The Radiation-Induced Addition of Acetaldehyde to Isobutylene[*]

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It has been found by the present authors that several ketones of the $CH_3CO(CH_2)_nH$ ($n=1, 2, 3, \cdots$) type can be synthetized by the radiation-induced telomerization of acetaldehyde to olefins, propylene[1] and ethylene[2] at room temperature with high G values. The mechanism can be ascribed to a chain telomerization reaction as follows,

$$CH_3CHO \rightsquigarrow CH_3\dot{C}O + H\cdot \qquad (1)$$

$$CH_3\dot{C}O + RCHCH_2 \longrightarrow CH_3COCH_2R\dot{C}H \qquad (2)$$

$$CH_3COCH_2R\dot{C}H + CH_3CHO \xrightarrow{k_d} CH_3COCH_2RCH_2 + CH_3\dot{C}O \qquad (3)$$

$$\text{or } CH_3COCHR\dot{C}H + RCHCH_2 \xrightarrow{k_p} CH_3COCH_2RCHCH_2R\dot{C}H \qquad (4)$$

and so on.

The first purpose of the present paper is to investigate the effect of the structure of taxogens on such a telomerization reaction, making isobutylene a taxogen of branched olefins. The second purpose is to analyze the products in detail so as to investigate the radical mechanism described above, because this monomer is easily polymerizable by a cationic mechanism.

Experimental

Materials.—Acetaldehyde was prepared by heating commercial paraldehyde, which had been purified by distillation at 70°C, with a small amount of concentrated sulfuric acid. The final product was again distilled in vacuo. Isobutylene was prepared by dehydrating commercial *t*-butyl alcohol with concentrated sulfuric acid at 70°C. Impurities were found to be less than 0.5% by the gas chromatographic method.

Procedure.—The sample was carefully deaerated by evacuation; then, while being kept at −80°C, it was enclosed and irradiated in a glass ampoule. Irradiation was carried out in the ampoule with a gamma-ray source (ca. 1000 curie Co-60) installed in the present laboratory. The dose rate was determined with a Fricke dosimeter.

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[*] Chain Telomerization Induced by Radiation. IV.

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

[2] K. Hirota, S. Iizuka, H. Ochi and M. Hatada, ibid., 36, 115 (1963).

For the detailed analysis of the irradiation products, a large amount of the sample (acetaldehyde/isobutylene=1.6; 200 g.) was irradiated at the dose rate of 4×10^4 r/hr. and the total dose of 5×10^7 r. After the irradiation, unreacted acetaldehyde and isobutylene were separated by distillation, and the residue obtained was fractionally distilled. Each fraction was analyzed by the use of a gas chromatograph (apparatus: Shimadzu GC-1A), an infrared spectrometer (Shimadzu AR-275), and a nuclear magnetic resonance spectrometer (Varian V-4300 B; field modulation, 40 Mc./sec.). In some cases they were derived to 2, 4-dinitrophenylhydrazone, whose melting point was determined. However, in most cases, 10 g. of the sample was irradiated in an ampoule (1.2 cm. in diameter; 15 cm. in length), and the products were analyzed. In the case of irradiation at a higher temperature, 5 g. of the sample was used in an ampoule (1.2 cm. in diameter; 5 cm. in length), the ampoule being get up in a small autoclave. After irradiation, each ampoule was opened, and unreacted acetaldehyde and isobutylene were carefully distilled out. The residue obtained was quantitatively analyzed by gas chromatography.

The effects of catalysts on the reaction were investigated, enclosing the catalysts prepared as follows; a) Nickel: nickel, prepared by decomposing commercial nickel formate (12 g.) for 2 hr. at 380°C, was evacuated for 2 hr. at the same temperature. b) Zinc oxide: commercial zinc oxide (5 g.) was evacuated for 2 hr. at 250~300°C. c) Alumina for chromatography (8 g.) was evacuated for 2 hr. at 350~400°C. d) Silica gel: silica gel for chromatography (8 g.) was evacuated for 2 hr. at 350~400°C. After irradiation, the ampoule was opened, and the catalyst was filtered off by a glass filter (G-4). The filtrate was analyzed by the method described above.

