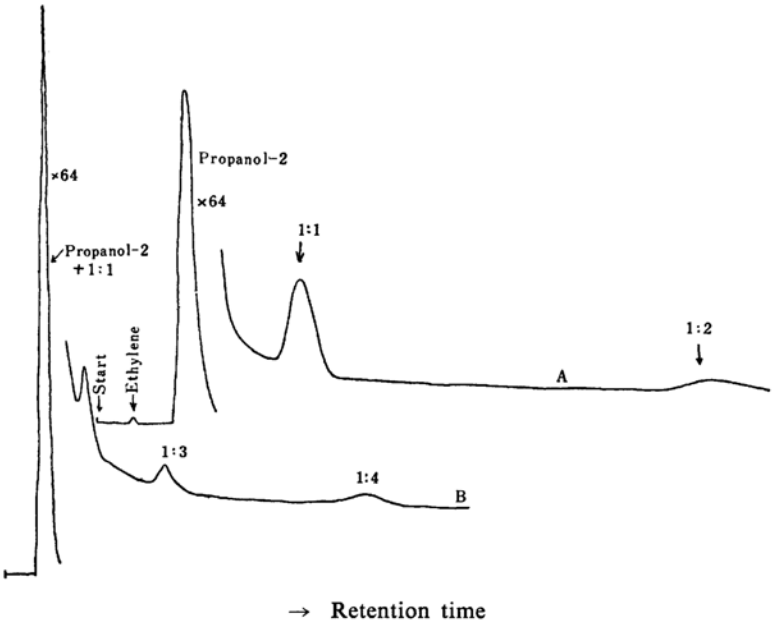
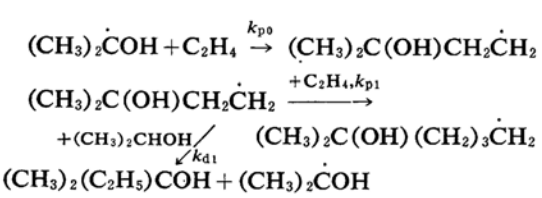


Fig. 1. Gaschromatograms of the samples after irradiation.
Curve A was obtained by using D. O. P. 3 m. column at 107°C.
Curve B was obtained by using H. V. O. 6 m. column at 180°C.



$$(CH_3)_2\dot{C}OH+C_2H_4 \xrightarrow{k_{p0}} (CH_3)_2C(OH)CH_2\dot{C}H_2$$

$$(CH_3)_2C(OH)CH_2\dot{C}H_2 \xrightarrow{+C_2H_4,k_{p1}} (CH_3)_2C(OH)(CH_2)_3\dot{C}H_2$$

$$+(CH_3)_2CHOH \swarrow k_{d1}$$

$$(CH_3)_2(C_2H_5)\dot{C}OH+(CH_3)_2\dot{C}OH$$

By a similar scheme $(CH_3)_2C(OH)(CH_2)_3$-$\dot{C}H_2$ will produce $(CH_3)_2$-$(OH)(CH_2)_3$ and $(CH_3)_2\cdot C(OH)(CH_2)_3CH_2CH_2\dot{C}H_2$ with velocity constants k_{d2} and k_{p2}, respectively, etc.

It is the object of the present paper to report that the expected telomerization proceeds even at room temperature.

Experimental

Commercial pure propanol-2 was used after distillation, while commercial ethylene (research grade) was used without further purification. No impurity was found in the gases by either gaschromatographical or mass-spectral analyses.

Every sample for irradiation was degassed and distillated into glass tubes (1.2 cm. in diameter; ca. 20 cm. in length), equipped with a breakable joints. After the tubes were sealed, they were irradiated by γ-rays from the Co-60 source (700 c) installed in this laboratory. Dosimetry was based on a ferrous oxidation yield of 15.5. After the irradiation, the samples were taken out through the breakable joint and were put through gaschromatographic analysis (Apparatus; Shimadzu GC1A type).

