

RADIOLYSIS OF 1,5,9-CYCLODODECATRIENE

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The present study of the Co-60 gamma ray radiolysis of cyclododecatriene was undertaken to compare its radiation stability with that of other cyclic hydrocarbons which differ in ring size and degree and arrangement of unsaturation.

Experimental

The irradiations were carried out at an intensity of approximately 2.0×10^5 rad/hr. A total of twenty-six samples were irradiated with total doses ranging from 4.75 to 157.5×10^6 rad. The ferrous sulphate dosimeter was used to calculate intensities. The radiation source was similar to that described previously (Burton, et al., 1955). The cis-trans-trans isomer of 1,5,9-cyclododecatriene used in this study was obtained from the Cities Service Company. Samples were pipetted into clean, Pyrex, break-seal tubes, degassed on a high vacuum system by alternate freeze-thaw cycles, and sealed under vacuum. Irradiations were carried out at approximately 18°C.

Analysis of the irradiated products was carried out as soon as possible after irradiation. Gases were collected and measured with a Toepler pump. Separations were made of gases which were non-condensable at -198°C. (liquid nitrogen), -120°C. (ethyl bromide mush) and -78°C. (acetone-dry ice). These were considered to be hydrogen, ethylene, acetylene, and a C_3 fraction identified by gas chromatography as a mixture of propene and propane. The Toepler pump was so designed that after measurement of the gas volume, the gas could be directly injected into the carrier gas stream of the vapor phase chromatograph. The total measured volume of gaseous products was injected into the carrier gas stream at one time. Analyses of products were made by standard gas chromatography with a four foot column of silica gel at 27°C. Nitrogen was used as a carrier gas in the hydrogen determinations and helium was used for all others. The products were identified by retention times based on comparisons with similar mixtures of known compounds. Similar results were obtained with a dimethylsulfolane on diaomaceous earth column packing (Perkin Elmer Vapor Fractometer). The results are given in Table I as the average values for 14 different samples irradiated for total doses of 4.75 to 157.5×10^6 rad. Over this dose range there is no dose dependence for the G values. The non-gaseous products were

not analyzed. Analysis with a column consisting of three inches of activated charcoal followed by three feet nine inches of silica gel with helium gas a carrier was used in an unsuccessful attempt to detect methane in the product gases.

Table I
Average G-Values of the Products of the Radiolysis of Cyclododecatriene

Product	G-Value	Retention Time	
		Observed ^a	Reported ^b
Acetylene	0.006 $\pm$ 0.0005	2.48	2.43
Ethylene	0.005 $\pm$ 0.0007	0.30	0.32
Propane ^c	0.0004 $\pm$ 0.0008	0.70	0.65
Propene		1.18	1.14
Hydrogen	0.437 $\pm$ 0.010		

^a Dimethylsulfolane on diatomaceous earth, helium, 32 cc./min., 38°, time in min. from air peak.

^b (Scholly and Brenner, 1961).

^c Includes less than 5% propene.

Results and Discussion

The data on the G-values for the gaseous radiolysis products from cyclododecatriene establish that the principal product is hydrogen ($G = 0.437$) and that gaseous ring cleavage products are formed in smaller amounts ($G = 0.015$). The $G(H_2)$ value is intermediate between values of 5.37 for cyclohexane and 1.2 for cyclohexene (Freeman, 1960) and values of 0.04 for benzene (Gordon and Burton, 1952) and 0.02 for cyclooctatetraene (Shida, et al., 1958). The G (cleavage products) of 0.015 is of the same order as values for benzene (0.020) and cyclooctatetraene (0.018), and cyclohexene (0.015).

There are two factors usually considered in accounting for the increased radiation stabilities of aromatic and alicyclic unsaturated hydrocarbons. These are resonance stabilization of aromatic compounds such as benzene and cage effects operative with the alicyclic types such as cyclooctatetraene (Franck and Rabinowitch, 1934). The absence of a planer structure in cyclododecatriene precludes resonance stabilization. It is, therefore, concluded that the low $G(H_2)$ value for this compound, as with other unsaturated alicyclic types, is to be attributed to cage effects. The presence of allylic hydrogen atoms accounts for the somewhat larger $G(H_2)$ as compared to that of cyclooctatetraene which has no such allylic hydrogen atoms.

The ring fragmentation products are somewhat unusual. The absence of butadiene, which was carefully checked, is noteworthy because cyclododecatriene can be considered to be a trimer thereof. The products formed require decomposition and fragmentation pat-

terns which are not yet completely understood. As with other cyclic hydrocarbons irradiated in the liquid state, only a limited variety of cleavage products are formed. All of the products identified have been observed as radiolysis products of other acyclic hydrocarbons.

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Summary

Cobalt-60 gamma irradiation induced decomposition of liquid cis-trans-trans 1,5,9-cyclododecatriene at 2×10^5 rad/hr. and total doses of 4.75 to 157.5×10^6 rad gives hydrogen ($G = 0.437$), acetylene ($G = 0.006$), ethylene ($G = 0.005$), and propane/propene ($G = 0.0004$). These $G(H_2)$ values are intermediate between those for cyclohexene ($G = 1.2$), benzene ($G = 0.04$), and cyclooctatetraene ($G = 0.02$) and the yield of cleavage products is of the same magnitude as for benzene and cyclooctatetraene. These low values indicate a stability attributable to cage effects.

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