Results and Discussion

Identification of the Irradiation Products.—Figure 1 shows the gas chromatograms of the irradiation products. The large peak, P_1, was easily assigned to acetaldehyde. The P_2 peak was separated into two peaks, P_{2-1} and P_{2-2}, by the use of a 3.0-m. column of dioctylphthalate at 120°C instead of a 5.3 m. column of high vacuum oil. The retention times of P_{2-1} and P_{2-2} agreed with those of methyl *t*-butyl ketone and methyl isobutyl ketone, which in turn correspond to two isomeric 1 : 1 telomers. The formation of two types of telomers had been found previously in the acetaldehyde and propylene system[1].

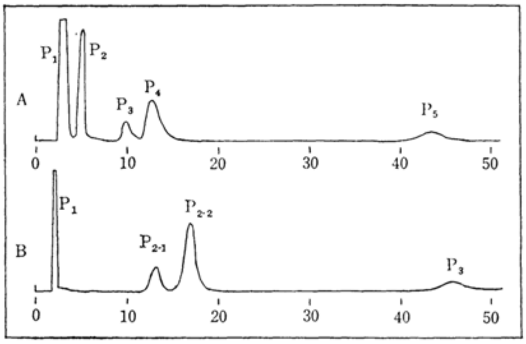


Fig. 1. Gas chromatograms of the irradiation products.

Curve A was obtained by using a high vacuum oil 5.3 m. column, and He as carrier gas (120 ml./min.) at 180°C.

Curve B was obtained by using a dioctyl phthalate 3.0 m. column, and He as carrier gas (120 ml./min.) at 120°C.

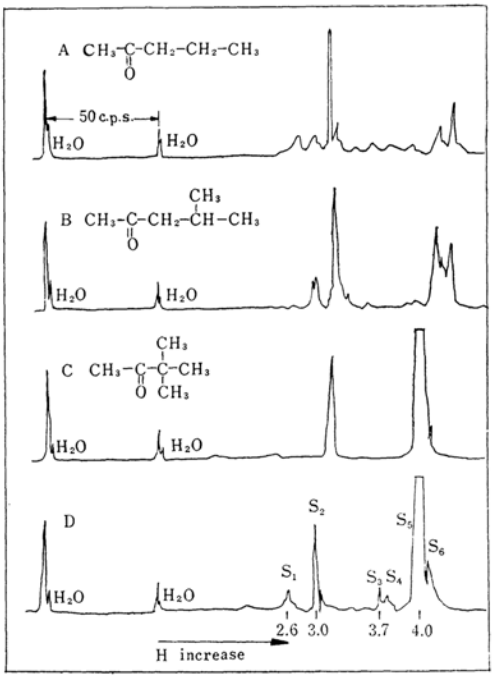


Fig. 2. NMR spectra of the second fraction of irradiation product and related compounds (40 Mc./sec.).

A Methyl *n*-propyl ketone

B Methyl isobutyl ketone

C Methyl *t*-butyl ketone

D The second fraction of irradiation product

From a large irradiated sample, two fractions were obtained by distillation. The first fraction (b. p., 114~117°C at 760 mmHg) corresponds to P_{2-2} and was identified as methyl isobutyl ketone, 1 : 1 telomer, by the retention time of the gas chromatogram, the boiling point and the melting point of its 2, 4-dinitrophenylhydrazone. The second fraction (96~101°C at 37~38 mmHg) corresponds to the P_4 peak. The reaction of this fraction with 2, 4-dinitrophenylhydrazine gave a red brown oily substance. The infrared spectrum of the second fraction showed a carbonyl band at 1720 cm^{-1} and isopropyl bands at 1150 and 1170 cm^{-1}.

