*The Gamma Ray-Induced Addition of Acetaldehyde to Cyclohexene and Normal Hexene**

By Motoyoshi HATADA, Jun'ichi TAKEZAKI and Kozo HIROTA

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In the present series of research papers[1] radiation-induced telomerizations have been studied, making gaseous olefins (ethene, propene and isobutene) the taxogens and acetaldehyde, the telogen, respectively; i. e., several methyl-alkyl ketones have been synthesized by the following reaction:

$$RCH{=}CH_2 + CH_3CHO \rightsquigarrow CH_3CO(RC_2H_3)_nH \quad (n=1, 2,.....) \quad (1)$$

However, since these research papers, as well as that published by others,[2] have been mainly interested in finding a new method of synthesizing ketones, the results are not suitable for a detailed discussion of the reaction mechanism. Especially, because of the small solubilities of gaseous olefins in acetaldehyde, the composition of the liquid part of the sample was not exactly the same as that of the gaseous part, resulting in a difficulty of drawing definite conclusions.

Such being the situation, it will be interesting to study the system where a liquid olefin perfectly soluble in acetaldehyde is used as the taxogen. Therefore, normal hexene-1 and/or cyclohexene is adopted as the taxogen in the present research. Thus, the reactivity of olefins other than α-olefins can be investigated at the same time. Second, according to the method of research hitherto published, it was difficult to discuss the point if the initial process 2 could be regarded as a single reaction brought about by irradiation.

$$CH_3CHO \rightsquigarrow CH_3\dot{C}O + H \quad (2)$$

In order to solve this problem, gaseous products are analyzed, as well as liquid products on samples the initial composition of which covers the entire range.

The research carried out along these lines will be reported on with reference to the reaction mechanism of this telomerization in general.

Experimental

Materials.—The acetaldehyde used was prepared from commercial acetaldehyde by the method described in previous reports.[1] Commercial cyclohexene was used after purification by distillation. Commercial *n*-hexene-1 was used without further purification. No impurity was detected in cyclohexene by gas chromatographic analysis, while the total amount of impurities in *n*-hexene-1 was found to be 5%. Mixtures of hexene and acetaldehyde were prepared and charged in vacuo into glass ampoules by a procedure reported on already.[1]

Irradiation.—The mixtures were irradiated at room temperature or at higher temperatures up to 180°C with gamma rays from a cobalt-60 source installed in our laboratory. The dose rate, which was determined by the use of a Frick dosimeter, was varied over the range from 1.4 to 9.7×10^4 r/hr.

The Analysis of the Liquid Products.—The liquid part of the irradiated mixture was subjected to both gas chromatographic and mass spectrometric analyses. The gas chromatograph used was an apparatus (the Shimadzu Model GCIA), the analytical conditions being as follows: column length, 5.25 m.; adsorbent, high vacuum oil; column temperature, 152°C; flow rate of the carrier gas (helium), 150 cm³/min.

The Analysis of the Gaseous Products.—The gaseous product was collected with an automatic töpler pump and was analyzed with a mass spectrometer (Hitachi RMU-5).

Results and Discussion

a) The Identification of the Liquid Products.—Only one new peak appeared in the gas chromatogram of the liquid part in the irradiated samples besides the peaks of acetaldehyde and cyclohexene. The fraction corresponding to this peak was collected and identified as methyl cyclohexyl ketone (McHK) by mass spectrometry. This substance is an addition product or a 1 : 1 telomer of acetaldehyde to cyclohexene. However, Mayo et al.[3] had reported that cyclohexanol was produced as the main product in the ultraviolet-irradiated

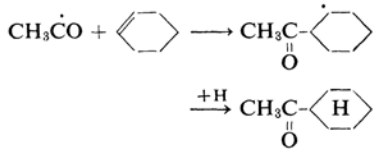
* Chain Telomerization Induced by Radiation. V. (A part of this paper was presented at the 14th Annual Meeting of the Chemical Society of Japan, Kyoto, April, 1961).

1) K. Hirota, M. Hatada et al., a) This Bulletin, **33**, 1682 (1960); b) ibid., **34**, 1644 (1961); c) ibid., **36**, 817 (1963); d) The IV Isotope Symposium (Japan), No. R-7 (1961), Kyoto.

