*Radiation-Induced Addition of Acetaldehyde to Ethylene**

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It was found by two of the present authors¹⁾ that several ketones of the type, $CH_3CO\cdot(C_3H_6)_nH$ ($n=1, 2, 3,\cdots\cdots$), can be synthetized by radiation-induced addition of acetaldehyde to propylene at room temperature with a maximum $G(-C_3H_6)$ value of 150. The mechanism could be ascribed to a following chain reaction, where acetyl radical which plays a role of the initiator is produced not only by irradiation but also by a result of chain transfer.

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

$$CH_3\dot{C}O + C_2H_3R \rightarrow CH_3COCH - \dot{C}HR \qquad (2)$$

$$CH_3COCH_2-\dot{C}HR + CH_3CHO \rightarrow CH_3COCH_2CH_2R + CH_3\dot{C}O \qquad (3)$$

$$CH_3COCH_2-\dot{C}HR + CH_2{=}CH_2 \rightarrow CH_3COCH_2CHRCH_2\dot{C}HR \qquad (4)$$

etc., where R denotes CH_3.

Such a kind of telomerization was later reported by Stoops and Furrow²⁾, who investigated the effect of methyl substitution of both telogen and taxogen, but detailed experimental conditions were not described. Radiation-induced telomerizations of similar type have been reported by several authors, who used different telogen (mercaptan³⁾, carbontetrachloride⁴,⁵⁾, alcohol⁶⁾, etc.), though their taxogen were the same and mostly ethylene. Nevertheless, the details of the research have not been described so extensively, except the recent of Takehisa et al.⁵⁾

It was found since then by the present authors that G values of such telomer formation, G(telomer), depend evidently on the temperature and pressure of the irradiated samples and also on the natures of telogens and taxogens. Especially such a dependency was shown when ethylene was adopted as the taxogen instead of higher olefins, and acetaldehyde as the telogen; moreover, G value of ethyl methyl ketone produced, 1 : 1 telomer of ethylene, reached more than 1000 even at room temperature, as reported in the preliminary paper⁷⁾. Therefore, it will be interesting to report the results of this telomerization, the experimental condition of which was varied over the ranges of pressure and temperature up to 50 kg./cm² and 110°C, respectively.

Experimental

Materials.—Acetaldehyde was prepared by heating commercial paraaldehyde, which had been purified by distillation at 70°C, with a small amount of concentrated sulfuric acid. The final product was again distilled under vacuum. Ethylene was obtained from the Takachiho Chemicals Co., and was purified by vacuum distillation. Impurities of ethylene thus treated were found to be within 0.5% by mass-spectrometric and gas chromatographic measurements.

Procedure. — Two different procedures were adopted according as the experiments were carried out at low or high pressure. In the first experiment, glass tubes were used as in the former reports. The pressure of ethylene in the tubes could not be determined absolutely. Therefore, a bomb equipped with a pressure gage was used in the second experiment. Both procedures and also the results will be described separately.

Experiment at Lower Pressure.—All the samples were carefully deaerated, and then enclosed in the glass tube, shown in Fig. 1. The following procedure was adopted in order to avoid polymerization of acetaldehyde when it was cooled with liquid nitrogen: 1) A measured amount (0.05 mol.) of acetaldehyde was introduced into A of the glass tube by cooling it at −78°C; 2) the tube was sealed off at B, and connected to the vacuum system at C; 3) a measured amount (0.027_4 mol.) of ethylene was introduced into D through C; 4) the tube was sealed off at E; 5) both liquid samples were mixed by opening the break-off tip.

The glass tube was put to irradiation of gamma-rays from the Co-60 source (1000 c.) of our laboratory. If not otherwise described, the irradiation was carried out at 7∼15°C. After irradiation, samples were taken out from the tube and their

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* Chain Telomerization Induced by Gamma-rays. III.

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

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

3) T. D. Nevitt, W. A. Wilson and H. S. Seelig, *Ind. Eng. Chem.*, 51, 311 (1959).