TABLE I. CHEMICAL SHIFT (δ) AND RELATIVE AREAS OF THE NMR SIGNALS*

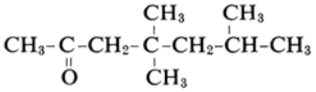
	$-CH_2-(\alpha)$		CH_3-CO		$-CH_2-(\beta)$		$-C-CH_3$	
	δ	Ratio	δ	Ratio	δ	Ratio	δ	Ratio
A	2.8 2.9	1.5	3.2	3.0	3.4 3.6 3.8 3.9	1.0	4.1 4.3	2.3
B	2.9 2.9	1.6	3.2	3.0			4.2 4.2	5.4
C			3.1	3.0			4.0	8.0
D	2.6	1.8	3.0	3.0	3.7 3.8	1.3	4.0 4.1	11.6

A: Methyl *n*-propyl ketons
B: Methyl isobutyl ketone
C: Methyl *t*-butyl ketone
D: The second fraction

$$\delta = \frac{H_{\text{sample}} - H_{\text{reference}}}{H_{\text{reference}}} \times 10^6$$

* One third of the area of the CH_3CO signal was taken as the unit of relative areas.

The NMR spectra (D, A, B and C) in Fig. 2 are that of this fraction and those of its related compounds, i. e., methyl *n*-propyl ketone, methyl isobutyl ketone and methyl *t*-butyl ketone. When one compares the D spectrum with the A, B and C spectra, it is apparent that each signal from S_1 to S_6 in D relates to the proton of the following groups; S_1 to $-CH_2-CO-$ (α-position), S_2 to CH_3-CO, S_3 and S_4 to $-CH_2-$ (β- and more portions) and/or $-CH-$, S_5 and S_6 to CH_3-C. Table I shows the chemical shift δ, taking water as the reference and with the relative areas of the signals making one-third of the area of the CH_3-CO signal as a unit. It can be estimated, therefore, that the second fraction contains substances of one CH_3CO-, one $-CH_2C$ (α) and four CH_3-C groups as well as a few $-CH_2-$ (β- and more positions) and/or $-\overset{|}{C}H-$groups. The mean molecular weight of these substances was determined to be 155 from the freezing point depression of benzene. On the basis of the results described above, the structure of the main substance in the fraction was reasonably estimated to be the 1 : 2 telomer; i. e.,



$$CH_3-\underset{\underset{O}{\|}}{C}-CH_2-\overset{CH_3}{\overset{|}{\underset{\underset{CH_3}{|}}{C}}}-CH_2-\overset{CH_3}{\overset{|}{C}}H-CH_3$$

(molecular weight : 156)

Although the minor products corresponding to the other peaks of the gas chromatogram were not isolated, it may be estimated that two peaks, P_3 and P_5, are due to the isomeric 1 : 2 telomer and 1 : 3 telomer respectively. It is possible, however, that the amount of isomeric 1 : 4 telomer was too small to be detected because of steric hindrance.

The Effect of the Dose on Yields.—The effect of the total dose on the yields of each telomer is shown in Fig. 3 where the dose rate was kept constant at 4.0×10^4 r/hr., while the molar ratio in the feed R, as defined by acetaldehyde/isobutylene, was kept constant at 1.5. After an induction period observed in the initial part of the curves, the amount of each telomer increased linearly. It is interesting to note that similar induction periods had been also observed in the gamma-ray-induced addition of acetaldehyde to ethylene[2] and of propanol-2 to ethylene[3]. It is not certain whether

