Life-time of the Propagating Radicals in the Radiation-Induced Telomerization of Ethylene with Propanol-2*

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In previous reports[1,2] the telomerization of an ethylene - propanol-2 mixture was investigated by using γ-rays as the initiating agent, and it was concluded that the telomers are produced by the following elementary reaction:

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

$$(CH_3)_2\dot{C}OH + C_2H_4 \longrightarrow (CH_3)_2C(OH)-CH_2-CH_2\cdot$$

$$\longrightarrow (CH_3)_2C(OH)CH_2-CH_3$$

$$\text{or } (CH_3)_2C(OH)-CH_2-CH_2-CH_2-CH_2\cdot$$

In the present research, the telomerization of the same system will be investigated by the use of electron beams from a Van de Graaff accelerator instead of γ-rays, adopting both intermittent and steady irradiation methods in order to determine the life-time of the chain-carrying radicals. The results will be given and compared with those of the previous reports.

Experimental

Materials.—Propanol-2 was dried over calcium hydride and was distilled before each use. Commercial ethylene (99.8%) was used without any purification.

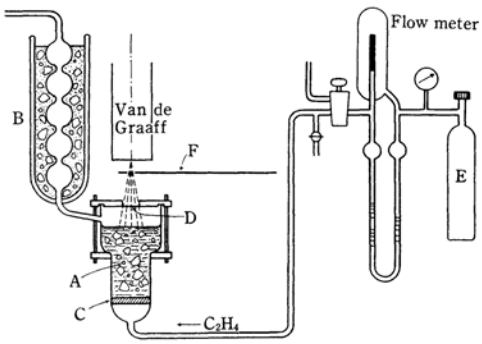

Fig. 1. Apparatus for electron beam irradiation.

Irradiation Procedures.—Figure 1 shows the apparatus for irradiation. Propanol-2 (80 ml.) was held in the irradiation vessel (A) (56 mm. ϕ in diameter) equipped with the condenser (B) kept at $-78°C$, a glass-filter (C) for bubbling ethylene into the vessel, and a window (D) made of aluminum film (0.1 mm. thick, 3.0 cm. in diameter), through which the electron beam penetrates into the irradiation vessel.

For the intermittent irradiation, the rotating sector method was used. A rotating aluminum disk (F) (4 mm. thick, 60 cm. in diameter) with two $\pi/6$ sector openings was placed between the irradiation windows of the Van de Graaff accelerator and the irradiation vessel. The ratio of the off-to-on time was kept constant at 5 throughout the experiments. The period of a whole cycle could be varied from 0.06 to 6.0 sec.

A spot electron beam (1.5 MeV, 100 μamp.) from the Van de Graaff accelerator (High Voltage Eng. Co.) was used for the irradiation. The dose rate was estimated to be 2.6×10^{22} eV. min^{-1} from the amount of oxalate ions produced by the irradiation of an aqueous solution of sodium formate, which was contained in a vessel with the same specifications as the irradiation vessel of propanol-2 and ethylene. This method was proposed and elaborately described by Hardwick and Guenter.[3]

Analysis.—After irradiation, samples were taken out and subjected to gas-chromatographic analysis. (Apparatus: Shimadzu GC1A)

Results

In the sample irradiated, *t*-amyl alcohol could be identified by the use of a 3.0 m. column of dioctylphthalate. The higher telomers found in the previous reports were not identified in the present experiment. In Fig. 2, the amount of *t*-amyl alcohol produced is plotted against the irradiation time. Without any inhibitor, as is indicated by the open circles in the figure, the amount of telomer increases linearly with the irradiation time. By the addition of 3.66×10^{-4} mol. of DPPH, some retardation was observed, as is indicated by the filled circles. The inclinations of the linear part of the two lines are equal, however.

By the use of a gas chromatograph equipped with a hydrogen flame ionization detector, several products other than *t*-amyl alcohol were

* Chain Telomerization Induced by Radiation. VII. Preliminary report: M. Hatada and K. Hirota, The 5th Meeting of Radiation Chemistry, Tokyo, 1962.

1) K. Hirota and M. Hatada, This Bulletin, 34, 1644 (1961).

2) M. Hatada and K. Hirota, Proceedings of the 4th Conference on Radioisotopes, 294 (1961), Tokyo.

3) T. J. Hardwick and W. S. Guenter, *J. Phys. Chem.*, 63, 897 (1961).