The initial ratios of propanol to ethylene in the sample were about ten if otherwise not described. These ratios will be denoted as R hereafter, which, however, is not necessarily equal to that in solution, because ethylene is hardly soluble.

Results

In the sample irradiated, *tert*-amyl alcohol (1 : 1 telomer) and *tert*-heptyl alcohol (1 : 2 telomer) were identified by the use of a 3.0 m. column of dioctyl phthalate, while *tert*-nonyl alcohol (1 : 3 telomer) and *tert*-undecyl alcohol (1 : 4 telomer) were also detected by the use of a 6.0 m. column of high vacuum-oil (Fig. 1). However, the existence of higher telomers will be estimated, especially when R is large, as is done in the discussions.

In Fig. 2, the amount of the 1 : 1 telomer produced is plotted against the irradiated time. After an induction period is observed in the initial part of the curve, a linear increase is found in the amount. It is interesting to note that a similar induction period was also observed4) in the gamma-ray-induced telomerization of acetaldehyde and ethylene. Such an effect may be due to the presence of some undetectable impurities, e. g. oxygen or other radical-scavengers. The G value calculated from the linear part of the curve is ca. 1.2×

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4) Cf. K. Hirota, H. Ochi and M. Hatada, *Isotopes and Radiation* (*Tokyo*), 3, No. 6 (1960). (Short communication).

10^2, suggesting that this reaction proceeds by a chain mechanism. Figure 3 shows the relation between *R* and *G* values of the product at 9°C, where other variables are kept constant. By use of the data of Fig. 3 molar fraction F_i of the 1 : *i* telomers to the total telomers is plotted in Fig. 4, making *R* as the ordinate. The full curves in the figure will be explained in the discussion.

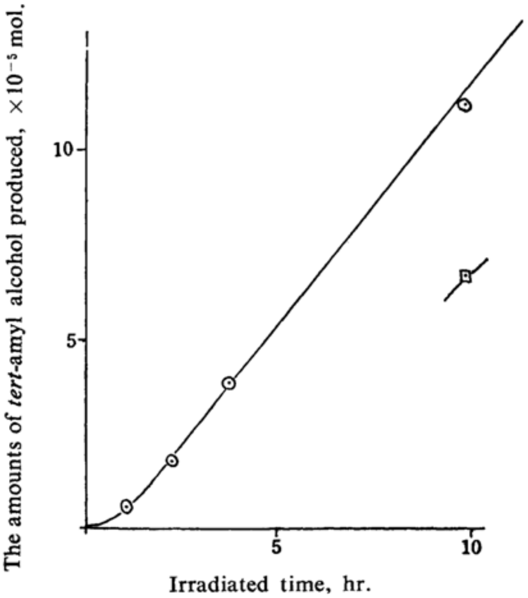

Fig. 2. The amounts of *tert*-amyl alcohol vs. irradiation time.
Dose rate, 5.7×10^4 r/hr.
$(CH_3)_2CHOH/C_2H_4(=R)$ in mole, 1 : 10
Irradiation temperature, 6°C

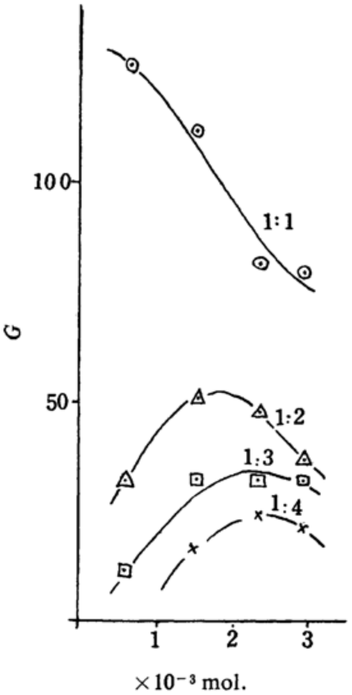

Fig. 3. *tert*-Alcohols produced vs. the amount of ethylene in the system.
Dose rate, 5.7×10^4 r/hr.
Energy absorbed, 8.5×10^{19} eV.
Irradiation temp., 9°C

