

SCAVENGER KINETICS IN THE RADIOLYSIS
OF CYCLOHEXANE-METHYL IODIDE
SOLUTIONS

By
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SECTION I

INTRODUCTION

Radiation chemistry is the study of the chemical effects produced in a system by the absorption of ionizing radiation. The radiations may come from radioactive nuclei (alpha, beta, or gamma rays), from particle accelerators (electrons, protons, deuterons, etc.) and from X-ray machines. The radiation dissipates energy by interacting with electrons in the system and each photon or particle can ionize or excite a number of molecules (via secondary electrons in the case of photons).

For the present study the source of radiation was a 400 curie Co^{60} source, emitting gamma rays of 1.17 and 1.33 mev. The mechanisms by which gamma rays interact with matter, namely photoelectric effect, Compton effect, and pair production, are well known.

The radiation chemistry of a number of hydrocarbon systems has now been studied. It is becoming evident that the product formation in the radiolysis of organic systems results from the direct production of product molecules as well as through the intermediate formation of ions and free radicals. Reactive solutes such as halogens, hydrogen halides, DPPH, O_2 , etc., have been used as scavengers in the measurement of free radical yields. In most cases, the effect of scavengers has been interpreted only qualitatively.

The present study deals with a quantitative treatment of HI-I₂ competition kinetics in the radiolysis of pure cyclohexane and cyclohexane-methyl iodide solutions. Rate equations, based on previously known mechanisms, were set up and their integration was done by numerical calculations using the second-order Runge-Kutta method on an IBM 709 computer.

Summary of the Previous Work

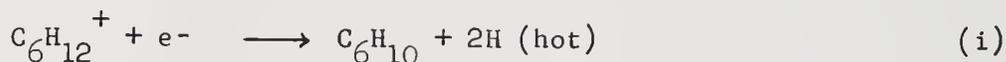
Radiolysis of the mixtures of liquid organic compounds dates back to 1931 when Schoepfle and Fellows¹ exposed a solution of benzene and cyclohexane to 170 kv cathode rays. They found that the hydrogen yield from cyclohexane decreases non-linearly with the addition of benzene. Since then cyclohexane has been the object of a number of investigations, e.g., in the pure state,⁴⁻¹⁰ with small concentration of solutes,^{8,11-16} and in mixtures.^{3,6-8,15}

The studies on pure cyclohexane have been concerned with the identification and yield of radiolysis products, and the role of scavengers. Hydrogen, cyclohexene, and bicyclohexyl are the major products.^{5,6,9,10,13} The use of iodine as radical scavenger in hydrocarbon radiolysis has been demonstrated by Fessenden and Schuler.¹⁹ They studied the effects of radiation on solutions of iodine in cyclohexane over the iodine concentration range of 5×10^{-6} M to 5×10^{-2} M. They found that the yield for the formation of alkyl iodide is independent of iodine concentration from 10^{-5} M to 5×10^{-3} M but is somewhat higher at higher concentrations. In the lower concentration region, the radiation yield, G(RI), is found to be 5.6 for both Co⁶⁰ gamma radiation

and 2 mev Van de Graaff electrons. It appears that the radiation chemical processes which are responsible for the ultimate chemical reactions are affected by the presence of high scavenger concentration in the substrate. At low concentrations, the presence of iodine does not complicate the physical processes resulting from the radiolysis.

The presence of hydrogen atoms in cyclohexane radiolysis has been detected directly by Smaller and Matheson⁴¹ and indirectly by Forrestal and Hamill¹⁰ and by Meshitsuka and Burton.¹⁴ Nash and Hamill³⁵ studied the hydrogen yield from solutions of cyclohexane-d₁₂ and hydrogen iodide. They observed an increase in the total hydrogen yield, as had been reported previously.^{10,12,16}

Toma and Hamill²² studied the mechanism of hydrogen formation in the radiolysis of cyclohexane and other hydrocarbons. They showed that the molecular yield of hydrogen can be accounted for by a mechanism of the type



When the thermal component of $G(\text{H}_2)$ in cyclohexane is suppressed by ca 10^{-2} M iodine, further addition of cyclohexene²³ continues to suppress $G(\text{H}_2)$. They found that addition of methyl iodide, however, continues to depress the somewhat correlated $G(\text{H}_2)$, $G(\text{C}_6\text{H}_{10})$, and $G(\text{C}_{16}\text{H}_{11}\text{I})$ by removing a common precursor of these products. They accounted for the effect of cyclohexene or benzene²⁴ in cyclohexane upon $G(\text{H}_2)$ by charge transfer processes as well as H atom scavenging.

