Effect of Dose-rate in the Radiolysis of Liquid Cyclohexane

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WHEN cyclohexane is irradiated with radiation of increasing linear energy transfer (L.E.T.) ($-dE/dx$), changes occur[1-6] in the yields of the major products, hydrogen, cyclohexene, and bicyclohexyl (Table 1).

Such effects are thought to be due to the competition between first- and second-order reactions

$$H\cdot + C_6H_{12} \rightarrow H_2 + C_6H_{11}\cdot$$

$$H\cdot + H\cdot \rightarrow H_2$$

$$H\cdot + C_6H_{11}\cdot \rightarrow C_6H_{12} \text{ (or } H_2 + C_6H_{10})$$

$$C_6H_{11}\cdot + C_6H_{11}\cdot \rightarrow \begin{cases} C_6H_{10}\cdot + C_6H_{12} \\ C_{12}H_{22} \end{cases}$$

of short-lived intermediate species (ions, excited molecules, and radicals), and mechanisms based on the competing reactions of hydrogen atoms,[3,4] and of excited molecules,[4,6] have been advanced.

Analogously with L.E.T. and dose-rate effects in aqueous solution[7,8] it is expected that similar trends in low-dose G-values for cyclohexane will be shown at high dose-rate as the dose-rate is is increased. It has been shown (ref. 9, Figure 4) that if the competing reactions of hydrogen atoms were the cause of a dose-rate effect:

$$k_1[C_6H_{12}] = 5 \times 10^7 \text{ sec.}^{-1}$$

$$2k_{1,1} = 3{\cdot}00 \times 10^{10} \text{ l.mole}^{-1} \text{ sec.}^{-1}$$

$$k_{1,2} = 1{\cdot}57 \times 10^{10} \text{ l.mole}^{-1} \text{ sec.}^{-1}$$

$$2k_{2,2} = 6{\cdot}78 \times 10^9 \text{ l.mole}^{-1} \text{ sec.}^{-1}$$

then for the plausible rate-constants given above, decreases in condensed product yields are to be expected in the dose-rate range 10^{25} to 10^{28} ev g.$^{-1}$ sec.$^{-1}$. By use of the Mount Vernon electron

TABLE 1

Liquid cyclohexane at 22—25°. Effect of linear energy transfer

Radiation	Energy (Mev)	Mean L.E.T. (kev/μm.)	$G(H_2)$	$G(C_6H_{10})$	$G(C_{12}H_{22})$	Ref.
^{60}Co γ-rays	—	$\sim 10^{-1}$	5·6	3·01	1·83	5
^{1}H	3·8	25·5	—	2·55	1·33	5
^{1}H	2·5	29·5	—	2·36	1·20	5
^{1}H	0·8	55	—	2·28	1·08	5
^{4}He	1·5	200	4·49	1·63	0·68	5
^{20}Ne	22	1250	5·89	1·5	0·55	5
^{235}U(n,f)	165	~ 4000	7·73	$<1{\cdot}5$	$<0{\cdot}4$	6

Doses 1·6—4·5 $\times$ 10^{19} ev g.$^{-1}$ over which range G-values were independent of dose.
Dose-rates 10^{17}—10^{21} ev g.$^{-1}$ sec.$^{-1}$ over which range G-values were independent of dose-rate.

TABLE 2

Liquid cyclohexane at 22—25°, G-Values at high dose-rate

	Dose-rate (ev $g.^{-1}$ $sec.^{-1}$)	Dose (ev $g.^{-1}$)	$G(C_6H_{10})$	$G(C_{12}H_{22})$	No. of experiments
Series 1:	*ca.* 2×10^{25}	$0{\cdot}25$—$1{\cdot}0 \times 10^{14}$	$2{\cdot}58 \pm 0{\cdot}16$	$1{\cdot}41 \pm 0{\cdot}04$	4
Series 2:	*ca.* 2×10^{25}	$0{\cdot}4$ —$1{\cdot}5 \times 10^{19}$	$2{\cdot}90 \pm 0{\cdot}2$	$1{\cdot}47 \pm 0{\cdot}1$	4

linear accelerator,[10] we have now achieved dose-rates in this range and have found changes in product yield ratios in the expected direction; however, at this stage other mechanisms cannot be precluded.

The irradiation vessel was an evacuated 6 mm.-bore glass U-tube joined at the top, with a constriction down to a 1 mm.-bore, 4 mm. long thin-walled tube in one arm, and with a magnetically-controlled closely-fitting plunger in the other. The plunger, of *ca.* 1 cm. diameter, was allowed to fall under gravity, at *ca.* 10 mm. $sec.^{-1}$, during irradiation, forcing the liquid through the capillary at *ca.* 700 mm. $sec.^{-1}$. The beam was focused and collimated to a 1 mm. square, irradiating the capillary section with 2 μsec. pulses of *ca.* 0·7 Mrad. per pulse, and the pulse repetition rate, 50 to 150 $sec.^{-1}$ was such that there was no overlap of irradiated volumes (of $\sim$2 μl.) during irradiation. This minimized the effects of secondary reactions and of heating by the beam. The total volume of 7—8 g. was irradiated to doses of $\sim 10^{19}$ ev $g.^{-1}$ at dose-rates of $\sim 2 \times 10^{25}$ ev $g.^{-1}$ $sec.^{-1}$ measured using approximate ferrous sulphate dosimetry[7] [$G(Fe^{3+})$ 7—8, extrapolated]. The following G values are based on $G(H_2) = 5{\cdot}6$.

These G-values are significantly lower than those in the first row of Table 1 and would be lower still if $G(H_2)$ were less than 5·6.

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