The Effect of the Type of Radiation on the Radiation-Induced Addition of Acetaldehyde to Cyclohexene[*]

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An earlier report[1] studied the gamma-ray-induced addition of acetaldehyde to cyclohexene; cyclohexyl ketone was the main product. The products were different from those when ultraviolet irradiation was carried out.[2] Since such a discrepancy might be caused by the difference in irradiation sources, the effect of the type of radiation will be investigated in the present report by comparing the results obtained by use of gamma-rays,[1] ultraviolet light, and electron beams.

Experimental

Materials.—Acetaldehyde was prepared by the method which has previously been described in the present series of studies. Commercial cyclohexene was used after distillation. Commercial DPPH was used without any further purification.

Irradiation Procedures.—For electron-beam irradiations, spot electron beams (1.5 MeV., 50 μamp) from a Van de Graaff accelerator were used. Figure 1 shows the apparatus for the irradiation. The sample (40 ml.) was irradiated in a vessel equipped with a magnetic stirrer, A, and an aluminum window, B, through which the electron beams penetrated into the vessel. During the irradiation, the sample was cooled with an ice water bath.

The dose rate was estimated to be 0.77×10^{20} eV./sec. by the use of a cerric-cerrous dosimeter in

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[*] Chain-Telomerization Induced by Radiation. VII. Presented at the Annual Meeting of the Chemical Society of Japan, April, 1963.

[1] M. Hatada, J. Takezaki and K. Hirota, This Bulletin, 37, 1661 (1964).

[2] P. de Mayo, I, B. Stothers and W. Templeton, *Can. J. Chem.*, 39, 488 (1961).

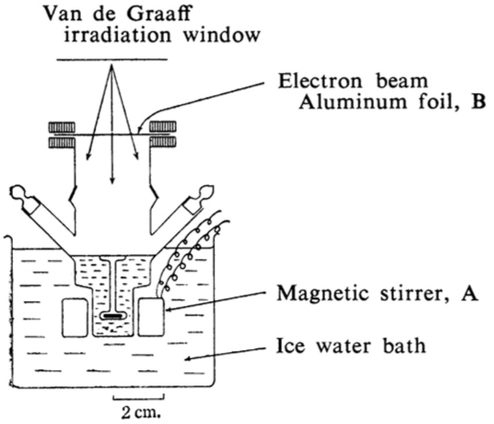


Fig. 1. Apparatus for electron beam irradiation.

the vessel used for the irradiation of the mixture. Details of the dosimetry will be described elsewhere.[3]

For the irradiation with an ultraviolet light, a high-pressure mercury lamp (Toshiba H400 P type) was used as the irradiation source. The sample (8 ml.) was degassed and distilled into a quartz tube under vacuum. Having been sealed off, the tubes were then subjected to the irradiation at 17°C for 5 hr.

Analysis. — After irradiation, the samples were subjected to gas chromatographic analyses, the conditions of which were as follows:

Column, P. E. G. 6000; column length, 3.0 m; carrier gas, He; flow rate, 60 ml./min.; column temperature, 180°C; apparatus; Shimadzu GCIB.

For the identification of the peaks which appeared in the gas chromatograms, a mass spectrometer (Hitachi RMU-5) and an infrared spectrometer (Shimadzu AR275) were used.

Results and Discussion

Identification of the Irradiation Products.— Typical gas chromatograms of the irradiated samples with γ rays,* electron beams, and ultraviolet are shown in Figs. 2a, 2b, and 2c respectively. The peaks which appeared in the gas chromatograms are designated as $P^i{}_\gamma$, $P^i{}_e$ and $P^i{}_{UV}$ respectively, where the subscripts denote the type of radiations while the superscripts, $i=1, 2, 3,\ldots\ldots$ denote the order in which the peaks appeared in the gas chromatograms.