Radiolysis of mixtures is more complicated and several processes

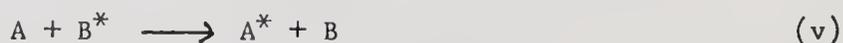
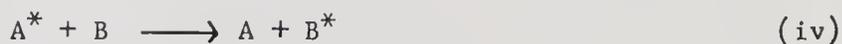
have been found to account for the over-all yields of products. Magee and Burton² suggested that ion-exchange processes may play a significant role in the radiation chemistry of mixtures. In a system consisting of molecules A and B, in which the ionization potential of A is less than that of B, the ionization, irrespective of the component primarily ionized, may be transferred to A. This greatly modifies the resultant chemical processes.

Manion and Burton³ irradiated four mixtures, namely toluene-benzene, cyclohexene-benzene, cyclohexane-benzene, and cyclohexane-cyclohexene by 1.5 mev electrons. The results obtained are consistent with an interpretation involving considerable emphasis on ion and excitation-transfer mechanisms. In a mixture of two components A and B, both are primarily affected by the ionizing radiation to produce A^+ and B^+ and of excited molecules A^* and B^* . If $I_A > I_B$ where I_A and I_B are the respective ionization potentials, then the process



may occur.

Either of the excitation-transfer processes



can occur dependent on the relative heights of the energy levels involved. The condition for most probable excitation transfer is that $E_A = E_B$ where E_A and E_B represent respective excitation energies. However, reaction (iv) is possible if $E_A > E_B$, the reference being to

the lowest excited states. In the case of toluene-benzene mixtures, the contribution of the excitation-transfer mechanism is unimportant, for the lower excited states make a negligible contribution to the total chemical effect. The primary chemical processes involve principally toluene, as is required by the ionization-transfer mechanism. In the radiolysis of cyclohexene-benzene mixtures, the two effects act in opposition, with cyclohexene playing a sacrificial role in protection of benzene ions and benzene offering sponge-type protection to excited cyclohexene molecules. In cyclohexane-benzene mixtures, benzene protects cyclohexane because it has both lower ionization potential and lower excitation energy. In cyclohexane-cyclohexene cases, limited evidence indicates just sacrificial protection by cyclohexene.

The role of ionic processes such as electron attachment, charge transfer and ion-molecule reactions has been emphasized by Hamill and coworkers. Williams and Hamill¹¹ studied the chemical effects of electron capture by solutes in hydrocarbons during gamma irradiation. They irradiated various samples consisting of cyclohexane, toluene and benzene as solvents and I_2^{131} , CH_3I^{131} , and $C_2H_5I^{131}$ as solutes. The observed yields could not be interpreted on the basis of positive charge transfer which may contribute whenever the ionization potential of the solvent exceeds that of the solute. This condition holds for cyclohexane as the solvent but not for benzene and toluene. They found that electron capture does appear to provide a consistent explanation of the observed results.

Schuler¹² extended the studies of Williams and Hamill¹¹ on dissociative electron capture by examining the effect on the hydrogen

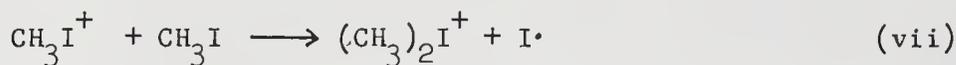
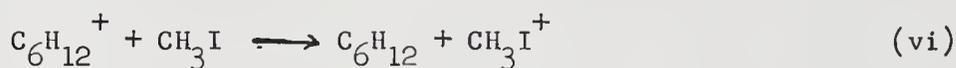
yield from cyclohexane of solutes similar to those which they used. He found that low concentration of solutes having high electron affinities such as iodine, alkyl halides, and sulfur dioxide decrease the hydrogen yield in the gamma irradiation of cyclohexane by about 40 percent. This decrease in hydrogen is ascribed to a transfer of energy to the solute, probably by an electron capture mechanism.