4) E. J. Henley and C. Chang, *J. Polymer Sci.*, 36, 511 (1959).

5) M. Takehisa, M. Yasumoto and Y. Hosaka, *J. Chem. Soc. Japan, Ind. Chem. Sec. (Kogyo Kagaku Zasshi)*, 65, 531 (1962).

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

7) K. Hirota and H. Ochi, *Isotopes and Radiation*, 3, 509 (1960).

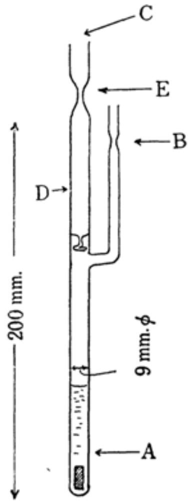

Fig. 1. Irradiation tube for experiments at lower pressure.

liquid part was analyzed by gas chromatography on a Shimadzu G-C 1A instrument by the use of a 3-m. column of dioctyl phthate at the flow rate of 120 ml./min. of helium. For analysis of 1 : 3 telomer, a 5.25-m. column of high vacuum oil was used at an operating temperature of 150°C and at the flow rate of 120 ml./min. of helium.

Experiment at Higher Pressure.—According to the preliminary run, it was found that acetaldehyde reacted with the inner surface of the autoclave made of stainless steel. Therefore, samples were introduced by the following procedures so as to prevent the direct contact of acetaldehyde with the wall :—Acetaldehyde was enclosed under vacuum in a glass ampoule which was then charged in another glass tube which has a small hole A at its side-wall. After the glass ampoule and tube were set up in the autoclave as shown in Fig. 2, an ethylene tank was connected via valves. Ethylene was introduced up to the desired pressure which was measured by a Bourdon gage. The autoclave was rocked and the upper end of the ampoule B was broken by shaking the autoclave upside down. After the time sufficient to reach the dissolution equilibrium of ethylene into acetaldehyde, the sample was irradiated through the wall of the autoclave with Co-60 γ-rays.

After cooling the autoclave down at 5°C and ventilating the unrecacted gas, the liquid product was taken out and put to the gas chromatographic analysis by making methylamyl ketone an internal standard. Operating condition of the gas chromatograph was similar to that of the first experiment.

Gelled part of the product was filtered, dissolved in carbon tetrachloride, and purified by the column chromatography using aluminum oxide as an adsorbent. The result of the elementary analysis is the purified gell was as follows :

Found : C, 81.2 ; H, 13.47. Calcd. for $C_{21}H_{42}O$: C, 81.21 ; H, 13.63%.

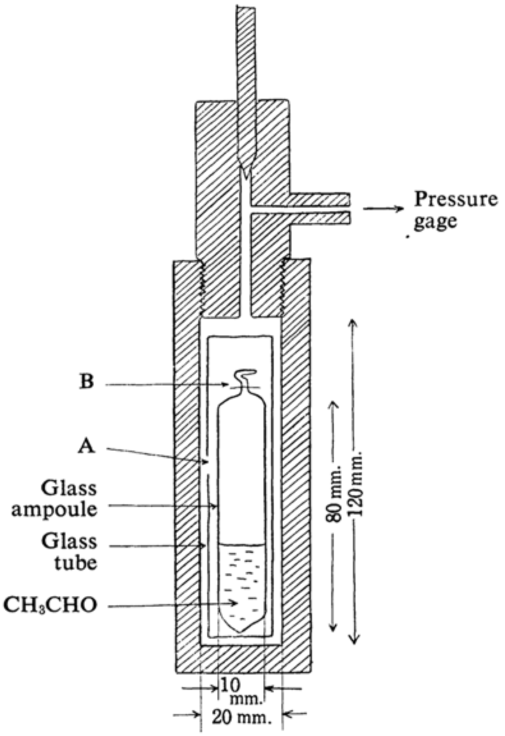

Fig. 2. Irradiation apparatus for experiments at higher pressure.