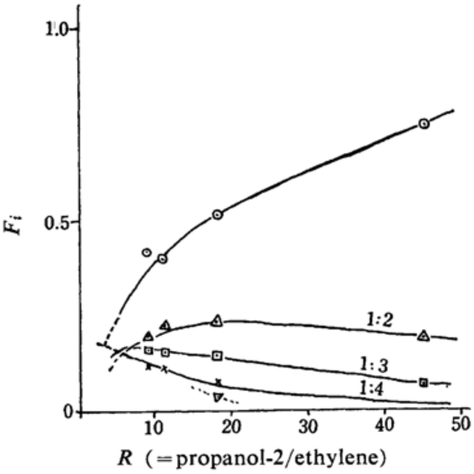

Fig. 4. Distribution of the telomers corresponding to the data of Fig. 3.
—— Calculated by

$$F_i=\frac{C_n R}{\prod_{i=1}^{n}(C_i R+1)}$$

▽ Assumed value for 1 : 5 telomer

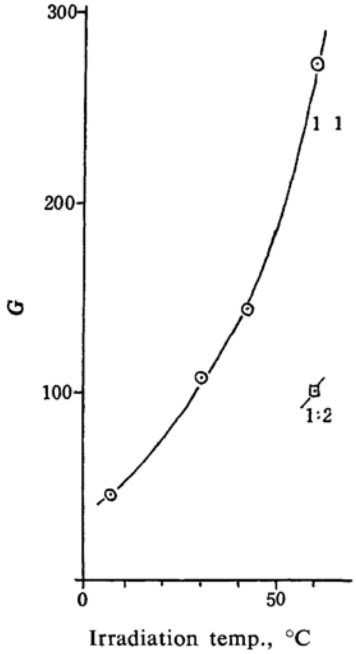

Fig. 5. *tert*-Amyl alcohols vs. irradiation temp.

Temperature dependency of G values on the amount of the products is shown in Fig. 5. It is clear that the higher is the reaction temperature, the more *tert*-amyl alcohol is produced and G value reaches about 300 at 60°C. Plots of logarithms of the G values vs. $1/T$°K give a straight line as shown in Fig. 6, by which an activation energy of 6.3 kcal./mol. can be determined. This value, however, is not necessarily that of the reaction, but is of complex nature, because the solubility of ethylene into alcohol changes when the reaction temperature is changed as is seen in our experiment.

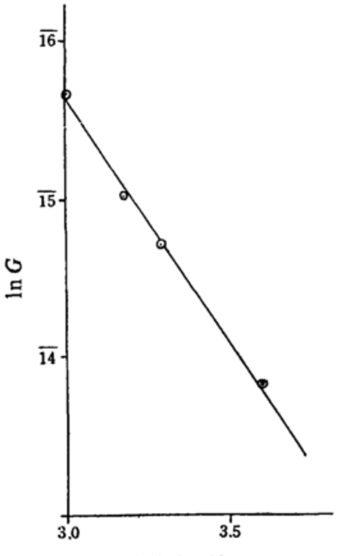

Fig. 6. ln G(*tert*-amyl alcohol) vs. $1/T$°K. $E_A = 6.3$ kcal./mol.

Discussion

If the telomerization proceeds by the reaction scheme shown in the introduction, the distribution of the telomers produced will be given as molar fractions F_i by the theoretical relation⁵⁾:

$$F_i = \frac{C_i R}{\prod_{i=1}^{n}(C_i R + 1)}$$

where C_n's$=k_{dn}/k_{pn}$ are transfer constants. Assuming that the molar ratio of alcohol to ethylene in the solution is the same as that (R) of the starting material and that higher telomers are produced though small in amount, chain transfer constants C_i's were calculated from the observed F_i's in the sample of $R=18$, and were found to be 0.062, 0.056, 0.073 and 0.12 for $i=1$, 2, 3 and 4, respectively, if G value of 1 : 5 telomer is assumed to be 8. The mean value of C_1, C_2 and C_3, i. e. 0.062, resembles Urry's average transfer constant, 0.057³⁾, obtained at 115~130°C, using di-*tert*-butyl peroxide as initiator. This means that the chain-propagating step of the radiation-induced reaction is similar to that of the reactions induced by chemical initiators, although the reaction temperatures, pressure and R values are different in the two reactions.