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

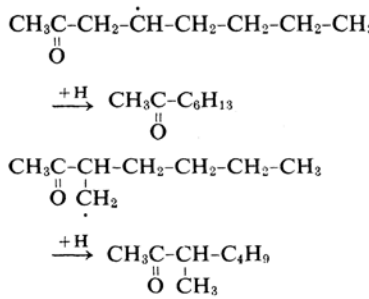
3) P. de Mayo, J. B. Stothers and W. Templeton, *Can. J. Chem.*, **39**, 488 (1961).

mixture of acetaldehyde and cyclohexene, especially when the latter was present in excess. However, no peak was found in the gas chromatogram of the present experiment over the region where the peak of cyclohexanol might be expected to appear. Therefore, the addition of the acetyl radical to cyclohexene will be the main process in the γ-ray irradiated system, as is shown by Eq. 3:



(3)

By a similar process, methyl *n*-hexyl ketone (MnHK) and methyl isohexyl ketone (MiHK) were found to be produced from the irradiated mixture of acetaldehyde and *n*-hexene-1. Both ketones are evidently the addition products of acetaldehyde and *n*-hexene-1. Apparently the mechanism of producing them will be the same as has been explained in the mixtures of aldehyde and lower olefins;[1] e. g., according as the acetyl radical attaches to the carbon-1 or the carbon-2 of *n*-hexene-1, followed by the addition of a hydrogen atom, MnHK or MiHK respectively, may be obtained as is shown below.



(4)

In both reactions, such products, which correspond to the higher telomers, could not be identified, partly because of their high boiling point as well as because of their small quantity caused by the difficulty of reaction. However, assuming the reaction to proceed by the mechanism already proposed, the methyl hexyl ketones mentioned above will be called 1 : 1 telomers hereafter.

b) The *G* Values of the Formation of Telomers.—In Fig. 1, the yield of the McHK produced in the mixture of acetaldehyde and cyclohexene is plotted vs. the irradiation time, keeping the dose rate at 7.4×10^4 r/hr. It is shown that, approximately, the yield increases linearly with the increasing dose. Similar curves could be obtained for the yields of MnHK and MiHK in the mixture of acetaldehyde and normal hexene, the *G* values of each

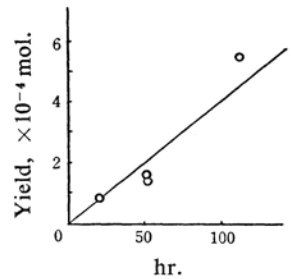


Fig. 1. The amount of McHK formation vs. irradiation time.

telomer were calculated from these curves. Generally speaking, MnHK was always produced most easily. This point will be discussed further in b).

However, it is noteworthy that *G*(MnHK) is larger than the value to be expected from *G*(1 : 1 telomer) of the mixtures of ethene,[4] propene[1] and/or isobutene[5] with aldehyde, because the *G*(1 : 1 telomer) decreases as the carbon number of the taxogens increases. Such a contradictory result may be explained by the possibility that the liquid part of the mixture contains much less olefin than would be estimated from its initial charge in the samples, as has been mentioned in the introduction.

The main components of the gas produced at room temperature by irradiation on the mixture of cyclohexene and acetaldehyde were found to be carbon monoxide, methane and hydrogen, as in the case of propene and acetaldehyde.[1a]

c) The Effect of the Dose Rate on *G*(Telomer)'s.—The *G*(telomer)'s thus obtained are plotted vs. dose rate *I* in logarithmic scales in Fig. 2, where the total dose is kept at 2.25×10^6 r, while the dose rate ranges from 10^4 to 10^5 r/hr. From the inclination of the lines, the *G*(McHK) is shown to increase in inverse proportion to the square root of *I*, while both *G*(MnHK) and *G*(MiHK) increase to the three-fourth power of *I*; i. e., the relation is expressed by a formula:

$$\log G = \text{Const.} - \alpha \log I \qquad (5)$$

where $\alpha=0.5$ for McHK and $\alpha=0.75$ for MnHK and MiHK respectively.

The fact that α has a value somewhat larger than 0.5 in the latter system suggests that a minor part of the reaction chain terminates in a monomolecular mechanism, as may be observed in the ionic mechanism.

4) K. Hirota, S. Iizuka, H. Ochi and M. Hatada, This Bulletin, **36**, 115 (1963).

5) K. Hirota, S. Iizuka and M. Hatada, *Annual Report of the Japanese Association of Radiation Research on Polymers*, **1**, 165 (1959); **2**, 169 (1960); This Bulletin, in press.