Mean molecular weight determined by the freezing-point method was found to be 410, though calculated value was given to be 310 from $C_{21}H_{42}O$.

Results and Discussions of the Experiment at Lower Pressures.—*Identification of the Products.*—Ethyl methyl ketone (EMK) and methyl-*n*-butyl ketone were found to be produced in the irradiated samples. They correspond to

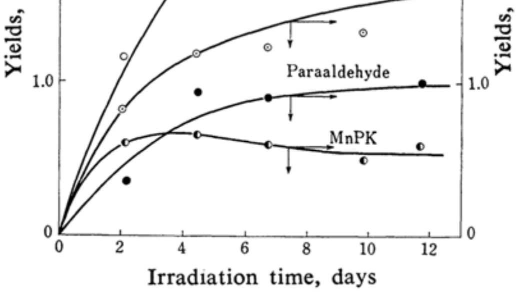

Fig. 3. The yields of EMK, MnBK vs. irradiation time.

Irradiation dose rate	1.3×10^4 r/h.
Ethylene	0.00411 mol.

1 : 1 telomer and 1 : 2 telomer, respectively, of acetaldehyde and ethylene. Both yields increase with irradiation time as shown in Fig. 3*. However, 1 : 3 telomer could not be identified. Besides a small amount of methyl-*n*-propyl ketone was found, which was probably produced by the termination of the following type:

$$CH_3COCH_2-\dot{C}H_2 + \dot{C}H_3 \rightarrow CH_3COCH_2\text{-}CH_2\text{-}CH_3 \qquad (5)$$

The methyl radical in Eq. 5 might be produced by thermal decomposition of acetyl radical, i. e.

$$CH_3\dot{C}O \rightarrow \dot{C}H_3 + CO \qquad (6)$$

or directly from acetaldehyde by irradiation, i. e.,

$$CH_3CHO \rightsquigarrow \dot{C}H_3 + \dot{C}HO \qquad (7)$$

Such reactions are very probable from the data of both photochemical and thermal decompositions of acetaldehyde[8].

Effect of Dose Rate on G(Ethyl Methyl Ketone).—The effects of dose rate I on the yield are shown in Figs. 4a and b. The G values were estimated from the initial inclination of the curves in Fig. 4a and logarithms of the G(EMK) are plotted against $\log I$ in Fig. 4b. From this plot, it is clearly shown that EMK is produced in proportion to -0.59 powers of I. This value is slightly smaller than -0.50 which will be derived under the assumption of a bimolecular termination of all the propagating radicals in Eqs. 3 and 4.

Effect of Irradiation Temperature on G(Ethyl Methyl Ketone). — Effect of irradiation temperature on the G(EMK) is shown in Fig. 5. The G values increase gradually with irradiation temperature. From their Arrhenius plots a relatively good straight line was obtained, and an apparent activation energy was determined to be 5.0 kcal./mol. from the inclination of this line. It will be interesting to compare this value with that of the system of ethylene and isopropanol (7.0 kcal./mol.)[7]. Such a smaller value may denote that hydrogen abstraction from acetaldehyde is easier than from isopropanol.

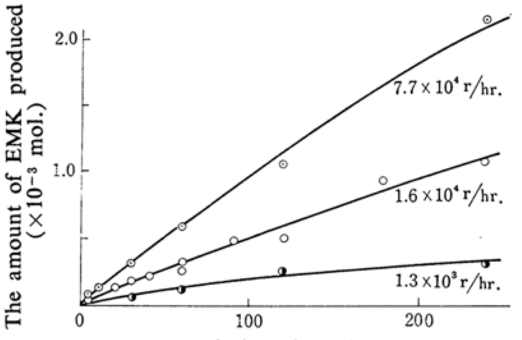

Fig. 4a. The amount of EMK produced vs. irradiation time.

