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RADIATION CHEMISTRY OF CYCLOHEXANE

IV. PRIMARY PRODUCT YIELDS IN THE IRRADIATION OF CYCLOHEXANE¹

P. J. DYNE AND J. A. STONE

ABSTRACT

The radiolysis of cyclohexane has been studied at low total doses and initial G values have been determined. Ninety-nine per cent of the evolved hydrogen has been accounted for in hydrogen-deficient products. Cyclohexene, bicyclohexyl, and cyclohexyl-hexene-1 have been identified as primary reaction products. Cyclohexyl-cyclohexene has been identified as a secondary reaction product. The use of high irradiation doses has been shown to lead to decreases in the initial G values of all primary products.

INTRODUCTION

A common feature of the reported product yields in the radiolysis of cyclohexane is the discrepancy between the hydrogen yield and the sum of the yields of hydrogendeficient products—principally bicyclohexyl and cyclohexene (1, 2, 3, 4). In all cases the total yield of hydrogen-deficient products is not great enough to account for the observed hydrogen yield. It is generally assumed that high molecular weight products are formed which have remained undetected. There are also disagreements on the identity and yield of some of the minor products.

Cyclohexene, a major product, reduces $G(H_2)$ and is itself destroyed in the radiolysis (5, 6). It follows that accurate initial G values for any product can only be obtained by working at low conversions and by extrapolations to zero dose, thus avoiding the complications of secondary reactions.

This paper describes analytical techniques for the identification and analysis of products at conversion of less than 0.01%. At these low conversions the primary products appear to be cyclohexene, bicyclohexyl, and 6-cyclohexyl-hexene-1. A good hydrogen balance is obtained, all but 1% of the hydrogen being accounted for.

EXPERIMENTAL

Materials

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Fisher Scientific Company Spectrograde cyclohexane was used as received. Gas-liquid chromatography showed three small impurity peaks before the main cyclohexane peak, but neither the sizes nor the shapes of these peaks were altered by γ -radiolysis. Cyclohexene (Eastman) was used as a solute.

Preparation of Samples

The 20-ml samples were contained in Pyrex tubes, 2.5 cm in diameter and 25 cm long, each equipped with a break-tip seal and a constricted side arm. The samples were pipetted

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Can. J. Chem. Vol. 39 (1961)

2381

into the tubes and were then degassed by the freeze-thaw technique. When the residual pressure was less than 5×10^{-6} mm, the sample tubes were sealed off at the constriction. The samples containing solute were made up in bulk and pipetted out as required.

Irradiation of Samples

The samples were irradiated at 22° C by Co-60 γ -rays. Dose rates were determined with the Fricke dosimeter, taking $G(\text{Fe}^{+++}) = 15.5$. Two irradiation facilities were used with dose rates of 4.8×10^{20} ev/liter minute, and 2.6×10^{19} ev/liter minute for cyclohexane at 22° C.

Product Analysis

The irradiated sample tubes were attached to a vacuum line and their contents frozen with liquid nitrogen. The gaseous products volatile at -196° C were then taken off with a Toepler pump and their volume measured with a McLeod gauge, the samples being thawed and refrozen to make sure that all the gas had been collected. Hydrogen was diffused through a heated palladium thimble, and the volume of the residual gas measured. In all cases it was found that this residue amounted to less than 1% of the initial volume. This was confirmed by mass spectral analysis of the collected gas.

The liquid products were analyzed by gas-liquid chromatography. Cyclohexene was determined using a 4-meter column of 3-mm internal diameter, containing firebrick on which was deposited 30% by weight of a silver nitrate/ $\beta\beta'$ oxydipropionitrile mixture as the stationary phase. The column was at room temperature, the sample injection end being at a slightly higher temperature. The results were checked quantitatively by infrared analysis, using the 717-cm⁻¹ cyclohexene band. Products of higher molecular weight than cyclohexane were separated on a 2.5 meter long, 2.5-mm internal diameter column containing 0.1% by weight of Apiezon-L grease on 200-micron diameter glass beads. This column, with a very low concentration of L-grease, gave better separations than a conventional column containing more grease. The more heavily loaded column must be used at a higher temperature to obtain the same separations in a comparable time. With the minimum amount of L-grease, the tailing of cyclohexane was greatly reduced, the less volatile components being eluted at lower temperatures with improved resolution. This column was at a fixed temperature for quantitative work but was temperature programmed for qualitative work.