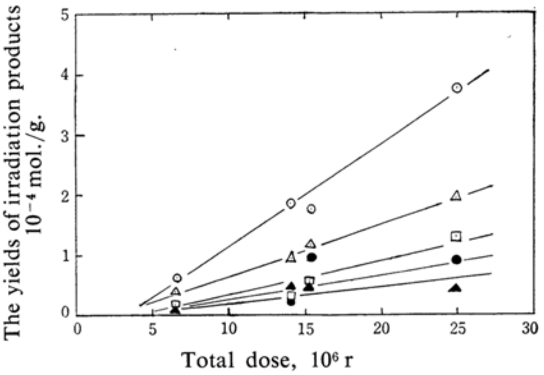


Fig. 3. Amounts of the irradiation products *vs*. total dose.
[acetaldehyde]/[isobutylene] ≒ 1.5
Dose rate 4.0×10^4 r/hr.
⊙, 1 : 1 ; ●, 1 : 1_{iso} ; △, 1 : 2 ; ▲, 1 : 2_{iso} ; ▣, 1 : 3 telomer

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[3] K. Hirota and M. Hatada, ibid., **34**, 1644 (1961).

or not this tendency is due to the presence of some undetectable impurities, e. g., oxygen or other radical-scavengers.

Generally speaking, the yields decreased by one or two orders of magnitude upon the substitution of isobutylene for propylene or ethylene as the taxogen. The reason for such a smaller reactivity of isobutylene will be discussed later.

The Effect of the Dose Rate on *G* Values.—In Fig. 4, the logarithms of the *G* values of the telomers, $G(1:n)$, are plotted against the logarithm of the dose rate. It is shown that in the cases of $G(1:1)$, $G(1:2)$ and $G(1:3)$, linear relations were otained, their inclination being nearly equal to −0.50, i. e., −0.47, −0.47 and −0.52 respectively. Since −0.50 is expected to occur in the case of the bimolecular termination of radicals, this finding seems to indicate a radical chain mechanism. However, $G(1:1_{\rm iso})$ and $G(1:2_{\rm iso})$ were not affected by the dose rate; thus suggesting a contrary thesis that these telomers were produced according to a mechanism different from that of the major telomers.

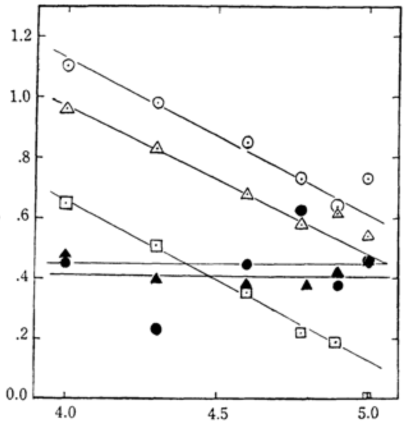


Fig. 4. log *G* vs. log (dose rate).
[acetaldehyde]/[isobutylene]≒1.5
Total dose; 1.5×10^7 r
⊙, 1 : 1; ●, 1 : $1_{\rm iso}$; ◬, 1 : 2;
▲, 1 : $2_{\rm iso}$; ⊡, 1 : 3 telomer

The Effect of the Molar Ratio in the Feed on *G* Values.—In Fig. 5, the *G* values of the telomers produced at 15°C are plotted against the molar ratio in the feed, taking both total dose and dose rate at constant values, i. e., at 2.2×10^7 r and 4.0×10^4 r/hr. respectively. It is shown that $G(1:1)$ was larger than the other *G*'s and that it increases markedly with the molar per cent of acetaldehyde, but that even its maximum value was smaller by one or two factors than the corresponding one when ethylene or propylene was adopted as the taxogen.