Forrestal and Hamill¹⁰ irradiated a number of liquid mixtures containing cyclohexane. They showed that the hydrogen yield can be divided into three components; one due to reactions of thermal H atoms, one to reactions of hot, high-velocity H atoms, and the third corresponding to hydrogen formed by molecular processes. In the case of radiolysis of cyclohexane-iodine mixtures with low iodine concentrations, they found that the decrease $G(\text{H}_2) = -2.0$ is matched by nearly equal $G(\text{HI})$ and is attributed to scavenging of thermal H atoms. They reported that the iodine concentration must be greater than 0.3 M in order to scavenge at least 99 percent of the available H atoms in cyclohexane. Forrestal and Hamill also presented considerable data on cyclohexane-methyl iodide system. They explained the effect of methyl iodide on $G(\text{H}_2)$ in a similar manner and found that their results with 0.1 electron percent or less added methyl iodide could be explained by competitive H atom scavenging by cyclohexane and methyl iodide. They postulated that the behavior in the 1-10 percent methyl iodide concentration range is due to dissociative electron capture by methyl iodide.

In their work on solutions of HI in cyclohexane- d_{12} which was mentioned above, Nash and Hamill³⁵ attributed the increase in the total hydrogen yield to dissociative electron attachment. At high concentrations

of ca 10^{-2} M, HI may become involved in electron capture or energy transfer processes.

Croft and Hanrahan²⁰ studied the iodine production in gamma radiolysis of cyclohexane-methyl iodide solutions. To explain the results, they postulated that the production of iodine in dilute solutions in cyclohexane is due to the ion-molecule mechanism similar to that proposed by Gillis, Williams and Hamill²¹



Upon neutralization of the product ion there results a "pocket" containing two methyl radicals and two iodine atoms which can undergo diffusion controlled recombination, giving ethane and iodine. Between 10-100 electron percent methyl iodide, the residual free radical production from cyclohexane would fall to zero and the efficiency of reaction (vii) would approach its value in pure methyl iodide.

Summary of the Present Work

The present work reports a series of experiments performed by irradiating pure cyclohexane with I_2 , HI, or both added initially. Cyclohexane-methyl iodide solutions having 20 to 99.9 volume percent cyclohexane were also irradiated with added I_2 or HI and without additives. The resulting iodine production or consumption during the course of radiolysis was plotted against dose in each case. The initial slopes of the graphs for those experiments in which no additives were added are designated as "Normal Rates" of the iodine production;

the initial slopes with added I_2 and with added HI are designated as "Minimum Rates" and "Maximum Rates", respectively. In the case of cyclohexane-methyl iodide solutions having 80 to 95 volume percent cyclohexane with added I_2 , the graphs are more interesting in that the iodine concentration actually decreases at first, comes to a minimum, and then increases.

During the investigations described here, it was found possible to predict quantitatively the curvature of graphs of iodine concentration vs dose on the basis of HI- I_2 competition kinetics. A simplified mechanism, based upon previous work, has been used. For pure cyclohexane, this mechanism includes the production of alkyl radicals, hydrogen atoms, and stable hydrocarbons within the "spurs" (hot spots) of the radiation tracks and reaction of the thermalized alkyl radicals and H atoms with HI or I_2 outside the track. For solutions of cyclohexane-methyl iodide, the mechanism includes the production of HI, I_2 , alkyl radicals and stable hydrocarbons inside the track and reaction of thermalized radicals with HI or I_2 outside the track. Differential rate equations, based on conventional kinetics, have been set up. The analytical integration of the equations appeared very cumbersome and has been carried out by numerical calculations using second-order Runge-Kutta method on an IBM 709 computer. These calculations provided a general procedure applicable to pure cyclohexane and with slight modifications to cyclohexane-methyl iodide solutions.