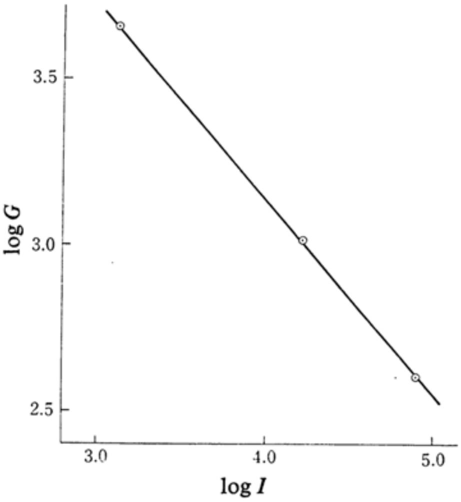

Fig. 4b. Log G vs. $\log I$.

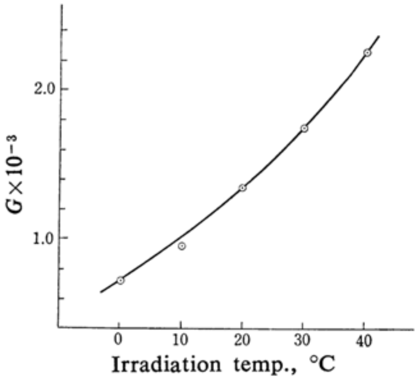

Fig. 5. G(EMK) vs. irradiation temperature.

Because if a bimolecular termination of the propagating radicals is assumed, the apparent activation energy of such a chain polymerization will be given generally by

$$E_a' = E_p - 1/2E_t \qquad (8)$$

where E_p and E_t denote the propagating and the terminating steps, respectively. In the present case E_t may be equated practically to zero. The above two values (5.0 and 7.0 kcal./mol.) however do not correspond exactly to E_p of Eq. 8 due to the change of solubility of ethylene into acetaldehyde with the reaction temperature. Nevertheless, since

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[8] Cf. E. W. R. Steacie, "Atomic and Free Radical Reactions", 2nd ed., Reinhold Publishing Corp., New York (1954), pp. 215—219, pp. 286—294.

* Since the amount of paraaldehyde is not reproducible, it may not be produced by irradiation. The data will therefore be omitted hereafter.

the temperature dependency on solubility of ethylene will be similar in both alcohol and aldehyde, the above conclusion on the difference of activation energy may be drawn.

Effect of Molar Percent of Ethylene in the Feed on G(Ethyl Methyl Ketone).—It is shown in Fig. 6 that the G(EMK) increases with increasing pressure of ethylene, the inclination of the curve decreases gradually. It will be interesting to study the behavior of G values at higher molar per cent. The investigation will be carried out in the higher pressure experiment.

Effect of Additives. — Presence of the air scarcely affected the yield of telomers but rather increased slightly. A small amount of DPPH inhibited the production of telomers perfectly, except that of paraaldehyde. Addition of water reduced the yield markedly; e. g. 20% decrease was found in the telomer formation by the addition of 2% water. Such a reducing effect of water may be ascribed to the hydration of acetaldehyde.

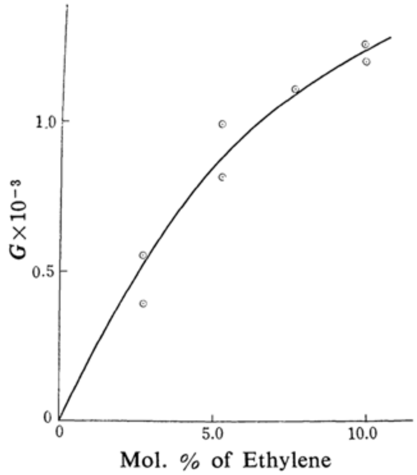

Fig. 6. G(EMK) vs. mol. % of ethylene.
Acetaldehyde 0.05 mol.
Dose rate 1.6×10^4 r/hr.
Irradiation time 1 hr.