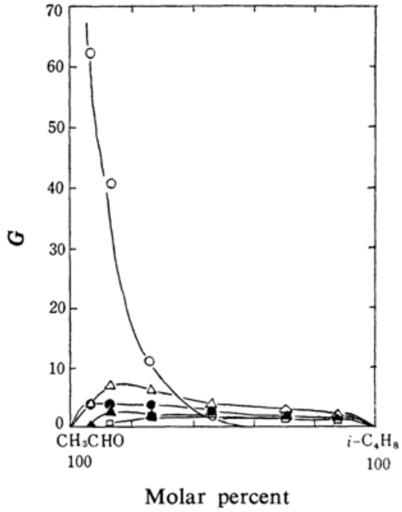


Fig. 5. *G* vs. molar percent.
Dose rate 4.0×10^4 r/hr.
Total dose 2.1×10^7 r
Irradiation temp., 15°C
⊙, 1 : 1; ●, 1 : $1_{\rm iso}$; ◬, 1 : 2;
▲, 1 : $2_{\rm iso}$; ⊡, 1 : 3 telomer

Another point to be mentioned is the finding that $G(1:1_{\rm iso})$ and $G(1:2_{\rm iso})$ did not depend on the molar ratio so markedly; this is the second fact which seems to be related to the mechanism of these products.

The Effect of the Irradiation Temperature on *G* Values.—The *G* values of telomers are plotted against the irradiation temperature in Figs. 6 and 7, where the R's are very different (1.5 and 15 respectively). The *G* values of the 1 : 1, 1 : 2 and 1 : 3 telomers markedly increased with the temperature below 100°C and show a maximum at a temperature between 110 and 150°C. The decrease in the *G* values of these products at higher temperatures may result from the decomposition of the acetaldehyde molecule, the acetyl radical and/or other intermediate radicals.

By plotting the logarithm of these values at a low temperature against $1/T$, relatively good straight lines were obtained. The apparent activation energies of formation were thus determined to be 6.5, 5.8 and 7.0 kcal./mol. for 1 : 1, 1 : 2 and 1 : 3 telomer respectively. These values are slightly larger than those observed in the case of acetaldehyde and ethylene[2), i. e., 5.0 kcal. for the 1 : 1 telomer. However, it seems that $G(1:1_{\rm iso})$ and $G(1:2_{\rm iso})$ remained constant in relation to the temperature, suggesting a low activation energy. This point will be taken up again below.

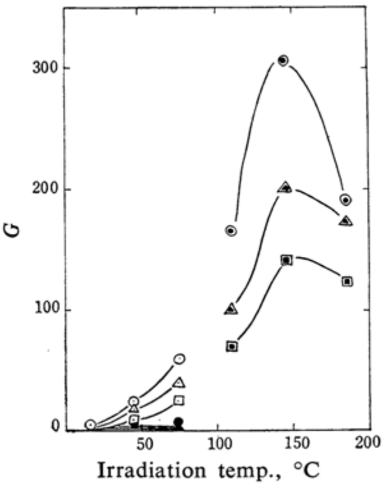


Fig. 6. G-values vs. irradiation temperature. (R≒1.5)
⊙, 1 : 1 ; ●, 1 : 1_{iso} ; △, 1 : 2 ; ▲, 1 : 2_{iso} ; ▣, 1 : 3 telomer
Dose rate 1.8×10^4 r/hr.
Total dose 7.4×10^6 r
⊙, 1 : 1 ; △, 1 : 2 ; ▣, 1 : 3 telomer
Dose rate 1.0×10^4 r/hr.
Total dose 1.0×10^6 r