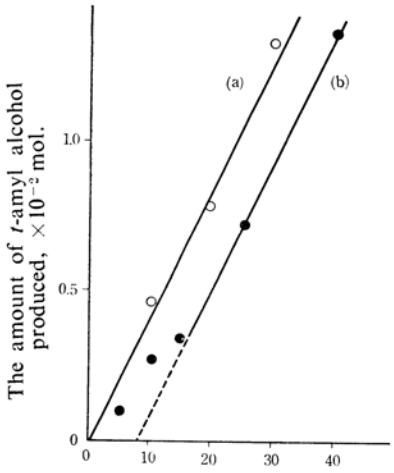

Fig. 2. The amount of *t*-amyl alcohol produced vs. irradiation time.
○ : without inhibitor
● : 3.6×10^{-4} mol. DPPH
Electron accelerating voltage : 1.5 MeV.
Electron beam current : 100 μamp.
Dose rate : 2.5×10^{22} eV./min.
Ethylene flow rate : 128 ml./min.

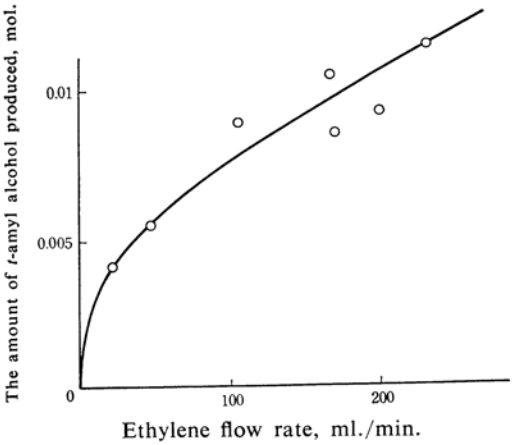

Fig. 3. The amount of *t*-amyl alcohol produced vs. flow rate of ethylene.
Isopropanol 80 ml.
Irradiation acc. volt : 1.5 MeV.
beem curr.: 100 μamp.
time : 30 min.

found to be produced. The details of the results will be published elsewhere.

In Fig. 3 the amount of the telomer produced after 30 min. of irradiation is plotted against the flow rate of ethylene. Up to the flow rate of 30 ml./min., the rate of telomer formation increases markedly with the flow rate of ethylene, but above this critical flow rate the rate of formation seems to increase linearly with the ethylene flow rate.

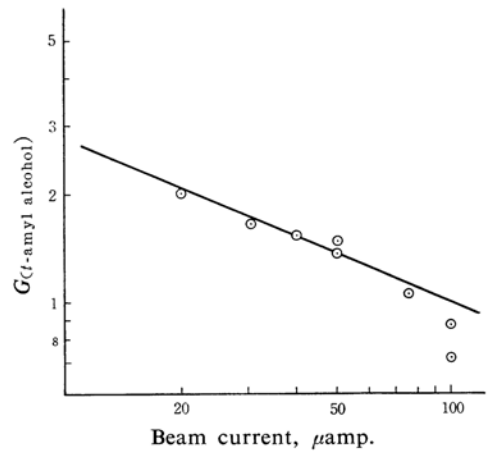

Fig. 4. $G_{(t\text{-amyl alcohol})}$ vs. electron beam current.
Ethylene flow rate : 128 ml./min.

In Fig. 4 the G value for *t*-amyl alcohol formation is plotted against the electron beam current in logarithmic scales. Since the dose rate depends linearly on the beam current, the G value for telomer formation is proportional to the $-1/2$ power of the dose rate.

The results of the sector experiment are shown in Fig. 5, in which the R_0/R_s is plotted

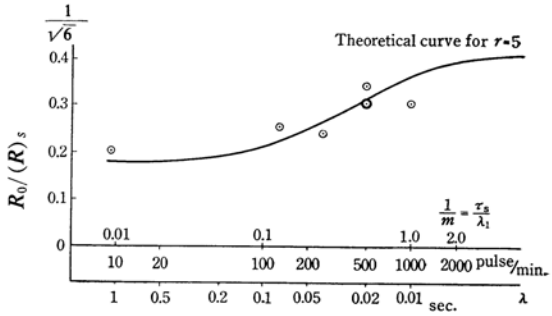

Fig. 5. Comparison of theoretical and experimental relative reaction rates.
Dose rate : 2.6×10^{22} eV./min.
Ethylene flow rate : 128 ml./min.

against logarithms of the pulse frequency in pulses/min. as the abscissa, where R_0 and R_s are the average radical concentration under intermittent and steady irradiations respectively and are assumed to be given by the amount of the telomer produced by irradiation. The theoretical curve shown in the same figure is plotted against λ_1/τ_s from the table by Burnett and Melville,[4] where λ_1 is the time when the beam is on, and τ_s is the mean life-time of the radicals.