However, exactly speaking, plots of F_i determined from the observed data vs. R do not lie on the full curves calculated from the above C_i's so completely as shown in Fig. 4. Similar comparison of the theory and experiment was better in the systems of acetaldehyde and propylene¹⁾ or isobutylene²⁾. The discrepancy in this system may be brought about by the assumptions adopted in the calculation i. e., G value of 1 : 5 telomer and neglect of the change of solubility of ethylene to propanol-2 with pressure. Though a better coincidence may be obtained by the introduction of solubility data, this correction could not be carried on, because of the absence of such data. On the other hand, production of higher alcohols, corresponding to 1 : i telomer ($i \gtrsim 5$), ought to be considered, as assumed to some extent in the calculation, because if they are completely neglected, the coincidence became more than that shown in Fig. 4.

The overall activation energy obtained above (6.3 kcal./mol.) nearly equals that of the abstraction reaction of hydrogen atom from α-carbon of propanol-2, i. e., 7.3 kcal./mol.⁶⁾ Considering the ambiguity included in the former value, such a degree of coincidence indicates that the step which produces the chain-carrying radical may be regarded as being the rate-determining one in the above mechanism.

In the irradiated samples containing a small amount of iodine (10^{-3} mol. in propanol-2), not even a trace of telomers was found, probably due to the radical-scavenging action of iodine. This finding may serve as an evidence of the radical mechanism as assumed by us. However, since formation of CH_nI^+ and CH_4OI^+ was recently observed mass spectrometrically by the ion-molecule reactions⁷⁾;

$$CH_n^+ + I_2 \rightarrow CH_nI^+ + I$$

$$\text{or} \quad CH_n^+ + I_2 \rightarrow CH_{n-1}I^+ + HI$$

$$CH_3OH^+ + I_2 \rightarrow CH_4OI^+ + I$$

an ion-scavenging action of iodine can be taken into account. It is possible therefore that some ion or ions also play some role in the

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5) Cf. C. Walling, "Free Radicals in Solution", John Wiley & Sons, New York (1957), p. 245.

6) A. F. Trotman-Dickenson and E. W. R. Steacie, *J. Chem. Phys.*, **19**, 329 (1951); *Quart. Rev.*, **7**, 198 (1953).

7) A. Henglein, *Z. Elektrochem.*, **64**, 1015 (1960).

present reaction, but probably in some intermediate step which preceeds the production of $(CH_3)_2\dot{C}OH$. Then the initiating step above the mechanism will be composed of several elementary ones.

Though the *G* value of this telomerization is of the same order of magnitude as the system of acetaldehyde and propylene or isobutylene, it is smaller by one or two orders of magnitude at the same temperature than that of the system where acetaldehyde was used instead of propanol-2[4]. This may be attributed to the difference in nature between the chain-carrying radicals, i. e., acetyl radical and isopropyl radical in both systems.

Summary

Tertiary amyl and higher tertiary alcohols have been synthetized at 6～60°C by irradiating gamma-rays on mixture of propanol-2 and ethylene enclosed in glass vessels. It has been found that as the irradiation temperature the *G* value of these telomers increases markedly, e. g. up to ca. 300 at 60°C. It has been concluded from the distribution of the telomers produced that this reaction proceeds by a chain mechanism, making isopropyl radical $(CH_3)_2\dot{C}OH$ as the chain-carrying radical. It has been estimated that the characteristic of gamma-rays will be found in the step prior to the production of the isopropyl radical. If the rays can play some role in this reaction.

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