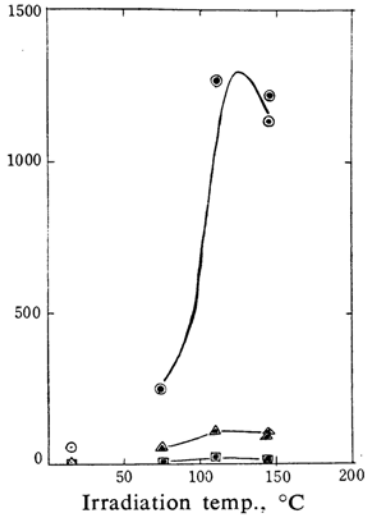
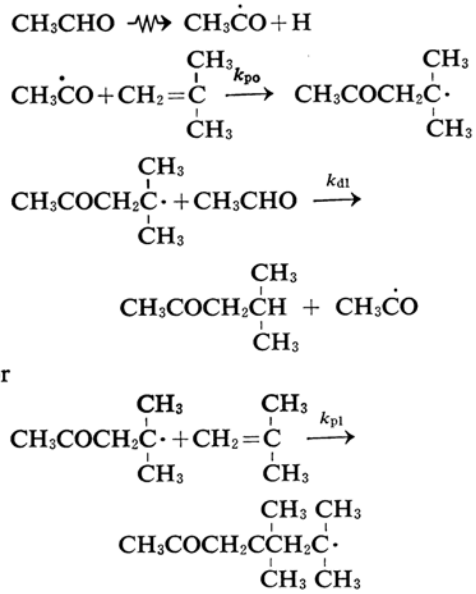


Fig. 7. G-values vs. irradiation temperature. (R≒15)
⊙, 1 : 1 ; △, 1 : 2 ; ▣, 1 : 3 telomer
Dose rate 4×10^4 r/hr.
Total dose 2.1×10^7 r
⊙, 1 : 1 ; △, 1 : 3 telomer
Dose rate 1.0×10^4 r/hr.
Total dose 1.0×10^6 r/hr.

Reaction Mechanism.—Considering the effects on the G(telomers) described above, it may be said that the major parts of the telomers are produced by the following chain schemes, which have been proposed by the present authors1,2) or by others4).



$$CH_3CHO \rightsquigarrow CH_3\dot{C}O + H$$

$$CH_3\dot{C}O + CH_2{=}\overset{\displaystyle CH_3}{\underset{\displaystyle CH_3}{C}} \xrightarrow{k_{p0}} CH_3COCH_2\overset{\displaystyle CH_3}{\underset{\displaystyle CH_3}{C}}\cdot$$

$$CH_3COCH_2\overset{\displaystyle CH_3}{\underset{\displaystyle CH_3}{C}}\cdot + CH_3CHO \xrightarrow{k_{d1}}$$

$$CH_3COCH_2\overset{\displaystyle CH_3}{\underset{\displaystyle CH_3}{C}}H + CH_3\dot{C}O$$

or

$$CH_3COCH_2\overset{\displaystyle CH_3}{\underset{\displaystyle CH_3}{C}}\cdot + CH_2{=}\overset{\displaystyle CH_3}{\underset{\displaystyle CH_3}{C}} \xrightarrow{k_{p1}}$$

$$CH_3COCH_2\overset{\displaystyle CH_3}{\underset{\displaystyle CH_3}{C}}CH_2\overset{\displaystyle CH_3}{\underset{\displaystyle CH_3}{C}}\cdot$$

and so on.

On the basis of the data in Fig. 5, the molar fractions F_n's, of the 1 : n telomers to the total telomers were calculated; they are plotted against R in Fig. 6. The lines in the figure indicate the theoretical curves based on the following equation;

$$F_n = \frac{C_n R}{\prod_{i=1}^{n}(C_i R + 1)} \qquad (C = k_{dn}/k_{pn})$$

which was derived by assuming the above scheme5). The chain transfer constants, C_n's, 0.6_0, 1.2_7 and 2.0 were selected as the most

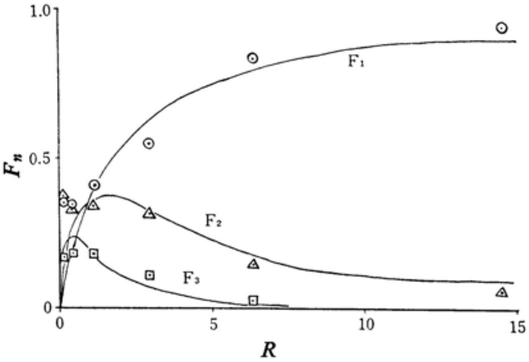


Fig. 8. Molar fractions of 1 : n telomers vs. molar ratio of acetaldehyde/isobutylene in the feed.