A simple hydrogen flame detector (7) was used, together with a split-stream device after the column. The output from the detector was fed through the 10⁹-ohm input resistor of an electrometer. Ten- λ samples of the irradiated material, without previous concentration, were injected directly onto the columns, the whole sample being passed through the detector. A new calibration curve was used for each series of analyses, standards and unknowns being run alternately. No standards were available for products other than cyclohexene and bicyclohexyl so their concentrations were obtained from measured peak areas, the peak area being assumed to be proportional to molar concentration.

A Consolidated 21-130 Mass Spectrometer was connected to the outlet of the chromatographic column by means of a heated, stainless steel capillary tube. Approximately 90%of the eluted sample passed through the detector, whilst the remaining 10% flowed through the capillary past a gold leak in the spectrometer sample introduction system. The capillary introduced a delay of the order of 5 seconds between the appearance of a chromatographic peak and the initial appearance of the mass spectrum due to the same component. The spectra were recorded on a recording oscillograph, the time taken to scan from mass

DVNE AND STONE: RADIATION CHEMISTRY

26 to mass 200 being of the order of 1 minute. Interpretable spectra were obtained when the desired component was present in the chromatographic eluent at a concentration of about 100 p.p.m. To obtain this concentration for the components which were present in very small amounts in irradiated samples, the following procedure was employed. A large sample (~ 0.5 ml) of irradiated material was injected, 20 λ at a time, onto the narrow L-grease column. Cyclohexane, which comprised 99.9% of the solution, was eluted rapidly at room temperature, leaving the higher-boiling components still at the column inlet. When sufficient material had been deposited on the column the temperature was raised gradually so that a good chromatographic separation was achieved and the mass spectra obtained. To ensure a rapid clearing of the spectrometer inlet system, and therefore no enhancement of the background spectrum, the temperature of the inlet system was maintained at 200° C and that of the spectrometer ion source at 250° C.

Samples from the chromatographic column were trapped out in micro infrared cells cooled in a solid CO_2 /acetone mixture. The spectra of these samples were obtained on a Perkin-Elmer model 21 machine equipped with a beam condenser.

RESULTS

1. Pure Cyclohexane

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The variation of $G(H_2)$ with dose, at a dose rate of 4.8×10^{20} ev/liter minute, is shown in Fig. 1. Each point on this curve represents the result of one measurement except for the initial G value, which was obtained from a series of measurements extrapolated to zero dose. At low doses a sharp decrease in $G(H_2)$ with increasing dose occurs, but at



F1G. 1. The variation of $G(H_2)$ with total dose.

higher doses the rate of decrease becomes smaller. The initial G value is 5.55. The decrease is clearly non-linear with dose. At the lower dose rate of 2.6×10^{19} ev/liter minute a similar decrease in $G(H_2)$ with dose was recorded. The initial G value was the same within experimental error, but at the lower dose rate the decrease was more rapid with increasing dose. Figure 1 represents a refinement on previously published data (3, 5).

The formation of cyclohexene as a function of dose is shown in Fig. 2. The initial G value is 3.27. At the higher doses shown in the figure the G value is beginning to decrease. A similar curve for bicyclohexyl is shown in Fig. 3. The initial G value is 1.95, and again at the higher doses this value decreases.



FIG. 2. The formation of cyclohexene.

Figure 4 shows the chromatograms obtained for all products of molecular weight higher than cyclohexane and cyclohexene. Figure 4(a) is from a sample of pure cyclohexane irradiated to the low dose of 2×10^{22} ev/liter; Fig. 4(b) is from pure cyclohexane irradiated to the much higher dose of 2×10^{24} ev/liter, and 4(c) is the chromatogram

2384

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DYNE AND STONE: RADIATION CHEMISTRY



FIG. 3. The formation of bicyclohexyl.

obtained from a solution of $4.5 \times 10^{-2}M$ cyclohexene in cyclohexane irradiated to 10^{23} ev/liter. Only the peak heights and areas in one chromatogram should be compared, as different-sized samples were used in the runs a, b, and c. The column was temperature programmed to give the series of peaks shown. These peaks may be conveniently divided into three groups, (i) those having retention times lower than that of bicyclohexyl, (ii) those with almost the same retention time as bicyclohexyl, and (iii) those with greater retention times than bicyclohexyl. The peak areas in each chromatogram are given in Table I in terms of percentages of the total area.

