RADIATION CHEMISTRY OF CYCLOHEXANE

II. DOSE RATE EFFECTS ON THE FORMATION AND DESTRUCTION OF CYCLOHEXENE¹

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ABSTRACT

Prolonged radiolysis of cyclohexane leads to a steady-state concentration of cyclohexene where G(cyclohexene) = 0. At concentrations greater than this steady concentration, cyclohexene is destroyed. It is shown that this steady-state concentration is a function of dose rate, varying approximately as the fourth root of the radiation intensity. A discussion of these and other observations indicates that dose rate and L.E.T. effects are observed in cyclohexane only if radical scavengers are present and that cyclohexene, a product of radiolysis, acts as a radical scavenger in irradiated cyclohexane.

INTRODUCTION

Cyclohexene and bicyclohexyl are the two major high molecular weight products formed in the radiolysis of cyclohexane. Dewhurst and Schuler (1) have shown that the initial G values (molecules formed/100 ev absorbed) for cyclohexene and bicyclohexyl are independent of the L.E.T. (Linear Energy Transfer)* of the irradiation. Dewhurst (2) showed that G(cyclohexene) decreases with dose (i.e. with increasing cyclohexene concentration) and, further, that in concentrated solution $(5 \times 10^{-4} \text{ moles/g})$, cyclohexene is destroyed. It follows that prolonged irradiation of cyclohexane or of solutions of cyclohexene in cyclohexane leads to a "steady-state" concentration of cyclohexene where G(cyclohexene) = 0. Dewhurst and Schuler (1) found some evidence that G(cyclohexene) fell off more rapidly with cyclohexene concentration at low dose rates, using a Co⁶⁰ γ -ray source, than at the higher dose rates obtained with electron and particle beams.

We have studied the formation and destruction of cyclohexene as a function of the dose rate, using $Co^{60} \gamma$ -rays and have shown that the "steady-state" concentration increases slowly with the dose rate. The dependence is less than a proportionality to the square root of radiation intensity and approximates to a fourth root dependence.

EXPERIMENTAL

Samples of cyclohexane (spectroscopic grade from various manufacturers) were irradiated in sealed glass vessels. The liquids were degassed by freezing, pumping, and thawing five times. Two Co⁶⁰ sources were used (3) having dose rates of 1.4×10^{19} ev/g hr and 9.6×10^{17} ev/g hr. These dose rates were established using the Fricke dosimeter, $G(Fe^{3+}) = 15.5$ ions/100 ev. Analysis for cyclohexene was done by infrared spectrophotometry of the 640 cm⁻¹ band of cyclohexene using a Perkin–Elmer, model 21, spectrometer. Path lengths of 0.2–4.0 mm were used with compensating cells containing pure cyclohexane for the thicker cells. The irradiations were made over an extended period of time (irradiations of up to 1400 hours at the low dose rate). The solutions were stored after irradiation and were all analyzed at one time together with a series of standard solutions of known concentration. The concentrations were determined by graphical interpolation from the measurements of the standard spectra. At the low

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^{*}Equivalent to the ionization density along the track.

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dose rates the range of the experiments was increased by irradiating solutions that already contained cyclohexene. These results fitted smoothly into the curves obtained in the irradiation of pure cyclohexane.

RESULTS

Most of the experimental results for the high and low dose rates are shown in Figs. 1 and 2 respectively. It should first be noted that at the lower dose rate cyclohexene is



FIG. 1. Formation and destruction of cyclohexene at a dose rate of 1.4×10^{19} ev/g hr.

destroyed at concentrations such as 3.0×10^{-5} moles/g where it is still being formed at the higher dose rate. A similar comparison can be made between our high dose rate results, where decomposition occurs at concentrations greater than 4.5×10^{-5} moles/g, and Dewhurst's results with an electron beam (1), where net decomposition is observed only at concentrations greater than 4.0×10^{-4} moles/g.