By a comparison of the retention times of the peaks obtained by different irradiation sources, some of the products may be assumed to be the same. They may be grouped in parentheses as follows:

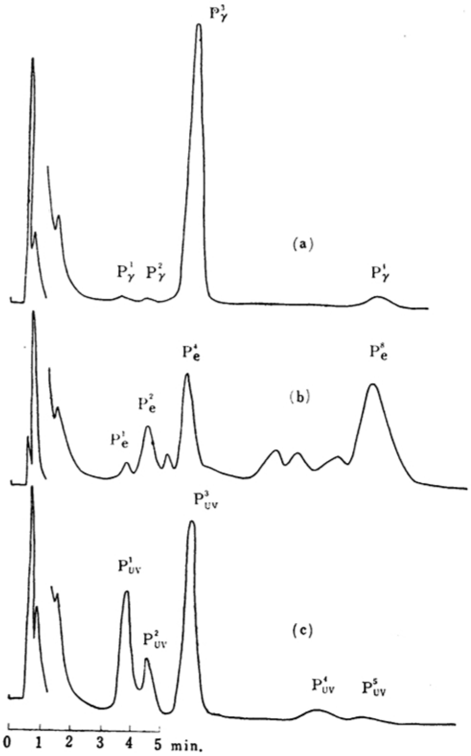
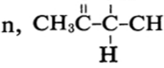
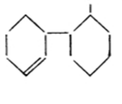


Fig. 2. Gas chromatograms of irradiated mixtures.
a) with γ-rays, b) with electron beams from the Van de Graaff accelerator, and c) with ultraviolet light from the high pressure mercury lamp.
Column: Polyethylene glycole 6000, 3.0 m.
Column temp.: 180°C
Carrier gas: He 60 cc./min.

$$A(P^1{}_\gamma, P^1{}_e, P^1{}_{UV}),\ B(P^2{}_\gamma, P^2{}_e, P^2{}_c),$$
$$C(P^3{}_\gamma, P^4{}_e, P^3{}_{UV}),\ D(P^4{}_\gamma, P^8{}_e, P^5{}_{UV})$$

The mass spectra and the infrared spectra of these fractions, A, C and D, are shown in Figs. 3a, 3b and 3c respectively, but the spectra of the fraction B were difficult to obtain because of its small yield as well as because of lack of a standard samples. The fraction A, which gives the same mass spectrum, infrared spectrum and retention time in the gas chromatogram as acetoin,  $CH_3\overset{O}{\overset{\|}{C}}-\underset{H}{\underset{|}{\overset{OH}{\overset{|}{C}}}}-CH_3$, is identified as this compound. The fraction C is assigned to be methyl cyclohexyl ketone (McHK) from the mass and infrared spectra shown in Fig. 3b. The D fraction is estimated to be 1-acetyl-2(3-cyclohexenyl)-cyclohexane,  in the mass spectrum and from

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[3] Y. Nakai et al., Annual Meeting of the Physical Society of Japan, 1963.

* Almost all the data on γ-ray irradiations in this report are reproduced from a former report[1] for the sake of comparison.

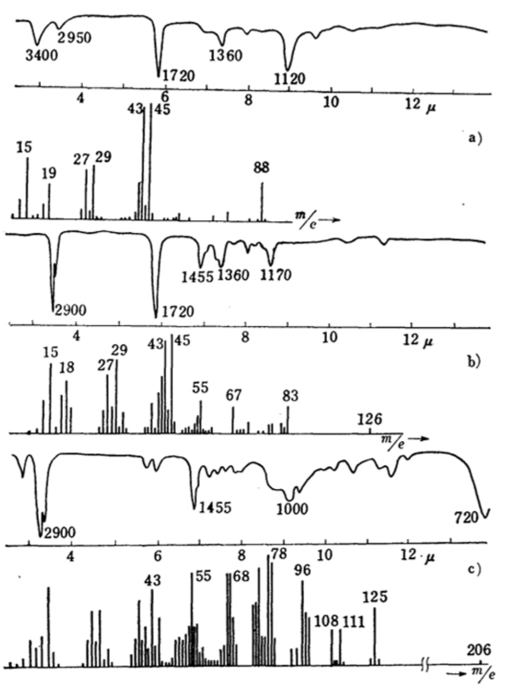
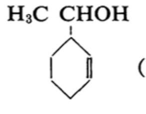