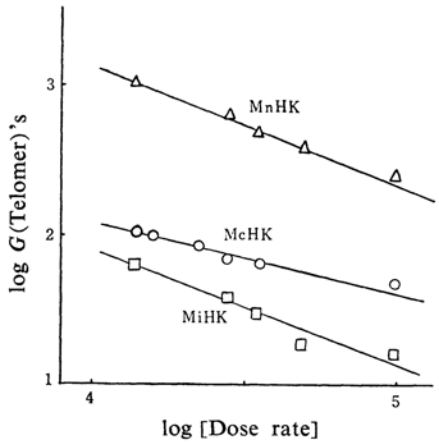


Fig. 2. Log [G(Telomer)'s] vs. log [Dose rate].
Total dose 2.25×10^6 r

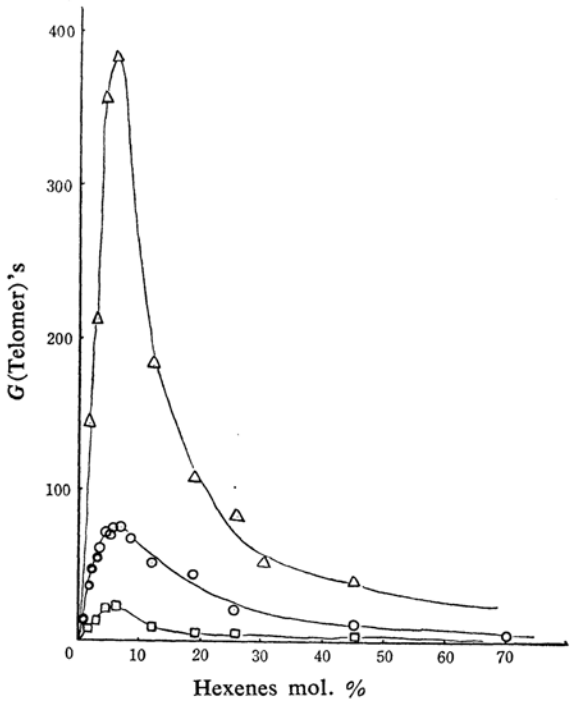


Fig. 3. G(Telomer)'s vs. mol. % of hexenes in the feed.
Dose rate 9.7×10^4 r/hr.
Dose 1×10^7 r
△ MnHK ○ McHK □ MiHK

d) The Effect of the Composition of the Feed on the G(Telomer)'s.—In Fig. 3, the G(1 : 1 telomer)'s obtained at the same dose rate (9.7×10^4 r/hr.) are plotted vs. the mole per cent of olefin in the feed. The curves thus drawn for the three telomers show a similar shape, with a maximum at ca. 5 mol.% of olefin concentration.

These curves may appear in the situation where some part of the acetyl radicals is consumed to form by-products and does not contribute to the production of methyl hexyl ketones.

The G(MnHK)$>G$(McHK)$>G$(MiHK) relation, mentioned in b), exists over the entire concentration range; i. e., MnHK is produced the most favorably, while MiHK is produced the least. This relation, contrary to Markownikoff's rule, may be an indication that telomerization proceeds by a radical chain mechanism, since the addition of the polar substance to the double bonds is known to follow Markownikoff's rule. Moreover, it will be noted that the G(MnHK)$>G$(MiHK) relation is concordant with the fact[2] that 1-olefin is more reactive than 2-olefin to aldehyde.

e) The Temperature Dependency on the G(Telomer).—The G(telomer)'s obtained at various temperatures take maximum values in both systems, e. g., at 70~80°C, as Figs. 4 a and 4 b show. Such maxima have already been observed in other systems where the taxogens were lower olefins,[2-4] but it could not be made clear that this decrease of G(telomer)'s in the high temperature region comes either from the instability of radicals or from the decrease in the solubility of the taxogens. Since hexenes are perfectly soluble in acetaldehyde, the decrease of G at the higher temperature may be ascribed to the decomposition of the acetyl radical because, the decomposition