Group i

For pure cyclohexane irradiated to a low total dose, Fig. 4(a), the estimated G value for all products in this group is 0.27.

An infrared spectrum of a trapped sample from group i showed an absorption band at 1634 cm⁻¹ corresponding to the C==C stretching frequency of hexene-1. The mass spectrum



FIG. 4. Gas-liquid chromatograms: (a) cyclohexane at low dose; (b) cyclohexane at high dose; (c) cyclohexane-cyclohexene mixture at low dose. Group i, peaks appearing before the bicyclohexyl peak; group ii, the bicyclohexyl group of peaks; and group iii, the peaks appearing after bicyclohexyl.

TABLE I Relative chromatographic peak areas from Fig. 4

Chromatogram No.	Relative chromatographic peak areas		
	4(<i>a</i>)	-4(b)	-4(c)
Group i Group ii Group iii	$ \begin{array}{c} 12\\ 88\\ 0 \end{array} $	$\begin{array}{c}14\\70\\16\end{array}$	

showed a parent peak at m/e = 166, together with fragment ions associated with both cyclohexyl and hexenyl groups. Unlike the spectrum of bicyclohexyl, the most intense peak of which is at m/e = 82, the peak at m/e = 83 was found to be the largest. This would suggest that a cyclohexane molecule substituted with a straight chain of mass 83 was present. Since the infrared spectrum showed that a cyclohexene group was not present the double bond must be in the side chain. The main chromatographic peak in group i is, therefore, most probably 6-cyclohexyl-hexene-1.

Group ii

Figure 4(a) shows that at very low doses a single peak is obtained. This peak is symmetrical with no sign of any other substance present. A symmetrical peak was obtained no matter how the column conditions were varied, showing that, in all probability, the

2386

DYNE AND STONE: RADIATION CHEMISTRY

identification of this peak as due to a single component, bicyclohexyl, was justified (see below). At higher total doses, however, this was not the case, as Fig. 4(b) shows. A second peak now appears together with the main bicyclohexyl peak, demonstrating that at higher doses a secondary reaction product appears. This we have identified as cyclohexyl-cyclohexene.

For a $4.5 \times 10^{-2}M$ cyclohexene solution, Fig. 4(c), a double peak is observed. The first maximum has the same retention time as bicyclohexyl whilst the second corresponds in position to the shoulder observed in 4(b). At attempt was made to trap the compound associated with the main peak in Fig. 4(a). However, the concentration of this product was too low for this to be possible. An infrared spectrum of the compound associated with the first part of the main peak in 4(b) was found to be identical with that of bicyclohexyl. The spectrum of the sample trapped during the elution of the whole peak showed a new absorption band appearing at 1642 cm^{-1} , corresponding to the C=C stretching frequency in a cyclohexene ring. The spectrum of the sample trapped during the elution of the main double peak of 4(c) showed the same band but in greater strength. From the chromatographic retention time and the infrared results, it would appear that this product, which appears as the radiation dose is increased, is a substituted cyclohexene.

The mass spectrum confirmed the above conclusions. The product provisionally identified as bicyclohexyl had a spectral pattern identical with that of a pure sample. The cyclohexyl-cyclohexene, although not fully resolved from the bicyclohexyl, showed a parent peak at m/e = 164, together with fragment ions associated with cyclohexyl groups at m/e = 83 and 82. In addition a strong fragment ion peak at m/e = 81 was deduced to be the cyclohexenyl ion formed by the rupture of the two ring molecule at the central C—C bond.

Group iii

This group contains the peaks due to compounds of higher molecular weight than bicyclohexyl. No peaks are found at low doses, but some do appear at higher doses and in cyclohexane-cyclohexene mixtures. This group of peaks may therefore be associated with secondary reaction products in pure cyclohexane and with products involving the reaction of cyclohexene in cyclohexane-cyclohexene mixtures. No correlation was attempted between the products found in chromatograms 4(b) and 4(c).

Attempts were made to trap samples of products in this group but without success. Mass spectra showed that cyclohexyl groups were present but no parent peaks could be detected.