Results and Discussion of the Experiments at Higher Pressure*.— *Effects of Irradiation Time on Telomer Yields.*—In addition to the 1 : 1 and 1 : 2 telomers described in the previous section, methyl-*n*-hexyl ketone (1 : 3 telomer) was found to be produced in the experiments at higher pressures. The effects of irradiation time on the yield of each telomer were shown in Figs. 7—9, where ethylene was charged at the initial pressures of 10, 20 and 50 kg./cm², respectively, to 0.05 mol. of acetaldehyde. The yields of 1−1 and 1−2 telomers increase approximately linearly with increasing dose, while tendency of the yield of 1−3 telomer is not so clear, as the value is too small.

Effect of Irradiation Temperature.—As can be shown by the data in Figs. 7—9, it may be clear that the effect of temperature is very small, especially at the pressure range higher than 20 kg./cm², if it ever exist. Such a result

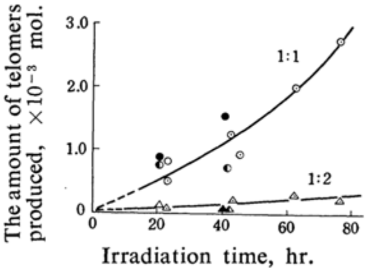

Fig. 7. The amount of telomers produced vs. irradiation time.
CH_3CHO 0.05 mole, C_2H_4 10 kg./cm²
Dose rate: 1.0×10^4 r/hr.
⊙△ room temp., ●▲ 75°C, ◐◭ 103°C

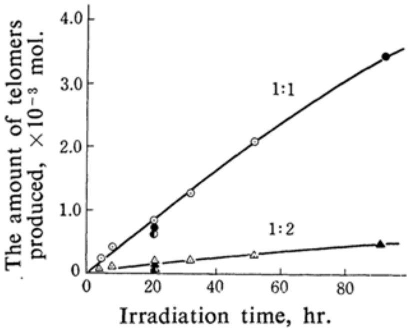

Fig. 8. The amount of telomers produced vs. irradiation time.
CH_3CHO 0.05 mole, C_2H_4 20 kg./cm²
Dose rate: 1.0×10^4 r/hr.
⊙△ room temp., ●▲ 75°C, ◭◐ 103°C

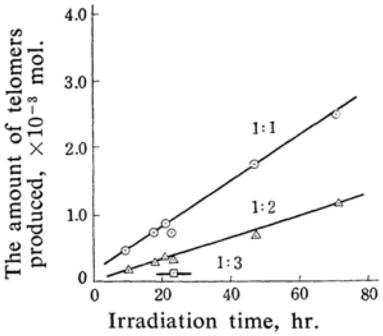

Fig. 9. The amount of telomers produced vs. irradiation time.
CH_3CHO 0.05 mole, C_2H_4 50 kg./cm²
Dose rate: 1.0×10^4 r/hr.
⊙△▣ room temp.

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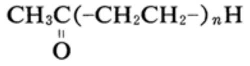
* According to a Germa Pat. 1077662 (Jan. 30, 1957), such telomers are produced without irradiation under the pressures higher than 35 atm. This effect was found to be negligibly small in the present experimental conditions.

is quite different not only from the low pressure experiment but also from the system of isopropanol and ethylene where *G*(telomers) increases with temperature up to 250°C[9]. These differences may be brought about by the less stability of acetyl radical than that of isopropyl radical, $(CH_3)_2\dot{C}OH$, as already mentioned[8].

Effects of Initial Pressure of Ethylene.—In order to investigate the effect of the initial pressure of ethylene on the yield of telomers, their *G* values at room temperature and 75°C are plotted against the initial pressure in Fig. 10. It is evident that the total $G(-C_2H_4)$ increases with increasing pressure up to 4000 at 50 kg./cm². However the *G*(1 : 1 telomer) has an optimum value and decreases above ca. 30 kg./cm² of the initial pressure. This optimum value seems to shift to the region of lower pressure when the irradiation temperature is 75°C. On the other hand, the *G*(1 : 2 telomer) increases in proportion to the ethylene pressure, and the *G*(1 : 3 telomer) to its second power. Such results ought to be expected from the reaction mechanism proposed above.