We have drawn an initial slope, equivalent to $G(C_6H_{10}) = 2.5$, equal to Dewhurst's

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FIG. 2. Formation and destruction of cyclohexene at a dose rate of 9.6×10^{17} ev/g hr.

value, on both Figs. 1 and 2. It can be seen that there is no significant change in the initial G-value with dose rate. The G-value indicated by the first point (at the lowest cyclohexene concentration) in Fig. 1 and in Dewhurst's Fig. 1 are between 3.0 and 3.2. The value of 2.5 must be regarded as a minimum value; it is possible that the true limiting G-value is 3.0 or higher.

We have calculated G-values for each successive pair of experimental points in Figs. 1 and 2 and for Dewhurst's experimental results. In Fig. 3 the G-values are plotted against the concentration of the first point, i.e. the one with lower concentration where G-cyclohexene is positive and the one with the higher concentration when G-cyclohexene is negative. This procedure is, we feel, preferable to drawing a smooth curve through the experimental points and measuring graphically the slopes of a series of tangents. Due to the fairly steep curvature of the plots of $G(C_6H_{10})$ vs. cyclohexene concentration this is a plot of minimum G-values ($G(C_6H_{10})$ and $G(-C_6H_{10})$ both having positive signs). The high initial points, G = 3.0-3.2 mentioned in the previous paragraph, are seen on the





FIG. 3. *G*-values for formation and destruction of cyclohexene as a function of cyclohexene concentration. See text for method of calculation.

graph. The locus of $G(C_6H_{10})$ vs. C_6H_{10} for the lower dose rate $(9.6 \times 10^{17} \text{ ev/g hr})$ experiments is also shown in Fig. 3. At this low dose rate $G(C_6H_{10}) = 0$ at a cyclohexene concentration of 2×10^{-5} moles/g and the largest observed value of $G(-C_6H_{10})$ is 1.6 at 6.1×10^{-4} moles/g. The largest observed value of $G(-C_6H_{10})$ at our higher dose rate of $1.4 \times 10^{19} \text{ ev/g hr}$ was 3.0 at 6.0×10^{-4} moles/g. Dewhurst reports a value of $G(-C_6H_{10}) = 2.3$ at 5.2×10^{-4} moles/g at the high dose rate obtained with the electron beam. This value is greater than that shown in Fig. 3 as it was derived from the initial slope of a smoothed curve.

The steady-state concentrations determined from Fig. 3 are given in Table I, which includes the relative concentrations and dose rates and shows that the steady-state concentration varies approximately as the fourth root of the dose rate. The term steady state is, perhaps, somewhat unfortunate as it implies that this concentration will never change. With very long irradiations, 10 or more times the highest doses used here, further reactions must be expected. The term refers only to the dose range of the present experiments.

TABLE I											
riation	of	steady-state	concen	tration	with	dose	rate				

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Dose rate, ev/g hr	Steady-state concn., moles/g	Relative dose rate	Relative concn.	(Relative dose rate) ^{1/2}	(Relative dose rate) ^{1/4}
9.6×10^{17} 1.4×10^{19} 5.2×10^{22}	2.0×10^{-5} 4.5×10^{-5} 4.2×10^{-4}	$^{1.0}_{14.5}_{5.4 imes 10^4}$	$\begin{smallmatrix}1.0\\2.25\\21.0\end{smallmatrix}$	$1.0 \\ 3.80 \\ 2.32 \times 10^2$	$\begin{smallmatrix}1.0\\1.94\\15.2\end{smallmatrix}$

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Irradiation of cyclohexane in a spent fuel-element γ -ray source, reported by Nixon and Thorpe (4), gave a concentration of 2.7×10^{-5} moles/g cyclohexene at a dose of 4.8×10^{21} ev/g, equivalent to G(cyclohexene) = 0.34. When compared with the initial G(cyclohexene) = 2.5 this low G-value indicates that the system was approaching a steady state. The steady-state concentration at their dose rate ($\sim 4 \times 10^{19}$ ev/g hr or perhaps somewhat less) (5) is, by interpolation from the data in Table I, $\sim 6 \times 10^{-5}$ moles/g.