Input data for a given experiment are the Maximum, Minimum, and Normal Rates of iodine production. An initial scavenger concentration (HI or I_2 , or both) is given to the computer, matching an actual

experiment. The ratio of rate constants $k_{\text{HI}}/k_{\text{I}_2}$ is used as an adjustable parameter, where k_{HI} and k_{I_2} are the rate constants for reactions of radicals with HI and I_2 respectively. For pure cyclohexane, the value of the H atom yield, which cannot be established directly from the present experimental results, has also been used as an adjustable parameter. The computed curves so obtained fit the experimental points quite well.

The results are summarized below:

For pure cyclohexane, variation of H atom yield affects the end point whereas the ratio $k_{\text{HI}}/k_{\text{I}_2}$ does not. A value of $k_{\text{HI}}/k_{\text{I}_2} = 0.71$ has been found for the best fit. The effective H atom yield used in the calculations depends upon the initial scavenger concentration. $G(\text{H}\cdot)$ has been found to be 0.70 to 1.43 for iodine scavenger concentrations of 0.31×10^{-3} M to 1.71×10^{-3} M. For HI scavenger concentrations of 2.11×10^{-3} M to 8.88×10^{-3} M, $G(\text{H}\cdot)$ is 1.40 to 1.74.

For cyclohexane-methyl iodide solutions with 20 to 95 volume percent cyclohexane, the H atom yield does not enter into calculations because methyl iodide is present in high concentration so that all H atoms react with methyl iodide in or near the spurs to produce HI. The value of $k_{\text{HI}}/k_{\text{I}_2}$ depends upon the concentration of the components of the solutions. For the range of solutions studied, the values of $k_{\text{HI}}/k_{\text{I}_2}$ have been found to be 0.55 to 0.98. For 99.9 volume percent solution, methyl iodide is not present in sufficient amounts to react with all the H atoms. Therefore, the H atom yield is also to be adjusted. For this case, $G(\text{H}\cdot)$ has been found to be 0.70.

The calculations also provided the yield of thermal alkyl radicals, and the yield of I_2 and HI within the radiation tracks.

SECTION II

EXPERIMENTAL METHODS

Apparatus

Samples for irradiation were deaerated on a vacuum line with a manifold shown in Figure 1. Preparation of a series of solutions with the same initial iodine concentration was facilitated by the use of a vacuum line buret.²⁶ The pump section of the vacuum line consisted of a Welch Duo-Seal fore-pump connected through a liquid nitrogen trap and a water condenser to a mercury diffusion pump. This arrangement pulled down the whole system to a pressure of about 10^{-4} mm of mercury. The pumps were connected to the vacuum line which consisted of the following: several 19/38 standard taper ground glass joints for introducing samples, a small calibrated tube (T, about 2 ml volume) for introducing measured amounts of gases, a mercury manometer (M) and a sub-manifold (S_1) for attaching and sealing off cells (C_1), all connected to the main manifold through stopcocks. Another sub-manifold (S_2) for attaching and sealing off sample cells (C_2) was connected to the vacuum line via a vacuum line buret (B) and a by-pass line as shown in the figure. The stopcocks above and below the buret have a teflon plug and o-ring seal, and require no grease. Kel-F fluorocarbon grease was used for all other stopcocks during the experimental work. Fifty ml round bottom Pyrex flasks (F) were used as sample reservoirs.