Fig. 3. Mass spectra and infrared spectra of fractions corresponding to the peaks appeared in the gas chromatogramms:
a) P^1_γ, P^1_e, P^1_{UV}, b) P^3_γ, P^4_e, P^3_{UV} and c) P^4_γ, P^8_e

the absorptions of ν_{CH_2,CH_3} (2900~2950 cm^{-1}) and ν_{CO}(1720 cm^{-1}) in the infrared spectrum in Fig. 3c.* Although the identification of this product is not so definite as the former two, it will be supported by the experimental results below.



(I)

In the present experiment, 1-cyclohex-2'-enylethan-1-ol(I) was not found as has been reported by Mayo²⁾, even when ultraviolet was used as the irradiation source. Since the separating factor of the column used in this experiment is not as large as that of Mayo's, there may be some ambiguity concerning the separation of (I) from McHK. However, this ambiguity is reduced to some extent by the fact that the absorption of ν_{OH} is not found in the infrared spectrum of this fraction. At any rate further experiments using higher resolution colums will be needed to elucidate this problem.

The Effect of the Irradiation Time on the Yields. — The amounts of the products are plotted against the irradiation time in Figs. 4-1 and 4-2, practically giving a linear increase of the amount of the products. However in the region of higher doses, the rates of formation decrease because of the decomposition of the products as a result of irradiation.

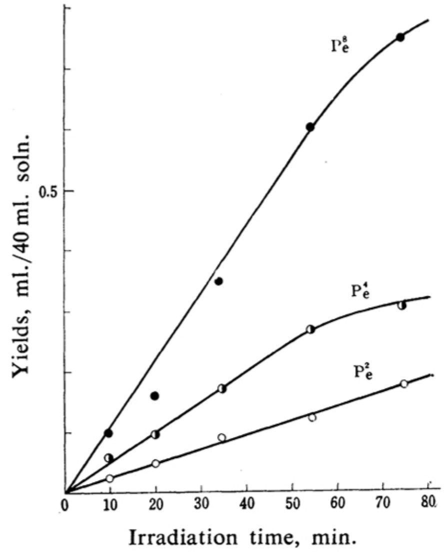


Fig. 4-1. The yields of products vs. irradiation time (electron beam irradiation).
Cyclohexene: 35 ml., Acetaldehyde: 5 ml.
Irradiation temp.: 0°C
Electron accelerating voltage: 1.5 MeV.
Electron beam current: .50 μA.

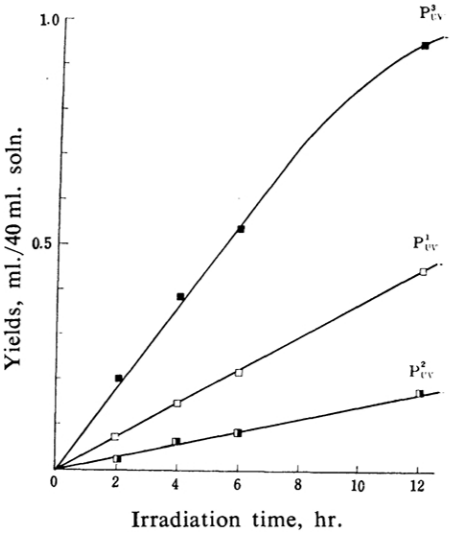


Fig. 4-2. The yields of products vs. irradiation time (ultra-violet light irradiation).
Cyclohexene: 2 ml., Acetaldehyde: 6 ml..
Irradiation temp.: 17°C

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* The absorption band at ν_{OH}~3300 cm^{-1} appeared in the IR spectrum of the fraction C. This band seems to be attributed to a trace of water condensed in the fraction collector from the atmosphere, and it seems to become significant when the fraction is difficult to collect effectively because of its lower vapor pressure.