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4) C. E. Stoops and C. L. Furrow, *J. Org. Chem.*, **26**, 3264 (1961).

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

TABLE II. CHAIN TRANSFER CONSTANTS OF RADIATION-INDUCED TELOMERIZATION

Telogen	Taxogen	C_1	C_2	C_3	Literature
CH_3CHO	C_2H_4	1.0	1.1	4.6	(2)
CH_3CHO	C_3H_6	0.86	1.64	6.1	(1)
CH_3CHO	i-C_4H_8	0.6	1.2_7	2.0	Present paper
$(CH_3)_2CHOH$	C_2H_4	0.062	0.073	0.12	(3)
CCl_4	C_2H_4		— 0.12(mean) —		γ-Ray initiation (6)
CCl_4	C_2H_4	0.08	0.9	3.2(?)	Peroxide-initiation at 70°C (7)

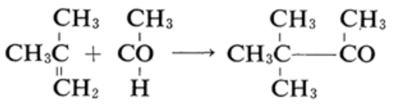
TABLE III. THE EFFECT OF THE PRESENCE OF CATALYSTS ON THE G VALUES OF TELOMERS

Dose rate: 4×10^4 r/hr.; total dose: 1.5×10^7 r

	Absence	Nickel	Zinc oxide	Alumina	Silica gel
1 : 1	17	7.4	2.5	3.1	5.7
1 : $1_{\mathrm{iso.}}$	3	—	—	—	—
1 : 2	13	1.9	0.9	7.0	3.4
1 : $2_{\mathrm{iso.}}$	3	0.2	0.1	1.3	0.6
1 : 3	7.5	0	1.0	5.7	2.1

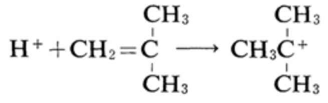
probable values. However, the observed values at a smaller R value do not lie on the calculated curves. This may be due to the errors caused by the use of $G(1:1)+G(1:1_{\mathrm{iso}})$ instead of $G(1:1)$ in this region*, and also to the approximation where the amounts of higher telomers ($n\geqq4$) were assumed. For the sake of comparison, chain transfer constants of similar reactions are shown in Table II. As ought to be expected, they are much larger than those in the case of polymerization and take values of an order of magnitude similar to those of peroxide initiation.

However, to summarize the effects of the dose rate, the molar ratio and the irradiation temperature on G values, the mechanism of producing the isomeric 1 : 1 and isomeric 1 : 2 telomers will be different from the above scheme, as has already been suggested. It is natural for the reaction to assume another mechanism; e. g., isomeric 1 : 1 telomer will be produced in accordance with the Markownikoff rule on the addition to a double bond as follows:

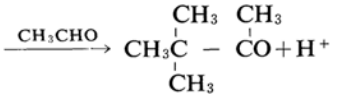


$$\mathrm{CH_3}\overset{\mathrm{CH_3}}{\underset{\mathrm{CH_2}}{\underset{\Vert}{\mathrm{C}}}} + \overset{\mathrm{CH_3}}{\underset{\mathrm{H}}{\mathrm{CO}}} \longrightarrow \mathrm{CH_3}\overset{\mathrm{CH_3}}{\underset{\mathrm{CH_3}}{\mathrm{C}}}\text{——}\overset{\mathrm{CH_3}}{\mathrm{CO}}$$

However, the production of the isomeric 1 : 2 telomer is difficult to explain by this mechanism. Therefore, the following ionic mechanism is more reasonable:



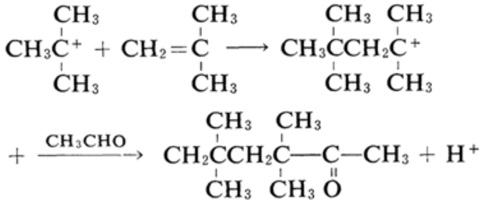
$$\mathrm{H^+ + CH_2}=\overset{\mathrm{CH_3}}{\underset{\mathrm{CH_3}}{\mathrm{C}}} \longrightarrow \mathrm{CH_3}\overset{\mathrm{CH_3}}{\underset{\mathrm{CH_3}}{\mathrm{C^+}}}$$



$$\xrightarrow{\mathrm{CH_3CHO}} \mathrm{CH_3}\overset{\mathrm{CH_3}}{\underset{\mathrm{CH_3}}{\mathrm{C}}} - \overset{\mathrm{CH_3}}{\mathrm{CO}} + \mathrm{H^+}$$

(i-1 : 1 telomer)

or



$$\mathrm{CH_3}\overset{\mathrm{CH_3}}{\underset{\mathrm{CH_3}}{\mathrm{C^+}}} + \mathrm{CH_2}=\overset{\mathrm{CH_3}}{\underset{\mathrm{CH_3}}{\mathrm{C}}} \longrightarrow \mathrm{CH_3}\overset{\mathrm{CH_3}}{\underset{\mathrm{CH_3}}{\mathrm{C}}}\mathrm{CH_2}\overset{\mathrm{CH_3}}{\underset{\mathrm{CH_3}}{\mathrm{C^+}}}$$

$$+ \xrightarrow{\mathrm{CH_3CHO}} \mathrm{CH_2}\overset{\mathrm{CH_3}}{\underset{\mathrm{CH_3}}{\mathrm{C}}}\mathrm{CH_2}\overset{\mathrm{CH_3}}{\underset{\mathrm{CH_3}}{\mathrm{C}}}\text{—}\underset{\mathrm{O}}{\underset{\Vert}{\mathrm{C}}}\text{—}\mathrm{CH_3} + \mathrm{H^+}$$

(i-1 : 2 telomer)

Such an ionic mechanism may be allowed, because isobutylene can be cationically polymerized by gamma-rays, according to Dainton et al.[8] Moreover, it may be explained on the basis of this ionic nature of isobutylene and on the basis of steric hindrance why the G values of this system are much lower than those when ethylene or propylene was used as the taxogen.

The Effect of the Presence of Catalysts on *G* Values.—Table III shows the effects of the presence of catalysts, i. e., nickel, zinc oxide, alumina and silica gel, on the G values of telomers to be produced at room temperature. The G values of all the telomers decreased whenever the catalysts were present. This finding suggests the possibility of the catalytic decomposition of acetyl and other intermediate radicals, but since several by-products were detected in the gas chromatogram, it can be concluded that aldehyde was also decomposed by the contact with these catalysts and was turned into the by-products.

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* Due to experimental reasons, these $G(1:1_{\mathrm{iso.}})$ and $G(1:1_{\mathrm{iso.}})$ values could not be determined separately.

6) M. Takehisa et al., *J. Chem. Soc. Japan, Ind. Chem. Sec.* (*Kogyo Kagaku Zasshi*), **65**, 531 (1962).

7) Ref. 5, p. 257.

8) E. Collinson, F. S. Dainton and H. A. A. Gills, *J. Phys. Chem.*, **63**, 909 (1959).

Summary

The radiation-induced addition of acetaldehyde to isobutylene has been found to proceed at room temperature; the G(telomer)'s are smaller by one or two orders of magnitude than those when ethylene or propylene is adopted as the taxogen, and they increase markedly with the temperature, reaching a maximum at 110～150°C.

It has been shown from the gas chromatographic and NMR analyses of the telomer produced that the radical chain mechanism proposed in former papers by the present authors is reasonable, although minor products seem to be formed in accordance to an ionic mechanism.

It has been found that the G values of all the telomers decrease in the presence of several solid materials, suggesting the catalytic decomposition of acetyl and other intermediate radicals.

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