4) G. M. Burnett and H. W. Melville, "Techniques of Organic Chemistry," Vol. IV, Interscience Publishers, New York (1953), p. 144.

Discussion

As is shown in Fig. 2, the formation of *t*-amyl alcohol was not inhibited completely, but it was retarded by the addition of DPPH. This retardation may be caused by the fact that, because of the high concentration of radicals produced by the electron beams of a high dose rate, DPPH can not inhibit the telomer formation effectively.

On the other hand, this retardation might be considered to be a contribution of some reaction paths which are not affected by the presence of DPPH. However, in the present research, these paths were assumed to play little part in the telomer formation.

The rate of initiation, v_i, was estimated approximately to be of the order of 10^{-5} mol. l^{-1} sec^{-1} from the following equation:

$$v_i = -\frac{d[DPPH]}{dt} \simeq \frac{\Delta[DPPH]}{\Delta t}$$

Where [DPPH] is the initial concentration of diphenylpicrylhydrazyl in mol. l^{-1} and Δt is the induction period in sec. assumed to be given by the intercept of curve b.

From the λ_1 scale of Fig. 5, where λ_1/τ_s is unity, τ_s is estimated to be 0.01 sec. This value is a little smaller than that estimated by Clingman in a similar telomerization reaction between *n*-butylmercaptane and *n*-octene,[5] although the chain-carrying radicals and dose rates are different in the two cases.

However, there remain some ambiguities which may arise from the shape of the electron pulses. The electron pulses used in the present research were not exactly square in shape, but were rather complicated, because each pulse consisted of a number of trigonometrical waves of 400 c./sec., which might be induced by the rotating magnetic field (400 c./sec.) of the generator of the Van de Graaff accelerator. However, since the frequency of pulses was very low compared to 400 c./sec., the pulse shape can be regarded as square.

If the dissolving or diffusion rate, k_s, of ethylene into propanol-2 and the rate of reaction 2, k, in the following scheme:

$$(E)_g \xrightarrow{k_s} (E)_s \qquad (1)$$

$$(P\cdot) + (E)_s \xrightarrow{k} (PE\cdot) \qquad (2)$$

are assumed to have a significant role in the reaction, the plots in Fig. 5 might be explained in terms of k_s. However, since it has been reported that the diffusion rate did not affect the sector curve in the system of *n*-butylmercaptane and *n*-octene,[5] the diffusion rate was assumed to be negligible in the present research.

By the use of the data obtained, the average concentration of radicals, R_s, the kinetic chain length, ν, and the rate constant of the termination reaction k_t, can be estimated to be of the order of 10^{-7} mol^{-1}, 10 and 10^9 mol^{-1} l. sec^{-1} respectively from the following relations:

$$\tau_s = [R_s]/v_i, \quad [R_s] = (v_i/k_t)^{1/2} \text{ and } \nu = \frac{v_p}{v_i}$$

The G value for telomer formation obtained in the present research is compared in Table I with that obtained in the γ-ray irradiation,

Table I. The effect of the dose rate on G(*t*-amyl alcohol)

Radiation source	Electron beams from the Van de Graaff Accelerator		γ-Rays from cobalt-60
Dose rate, I (eV./min.)	7.2×10^{22}	5×10^{22}	8×10^{16}
$I_e/I\gamma$	960	780	1
G(*t*-amyl alcohol)	1.6$_7$	2.0	250

as has already been reported.[1] The G value in the present paper is smaller than that in the former by a factor of 10^2. This can be explained as being caused by a higher dose rate of the electron beam, considering that G (telomer) depends on the $-1/2$ power of the dose rate. There are some ambiguities in this comparison, however, which come from the non-uniformity of the dose rate in the present system caused by the weaker penetrating power of the electron beams.

Conclusion

It has been found that the 1:1 telomer, *t*-amyl alcohol, is produced by electron irradiation, and that it has a G value smaller than that obtained by γ-irradiation. The average life-time of the radicals of the rate-determining step has been estimated to be 0.01 sec. by the rotating sector method.

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