The Effect of the Compositions of the Feed on the Yields.—The results are shown in Fig. 5, where the yields of the products are plotted against the volume percent of cyclohexene. For the methyl cyclohexylketone formation, the concentration of that cyclohexene in the feed which gives a maximum yield of McHK seems to depend on the type of radiation. It reaches its highest value at 40% in the electron irradiation, at 25% in ultraviolet irradiation, and at 10% in the γ-ray irradiation.

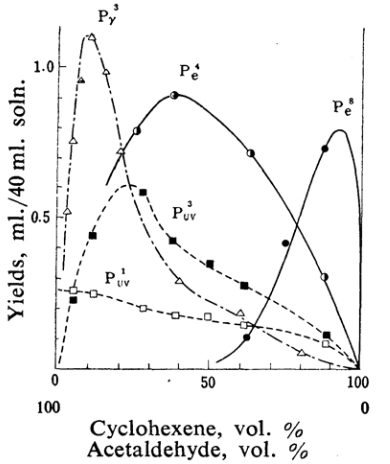


Fig. 5. The yields of products vs. cyclohexene in the feed.

Acetoin was produced most favorably in pure acetaldehyde. The yield of 1-acetyl-2-(3-cyclohexenyl)cyclohexane reaches a maximum in the cyclohexene-rich mixture (ca. 90%). These relations between the yields and the cyclohexene fraction in the feed seem to be reasonable judging from the structure of the product molecules.

The Temperature Dependencies on the Yields.—The yield of McHK increases with the rise in irradiation temperature in the case of ultraviolet irradiation, as Fig. 6 shows. The Arrhenius plot for the McHK formation gives an overall activation energy of 3.5 kcal./mol., which is approximately equal to that obtained in the γ-ray irradiation. This coincidence indicates that the mechanism of the McHK formation is the same in both systems.

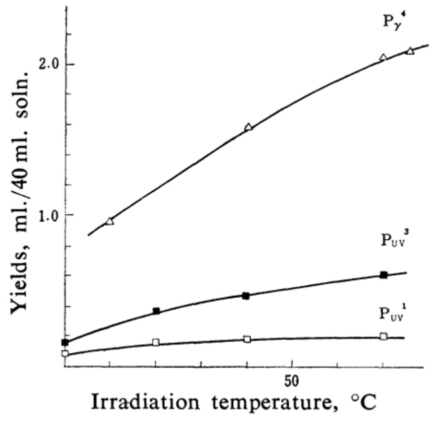


Fig. 6. The yields of products vs. irradiation temperature.

The Effect of the Dose Rate on the Yields.—The effects of the dose rate of the electron beams on the formation of McHK and 1-acetyl-2-(3-cyclohexenyl)cyclohexane are shown in Fig. 7. The yield of McHK is proportional to 1/2 power of the beam current, while that of 1-acetyl-2-(3-cyclohexenyl)cyclohexane is proportional to 1. The reason for this will be discussed below.