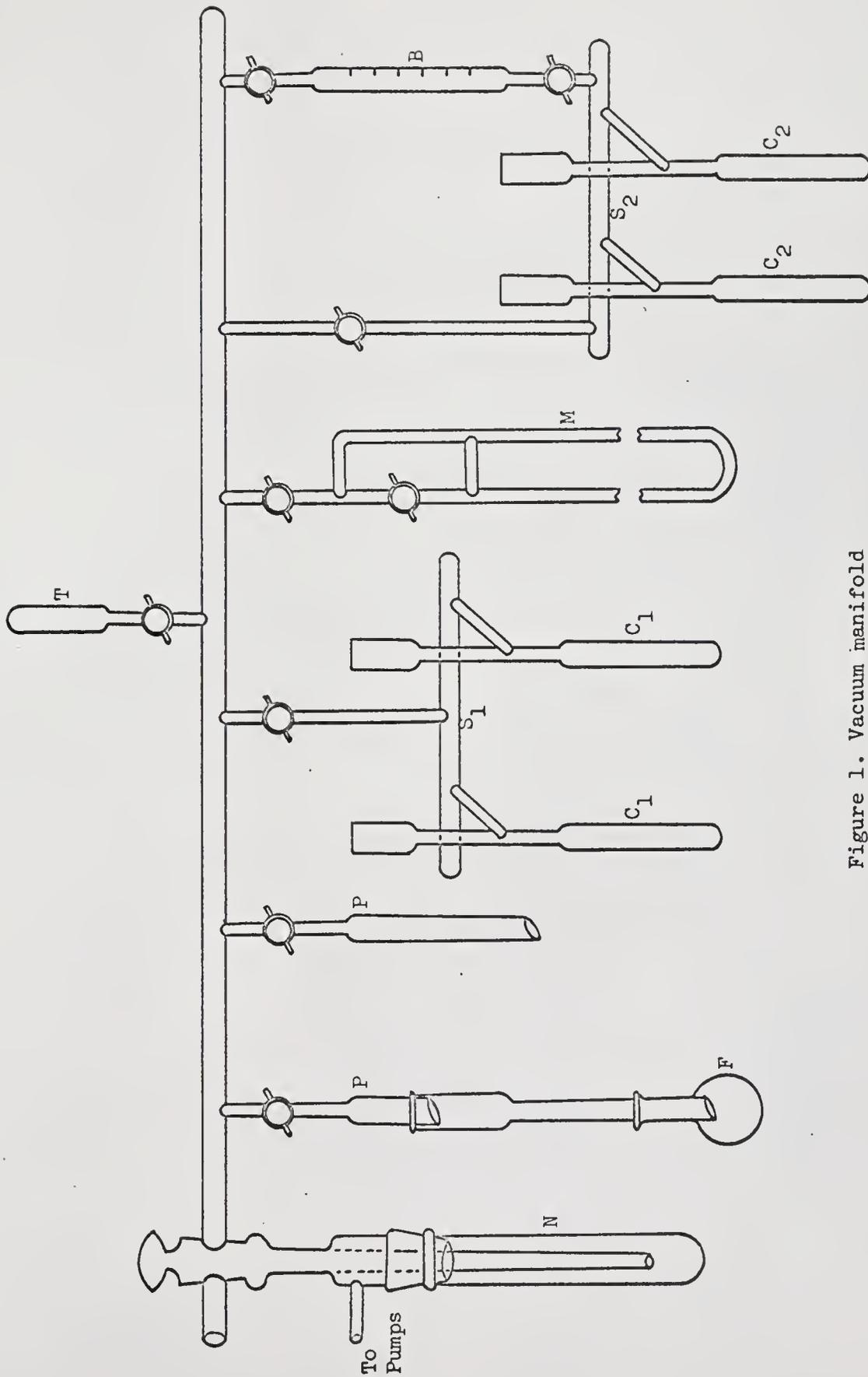


Figure 1. Vacuum manifold

For all radiolysis experiments, except for those used for HI determination, irradiation vessels (C_1 , C_2) were 13 x 100 mm test tubes, with attached spectrophotometer cells. The spectrophotometer cells were made from square Pyrex tubing. Irradiations were performed at $25 \pm 2^\circ\text{C}$. using a modified Firestone-Willard type 400 curie Co^{60} source described previously.²⁷ Iodine was analyzed spectrophotometrically using a Beckman DU spectrophotometer. Hydrogen iodide was analyzed by extracting with distilled water and the aqueous layer was separated by a separating funnel²⁸ of a special type.

Purification of Materials

Phillip's "pure grade" cyclohexane was passed through silica gel before use. Methyl iodide (Eastman Organic Chemicals) was passed through alumina, distilled on a Todd still and passed through alumina again. "Baker analyzed" reagent grade iodine and hydriodic acid were used without further purification. Pyrex glass wool used in the vacuum line was purified by washing with carbon tetrachloride and then heating to 560°C in an annealing oven. Water used during the experiments was purified by distilling ordinary distilled water in the presence of alkaline potassium permanganate.