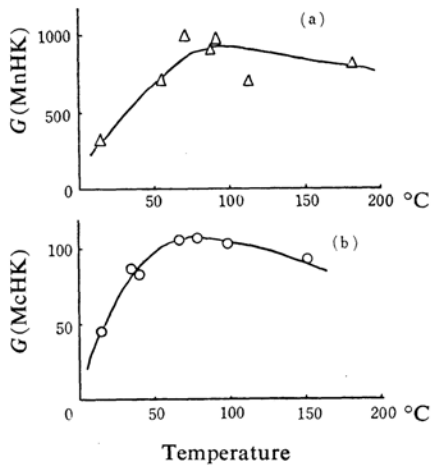


Fig. 4. G(Telomer)'s vs. irradiation temperature.
△ MnHK ○ McHK

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

with the activation energy of 15 kcal.,[6] proceeds more favorably at the higher temperature. Such an explanation will also be reasonable on the basis of the experimental finding that the shapes of both curves are the same, irrespective of the taxogen.

In order to determine the overall activation energy of formation, the logarithmus of the $G(1:1$ telomer)'s was plotted against $1/T$. The activation energies thus determined in the region of room temperature were 4.3 kcal./mol. for MnHK and 3.7 kcal./mol. for McHK respectively. They practically correspond to the activation energy of the propagation step, if a bimolecular termination of the propagating radical with a negligibly small activation energy is assumed. However, it is noteworthy that the values actually observed are smaller in this system than those in the system where the taxogens were ethene (5.0 kcal.)[4] or isobutene (6.5 kcal.).[5] The values may be ascribed to the decrease in the solubility of lower olefins with the temperature, so that their initial concentration in the liquid part of the samples decreased more than in the feed.

f) Gases Produced by Irradiation on the Mixture of Cyclohexene and Acetaldehyde.—As has already been mentioned, hydrogen, methane and carbon monoxide were the main gaseous products. They were produced in almost equal amounts, as is shown by Fig. 5, by the irradiation of samples rich in acetaldehyde, although the latter two components decrease with an increase in the cyclohexene fraction in the initial mixture. These may be explained easily by the decomposition of acetaldehyde: $CH_3CHO \rightarrow CH_4+CO$, and the primary process may be the one designated by Eq. 6, as well as by the direct scission of the C–C bond.

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

The slight difference between $G(CH_4)$ and $G(CO)$ may be caused by the recombination of methyl radicals into ethane, whose formation is favorable in the aldehyde-rich region, $G(C_2H_6)$ being, however, experimentally difficult to determine.

The $G(H_2)$~composition curve has a minimum in the middle region. This is because hydrogen is produced as the by-product of the telomerization as well as by the decomposition of cyclohexene, the $G(H_2)$ value of cyclohexene-rich samples was 1.3, which agreed well with that ($G(H_2)=1.2$) obtained by Freeman[7] in the γ-ray irradiation on pure cyclohexene. On the other hand, hydrogen may be produced by the decomposition of acetaldehyde, e.g., $CH_3CHO \rightarrow H_2+CH_2C{=}O$. Since $G(H_2)$ nearly equal to $G(CO)$ in the acetaldehyde-rich region, the $G(H_2)$ produced from acetaldehyde in the middle region may may be given approximately by the value of $G(CO)$. If so, $G(H_2)$-$G(CO)$ as shown by the dotted line α in Fig. 5 can be regarded as the $G(H_2)$ from cyclohexene only.

In short, considering the magnitude of $G(H_2)$, $G(CO)$ and $G(CH_4)$ in Fig. 5, radiation-induced decompositions of aldehyde and cyclohexene may be said to proceed parallel with the telomerization.

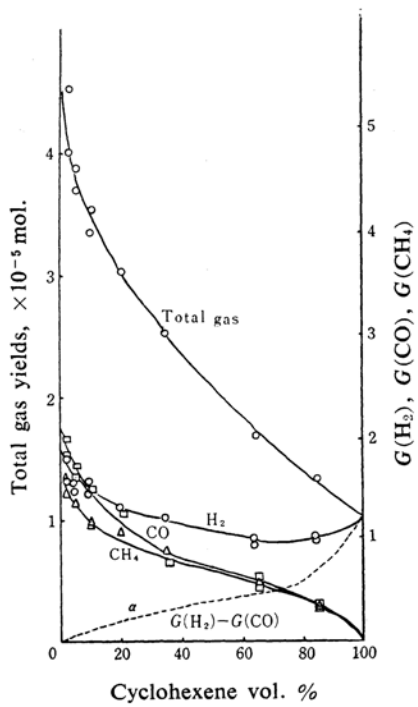


Fig. 5. G(gases) vs. cyclohexene vol. % in the feed.

g) The Effect of Benzene and Cyclohexane Added to the System.—Since benzene is known to act as a scavenger of hydrogen atoms, the dilution of the samples with benzene may give us knowledge of the fate of the hydrogen atoms produced in Eq. 2. The experiment is interesting from the viewpoint of increasing the yield of telomers, because the hydrogen produced in Eq. 2 might be captured, otherwise it would act as a terminating agent.