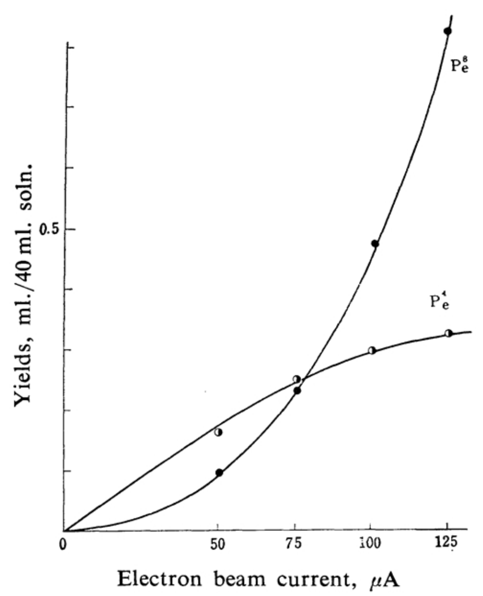
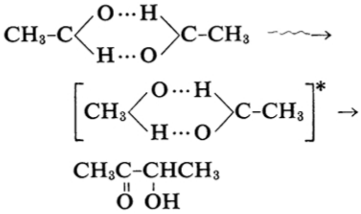


Fig. 7. The yields of products vs. electron beam current.
Cyclohexene: 30 ml., Acetaldehyde: 10 ml.
Irradiation time: 20 min.
Irradiation temp.: 0°C
Accelerating voltage: 1.5 MeV.

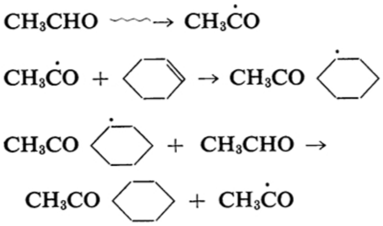
The Effect of Additives.—When ultraviolet was used as the irradiation source, the peaks P^1_{UV} and P^2_{UV} in the gas chromatogram were not affected by the addition of DPPH, but P^3_{UV} decreased markedly. However, when the electron beams were used as the irradiation source, the peaks P^1_e, P^2_e and P^3_e were not changed, while P^4_e and P^8_e decreased markedly upon the addition of DPPH.

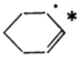
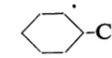
The Reaction Mechanism of Acetoin Formation.—Acetoin was formed by ultraviolet and electron beam irradiations in the acetaldehyde-rich mixture, but it was formed in only a small quantity by the γ-ray irradiation. As has been mentioned above, the formation of acetoin was not inhibited by the addition of DPPH. These facts indicate that acetoin was formed via a bimolecular process 1 which involves the excitation of the acetaldehyde dimer thus, forming a chelate ring. This reaction does not proceed via a chain mechanism, so it plays only a minor role in the case of the γ-ray irradiation, where the dose rate is significantly lower than in the other.



(1)

Methyl Cyclohexylketone.—McHK was formed by γ-ray, electron beam and ultraviolet irradiations. Its formation was inhibited by the addition of DPPH, and its rate of formation depends on the 1/2 power of the dose rate. On the basis of these results, McHK formation may be attributed to the following radical chain process, as was suggested in a previous report:[1)]



Fraction C (1-Acetyl-1-(3-cyclohexenyl)-cyclohexane).—This productwas formed only when a cyclohexene-rich mixture was irradiated with electron beams. The formation of this compound was inhibited by the addition of DPPH, and its rate of formation depends on the first power of the dose rate. Consequently, this fraction was formed by a recombination reaction of the two radicals, probably * and -COCH$_3$.

The fact that this product is formed in only a small amount in the two types of radiation other than that of electron beams may stem from the situation that the radicals which react to form this fraction are not produced effectively in the case of ultraviolet irradiation because cyclohexene does not absorb the ultraviolet light of this wavelength region, and that the concentrations of these radicals are small in the case of γ-ray irradiation because of its low dose rate.

Summary

Several kinds of products have been found to be formed from mixtures of cyclohexene and acetaldehyde by the irradiation of γ-rays, electron beams, and ultraviolet. Both the yields and the kind of product seem to depend on the type of radiation because of their dose rate and bond-dissociating power.

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* It has been reported that the cyclohoxenyl radical may be produced by irradiating cyclohexene at −198°C with electron beams from the Van de Graaff apparatus. Cf. S. Ohnishi and I. Nitta, *J. Chem. Phys.*, 39., 2848 (1963).