High Molecular Weight Products. — At the highest pressure, a small amount of white gelled product was obtained. This substance is soluble in carbon tetrachloride, benzene, toluene and hot ethanol, and has a melting point of 65~66°C. The infrared spectrum of this substance is shown in Fig. 11. Strong absorption at 1710 cm⁻¹ indicates the presence of carbonyl group. Besides, taking the data of elementary analysis of this substance into account, it is considered to be a mixture of telomers differing in *n*; e. g.



$$CH_3C(O)(-CH_2CH_2-)_nH$$

where *n* can be estimated to be 9.5 as an average value from the molecular weight as mentioned above.

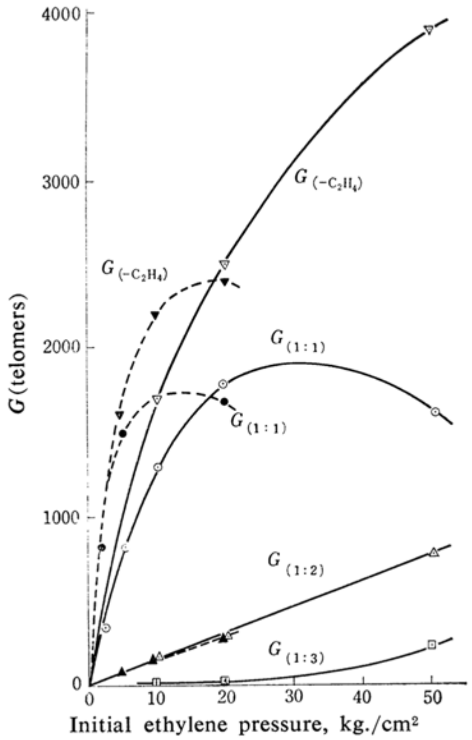


Fig. 10. *G*(telomers) vs. initial ethylene pressure.
⊙△▽⊡ room temp., ●▲▼ 75°C

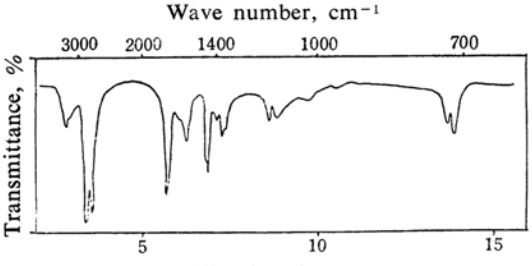


Fig. 11. Infrared spectrum of the gelled product (using KBr disk method).

General Discussion

As discussed in the previous two sections, it is evident that the present telomerization proceeds according to the chain mechanism shown by Eqs. 1—4, regenerating the acetyl radical by a chain-transfer. Such a radical mechanism is in good agreement with the inhibiting effect of DPPH. Another confirmation of this mechanism may be quantitatively shown by the distribution of the telomers produced, as already done in the former papers.

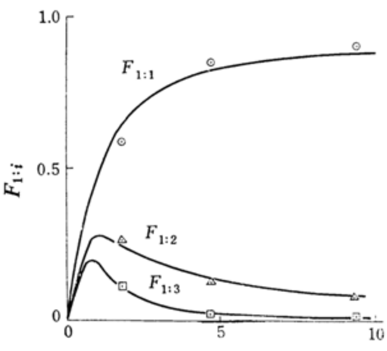


Fig. 12. Molar fraction of produced ketones vs. *R*. 1 : *n* means the ketone produced by one mole of acetaldehyde and *n* moles of ethylene.

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[9] M. Hatada and K. Hirota, The 4th Isotope Conference of Japan, Kyoto (Oct. 1961).