The experiment was carried out on various mixtures of aldehyde (A), cyclohexene (B) and benzene (C), keeping the amounts of A and B+C respectively constant. As is shown by the full line in Fig. 6, the G(McHK) became, contrary to expectation, slightly smaller upon the addition of benzene over the whole range of composition expressed by the electron fraction than that denoted by the dotted line

6) Cf. E. W. R. Steacie, "Atomic and Free Radical Reactions," 2nd ed., Reinhold Publishing Corp., New York (1954).

which was calculated under the assumption that benzene plays the role of a mere diluent.

It might be possible that the above tendency comes, rather, from an energy transfer to benzene molecules from excited cyclohexene molecules, which can easily react with acetyl radicals. If this be true, the addition of cyclohexane to the feed might increase the G(McHK), because cyclohexene would behave also to some extent as an energy acceptor from the excited cyclohexane. This reasoning may be justified by the fact that cyclohexane is regarded as acting as an energy donor in the cyclohexane-benzene mixture.[7,8] However, as the broken line in Fig. 6 shows, in the systems where cyclohexane was added to the mixture, a curve was obtained which is also concave upward but slightly different in shape from the systems where benzene was added. In order to explain these findings, it is not necessary to assume that the excitation of the cyclohexene molecule is important in the production of methyl hexyl ketones.

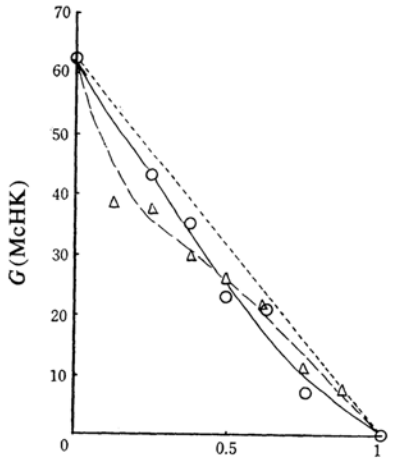


Fig. 6. G(McHK) vs. electron fraction of the additives.

Cyclohexene+Additive: 0.2 ml.
Acetaldehyde: 1.8 ml.

Dose rate 8×10^4 r/hr., dose 5×10^6 r

○ Benzene △ Cyclohexane

In summarizing the conclusions obtained from c) to g), it can be said that the mechanism of the telomerization of the aldehyde-olefin mixture is generally expressed by the radical mechanism hitherto proposed.[1]

Summary

By the radiation-induced telomerization of acetaldehyde-hexene mixtures, McHK has been produced when cyclohexene is used, while MnHK and MiHK have been produced when normal hexene is used. The G(MnHK) at room temperature has been found to be 400 (dose rate $=9.7\times10^4$ r/hr.), which is larger by a factor of ten than the G(MiHK) and the G(McHK). Irrespective of the dose rate, a G(MnHK)$>G$(McHK)$>G$(MiHK) relation always exists.

It has been found that: (i) the G(MnHK) value, as well as the G(MiHK) and the G(McHK) values, increases with the rise in temperature, they all show however, maxima at 70~80°C, because of the thermal decomposition of the acetyl radical, (ii) sharp maxima are shown in the curves of G(telomer) vs. initial composition at 5 mol.% of hexenes, (iii) the analytical data of the gaseous products establish that the radiation-induced decomposition of aldehyde and hexene occurs in parallel with the telomerization, and (iv), upon the addition of benzene or cyclohexane to the system, the G(telomer)'s decrease slightly in both systems, suggesting that they act as diluents rather than as agents of the energy transfer.

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Osaka Laboratories
Japanese Association for
Radiation Research on Polymers
Neyagawa, Osaka (M. H. & J. T.)

Science Faculty
Osaka University
Nakanoshima, Osaka (K. H.)

7) G. R. Freeman, *Can. J. Chem.*, **38**, 1043 (1960).
8) J. P. Manion and M. Burton, *J. Phys. Chem.*, **56**, 560 (1952).