DISCUSSION

Two different, but closely related, effects have to be explained; the invariance of initial yields with L.E.T. and with dose rate, and the variation of yields with dose rate in the presence of cyclohexene. It is well known that both L.E.T. and dose rate effects are generally due to a competition between reactions $R + R \rightarrow$ products, P_1 involving two precursors (free radicals) and reactions $R + S \rightarrow$ products, P_2 involving one precursor and a stable molecule S present in macro quantities. The products P_1 and P_2 may consist of more than one species. Variations in yield with L.E.T. occur because the balance of the competition is largely determined by the initial distribution of the precursor R. The chief features of the radiation chemistry of water are explicable in these terms.

Variations of yields with dose rate occur, in general, because the steady-state concentration of precursors is determined by functions involving the dose rate and the square root of the dose rate: the square root arising from the bimolecular removal of precursors in a reaction $R + R \rightarrow P_I$. This situation occurs if the precursors are reacting homogeneously, track effects being absent (as in photochemistry).

The chief experimental observations to be correlated and explained are:

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1. The initial yield of hydrogen from cyclohexane is independent of L.E.T. and dose rate. This was demonstrated by Schuler and Allen (6).

2. The initial yield of cyclohexene is also independent of dose rate and L.E.T. This may be stated, using E for cyclohexene, as (dE/dt) $(E \rightarrow 0) = k_1I$, where I is the dose rate. This also expresses the fact that dose rate and/or L.E.T. effects are observed only in the presence of cyclohexene.

3. The yield of cyclohexene from unimolecular processes $C_6H_{12} \rightarrow C_6H_{10} + H_2$ has a *G*-value less than 1.0; the major fraction of the yield ($\sim 2/3$) is produced by bimolecular processes, probably the disproportionation of cyclohexyl radicals, $2C_6H_{11} \rightarrow C_6H_{10} + C_6H_{12}$. This conclusion was reached by Dewhurst (2) from studies of the yield of cyclohexene in the presence of oxygen (1) and is in agreement with the measurements made by Dyne and Jenkinson (7) of the yield of deuterium produced in unimolecular processes from C_6D_{12} .

4. The steady-state concentration of cyclohexene varies slowly with radiation intensity, approximately as the fourth root of I, i.e. $E_s \simeq k_2 I^{1/4}$.

5. The yield of cyclohexene drops very sharply with cyclohexene concentration at the lower dose rates. Cyclohexene inhibits its own formation very effectively, more effectively than it reduces the yield of molecular hydrogen.

The invariance of the hydrogen yield with L.E.T. can be simply explained. Hydrogen is presumably formed by $H + C_6H_{12} \rightarrow H_2 + C_6H_{11}$; this is essentially the scavenging reaction $R + S \rightarrow$ products, where S is present at a very high concentration—so high that the probability of the recombination reaction $H + H \rightarrow H_2$ is very small. It should also be noted that the scavenging reaction gives one molecule H_2 for one hydrogen atom

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while the recombination reaction gives one molecule H_2 for two hydrogen atoms. If the two reactions rates were comparable then the hydrogen yield would *decrease* with increasing L.E.T. as the probability of bimolecular recombination would increase.

The invariance of the initial yield of cyclohexene with L.E.T. may arise from the opposite circumstance; all the precursors of cyclohexene react $R + R \rightarrow$ products (e.g. cyclohexene) and the scavenging reaction is non-existent. Scavengers (cyclohexene itself, for instance) may be formed during the radiolysis. Changes in yield with L.E.T. would then be observed in solutions containing cyclohexene but not in pure cyclohexane. This is in agreement with experiment. The variation in yield of bicyclohexyl with dose rate, which is similar to the behavior of cyclohexene observed by Dewhurst and Schuler (1), would be explained similarly.

With reference to the steady-state concentration, it is not possible to distinguish properly between L.E.T. and dose rate effects. The dose rate variation has been observed with $Co^{60} \gamma$ -rays. No α -particle or proton beam experiments have been reported in which the total dose rate was varied or in which the irradiation was carried to a sufficiently high dose rate for the observation of the radiation steady state.