2. Cyclohexane-Cyclohexene Mixtures

Samples of a 4.5×10^{-2} M cyclohexene solution were irradiated at the higher dose rate for varying doses up to 10^{23} ev/liter. The gaseous product volatile at -196° C was more than 99% hydrogen. The initial $G(H_2)$ was 4.76. This value was constant over the dose range studied.

The determination of a G value for the production of cyclohexene was difficult. A value of 0.6 ± 0.3 was obtained. The large error was due to the fact that at the doses used only a small change in cyclohexene concentration occurred.

G(bicyclohexyl) could not be determined since complete resolution from the peak assigned to cyclohexyl-cyclohexene could not be obtained. Both peak areas were measured together and the total area was calibrated against that for pure bicyclohexyl. A total G value of 1.3 was found. The sensitivity of the chromatographic detector for bicyclohexyl only was determined, and so the error involved in using this calibration was not

2387

known. With the type of detector used the error is, however, probably small. By visual inspection of the peak shape (Fig. 4(a) group ii), it is seen that bicyclohexyl constitutes roughly 55% of the total area, which would correspond to a G value of 0.72.

The analyses for products in groups i and iii were less accurate. The G values obtained were 0.13 and 0.15 respectively.

DISCUSSION

The results obtained for the product yields in the radiolysis of pure cyclohexane by Co-60 γ -rays are summarized in Table II.

TABLE II				
Initial G values for products in the irradiation of				
pure cyclohexane				

Product	G	
Hydrogen Cyclohexene Bicyclohexyl Cyclohexyl-hexene-1	$5.55 \pm 0.05 \\3.27 \pm 0.06 \\1.95 \pm 0.06 \\0.27 \pm 0.05 \end{bmatrix}$	Hydrogen equivalent = 5.49

All these results were obtained by extrapolation to zero dose since it was shown that the G values of all products decrease with increasing dose. An excellent hydrogen balance has been obtained showing that in the initial stages of radiolysis, i.e. at very low doses, a simplicity of products is observed. No dienes or high molecular weight products are observed and indeed none need be invoked since there is no hydrogen deficit.

At higher doses complications arise. The G values of all the initial products decrease and secondary reaction products appear. Cyclohexyl-cyclohexene is one which has been definitely identified. High molecular weight products appear and the hydrogen deficit becomes greater. Dyne and Fletcher (6) have shown that, on prolonged radiolysis of cyclohexane, the cyclohexene reaches a limiting concentration when its rate of formation is equal to its rate of disappearance. In the present work it has been shown that the radiolysis of a mixture of cyclohexane and cyclohexene results in a decrease in G(cyclohexene)of about 2.7, but the decrease in $G(H_2)$ is only 0.9. This implies that the disappearance of cyclohexene is not brought about simply by the addition of hydrogen to the double bond, but some other reaction must be occurring. Since cyclohexyl-cyclohexene is a secondary product, some substitution at a saturated carbon atom takes place.

These results differ somewhat from those of Waight and Walker (8), who found lower yields of bicyclohexane and cyclohexene (1.6 and 2.4 respectively). The dose rate of their irradiation was about one tenth of the dose rate used here and, at the doses used (6×10^{22}) ev/liter), it is consequently likely that their G values for these products would be significantly lower than the true initial value. We do not observe cyclohexyl-cyclohexene as a primary product.

REFERENCES

1. H. A. Dewhurst. J. Phys. Chem. 63, 813 (1959).

- - 3.
 - 4. 5.

 - 6. 7.
- H. A. DEWHURST, J. Phys. Chem. 63, 813 (1959).
 A. C. NIXON and R. E. THORPE. J. Chem. Phys. 28, 1004 (1958).
 G. R. FREEMAN. J. Chem. Phys. 33, 71 (1960).
 T. D. NEVITT and L. P. REMSBERG, J. Phys. Chem. 64, 969 (1960).
 W. S. GUENTER, T. J. HARDWICK, and R. P. NEJAK. J. Chem. Phys. 30, 601 (1959).
 P. J. DYNE and J. W. FLETCHER. Can. J. Chem. 38, 851 (1960).
 I. G. MCWILLIAM and R. A. DEWAR. Gas chromatography. *Edited by* D. H. Desty. Butterworths, J. London 1058. London. 1958
 - 8. E. S. WAIGHT and P. WALKER. J. Chem. Soc. 2225 (1960).

2388