Molar fractions of 1 : *i* telomer, F_i, are plotted against the ratio of acetaldehyde/ethylene(R) as the abscissa in Fig. 12, making both total dose and dose rate constant. In evaluating R, the absorption coefficient of Ostwald was assumed to be five irrespective of pressures. The lines in the figure indicate the calculated curves from the following equation,

$$F_i=\frac{C_iR}{(C_iR+1)} \tag{9}$$

where C_i's, chain transfer constants, are assumed to be 1.0, 1.1 and 4.6, respectively as the most probable values. These numerals resemble to those obtained in the system of acetaldehyde and propylene, but are quite different from those obtained in the system of isopropanol and ethylene (cf. Fig. 13). In the latter system, the change of C_i's against i is small as well as their magnitude. This difference, therefore, is a result to be characterized by the nature of the taxogens.

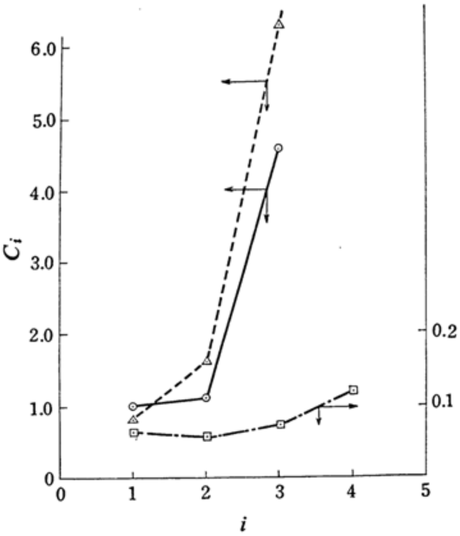

Fig. 13. Chain transfer constant C_i vs. i of the various systems.
⦿ $C_2H_4+CH_3CHO$ △ $C_3H_6+CH_3CHO$
▣ $C_2H_4+(CH_3)_2CHOH$

As mentioned already, the apparent activation energy, 5.0 kcal./mol., obtained between 0 and 40°C seems to correspond approximately to that of the abstraction reaction of hydrogen atom from CHO group of acetaldehyde. However, in the experiment at higher temperature and pressure a smaller temperature dependency or rather independency of temperature was observed on G(telomers). This may probably be ascribed to the increasing occurrence of thermal decomposition of acetyl and/or $CH_3\cdot COCH_2\cdots\cdots\dot{C}H_2$ radicals at higher temperature. Because though telomers of the type as mentioned in Eq. 5 may be produced, the decomposition of acetyl radical, followed by stabilization into CH_4+CO, will contribute to decrease the yield of telomers.

It must be pointed out finally that by the present experiment the acetyl radical seems to be not so unstable as assumed in the photochemical decomposition of acetaldehyde[10]. This conclusion is in agreement with the finding that the activation energy of the decomposition 7 is 9.6 kcal.[11]; i. e., acetyl radical would react with ethylene more easily from the standpoint of the activation energy.

Summary and Conclusions

(1) It has been found that radiation-induced addition of acetaldehyde to ethylene occurs at room temperature with a relatively high $G(-C_2H_4)$, e. g., 4000 at the initial pressure of 50 kg./cm² of ethylene, and that the production of 1 : 2 telomer is more favorable than that of 1 : 1 telomer at higher pressure of ethylene. In order to obtain higher G values of 1 : 1 telomer, it has been shown to be unnecessary to make the initial pressure of ethylene higher than 10 kg./cm², and also to elevate the irradiation temperature much higher than room temperature.

(2) It has been confirmed that a major part of the telomerization proceeds by a chain mechanism, which accompanies a chain-transfer process simultaneously, acetyl radical playing a role of the chain-carrying radical as well as role of initiator. Moreover it has been pointed out that the acetyl radical reacts with ethylene more easily than decomposes, though the decomposition is assumed to occur dominantly in the photochemical and thermal decomposition of acetaldehyde alone[8].

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[10] E. I. Akeroyd and R. G. W. Norrish, *J. Chem. Soc.*, **1936**, 890; N. Imai and O. Toyama, This Bulletin, **33**, 1120 (1960).

[11] F. E. Blacet and D. E. Loeffler, *J. Am. Chem. Soc.*, **64**, 893 (1942). Older data give also the value between 8.3 and 10 kcal./mol.[8]