Dose rate effects in γ -ray irradiations can occur only when radicals (or precursors) have an appreciable probability of escaping from the spur in which they were formed and of reacting with radicals produced in other spurs. Homogeneous kinetics, as in photochemistry, are then applicable. A competition between $R + R \rightarrow P_1$ reactions (second order in R) and $R + S \rightarrow P_2$ reactions (first order in R) will give rise to dose rate dependence of the yields of P_1 and P_2 and of the disappearance of S. The present evidence suggests that cyclohexene is the scavenger S as its presence generates the dose rate effects. The effectiveness of cyclohexene in the inhibition of its own formation suggests, also, that in the $R + R \rightarrow P_1$ reactions, P_1 includes cyclohexene. Cyclohexene is destroyed in the scavenging reactions and in some of these same reactions it destroys its own precursors. As G(cyclohexene) falls more rapidly than $G(H_2)$ with cyclohexene concentration (i.e. the reduction in $G(H_2)$ is not equivalent to the reduction in G(cyclohexene)), cyclohexene must presumably be reacting with other precursors as well as with hydrogen atoms.*

Schuler (8), using a variety of ionizing radiations, measured the disappearance of iodine in cyclohexane solutions and equated this yield with the total radical yield. The radical yield obtained with 33-Mev helium ions is about 30% less than that found in electron beam irradiations. Compared with the effects in water this is a small change in yield with L.E.T. Under the particular experimental conditions used (dose rate, scavenger concentration, etc.) the scavenging reaction is dominating the recombination reaction over the whole L.E.T. range. Detailed studies of scavenging, similar to those done by Charlesby and Lloyd (9) on anthracene are needed to put this and other observations (such as those presented in this paper on cyclohexene) on a quantitative basis.

The relations $dE/dt.(E \to 0) = k_1I$ and $E_s \simeq k_2I^{1/4}$ are reduced, approximate forms of the general rate equation dE/dt = F-D where F is the rate function for all processes forming cyclohexene and D the rate function for all processes destroying cyclohexene. Both these rates F and D are likely to be functions of E and I. We may speculate on the form of F and D, as follows. The $I^{1/4}$ function is probably derived from the $I^{1/2}$ dependence found in many radical chain mechanisms. The relation $E_s \simeq k_2 I^{1/4}$ is possibly

*This conclusion is contrary to the argument given by Dewhurst, who equates the change in hydrogen yield with the value of $G(-C_6H_{10})$ at a concentration of 5.2×10^{-4} moles/g. The correct value for the comparison is $[G_{\text{Inttal}}(C_6H_{10}) + G(-C_6H_{10})]$ and this is greater than the reduction in hydrogen yield.

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a simplification of $E_{s^2} \simeq k_2^2 I^{1/2}$. This equation is a reduced form of the relation D = Fwhen $E = E_s$. Now F, the processes of formation, are likely to be proportional to I; they are certainly so when E = 0. The process of destruction is likely to be a reaction of cyclohexene with a reactive intermediate with a rate governed by k.E.R where R is the steady-state concentration of this intermediate. If this is the intensity-dependent process, it may have the form $k'' E I^{1/2}$. The relation $E_s^2 \simeq k_2^2 I^{1/2}$ can be rearranged to $E_s I^{1/2} \simeq k_2^2 I/E_s$ which we identify with D = F. Now F cannot be inversely proportional to E as $E \to 0$ —it must have a form of the type: $k_2^2 I/(k_3 + E)$, in which k_3 is sufficiently small that E quickly becomes the dominating term in the denominator.

The true rate equations must be more complex than this. We know that there are two processes, one unimolecular, the other bimolecular, forming cyclohexene, i.e. $F = F_1 + F_2$, each presumably having a different dependence on E and I. There may again be more than one process destroying cyclohexene. The sum of all destruction $\Sigma_1 D_1$ and formation processes are related by $\Sigma_1 D_1 = F_1 + F_2$ at the steady state. The relation $E_s I^{1/2} \simeq k_2^2 I/(k_3 + E)$ is a simplification of this relation which is observed over a possibly limited range of values of E and I.

In summary, the chief conclusion of this study is that, in liquid cyclohexane, scavengers must be present before dose rate and L.E.T. effects are observed and that a major product of the radiolysis, cyclohexene, acts as a scavenger.

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