The apparatus such as burets, measuring flasks, sample flasks, and irradiation vessels were washed with distilled water and acetone and then heated in an oven.

Preparation of Samples

General procedure

The general procedure of filling all irradiation vessels was the following: a 4 ml volume of the required sample was measured into a small round bottom flask (F) fitted with a female 19/38 joint. After adding about one gram of phosphorus pentoxide, the flask was connected to the vacuum line through a column of phosphorus pentoxide and a stopcock. The sample was then frozen in liquid nitrogen and evacuated. To remove air from the sample as thoroughly as possible, it was melted, refrozen and pumped several times. The main section of the vacuum line was isolated from the pump section by closing the stopcock. The sample was then transferred to the irradiation vessel. Two or more melting, freezing and pumping cycles were performed and the sample sealed off at a constriction.

Samples containing iodine

Samples containing iodine were prepared by diluting a stock solution of iodine in cyclohexane to a volume of 4 ml. The solution was then used to fill the irradiation vessels as described above. Iodine concentration in the sample was verified spectrophotometrically. To prepare several samples containing the same initial iodine concentration, a stock solution of about 25 ml was degassed in a flask connected to the vacuum line. This solution was then transferred to the buret (B) and homogenized by a small stirring magnet placed inside it. Four ml samples were then transferred to the irradiation vessels (C_2).

Samples containing hydrogen iodide

Dry hydrogen iodide was produced by dehydrating hydriodic acid. The hydriodic acid was frozen to liquid nitrogen temperature in a round bottom flask and phosphorus pentoxide added on top of it. The flask containing the frozen acid was then attached to the vacuum line through phosphorus pentoxide column and degassed. The hydriodic acid was allowed to melt and interact with P_2O_5 , and the hydrogen iodide released was collected in another round bottom flask connected to the line. This collected hydrogen iodide was degassed and stored at liquid nitrogen temperature until used. To obtain a known quantity of hydrogen iodide, the gas was taken in the calibrated tube (T) at a known pressure and temperature and then transferred to the sample.

Irradiation of Samples

Irradiation of samples was performed by placing them, in the same irradiation geometry, directly adjacent to the source capsule. Reproducible geometry was assured by using a special aluminum rack.

Post-Addition of Iodine to Irradiated Samples

In several experiments, iodine was to be added to the sample after irradiation. The procedure used was the following: the irradiation vessel was fitted with a break-seal and connected to the vacuum line. The required sample was transferred to the vessel as described earlier and sealed off. After irradiating the sample, the other side of the break-seal was connected to the vacuum line and evacuated. A known amount of iodine in the same solvent was degassed. The break-seal was broken by a small magnetic hammer and the degassed iodine solution transferred to the irradiated sample kept frozen

throughout the experiment. The sample was then melted, thoroughly shaken, refrozen and kept frozen until used.

Determination of Hydrogen Iodide

Hydrogen iodide formed during irradiation was determined by first opening the frozen sample in distilled water and thoroughly shaking it. The aqueous layer was separated and any iodine present in it was removed by washing several times with cyclohexane. The aqueous portion was then slightly heated to remove any cyclohexane until a clear solution was obtained. It was then diluted to a known volume and the concentration of HI determined spectrophotometrically by Beckman DU spectrophotometer at a wave length of 226 $m\mu$ and using $\epsilon = 13,000$.

SECTION III

EXPERIMENTAL RESULTS

In this study the current practice of expressing radiation yields as G values has been adopted. G value is defined as the number of molecules of a substance produced or consumed per 100 ev deposited in the system. Yields are based on the ferrous sulfate dosimeter⁴² [$G(\text{Fe}^{+++}) = 15.6$]. Since concentration and time had to be used for theoretical calculations as iteration parameters on a digital computer, it became necessary to use other convenient units. It was chosen to state concentrations as micromoles per 4 ml sample and to use time in minutes which is proportional to radiation dose.

The dosimetry on the source was originally done on January 1, 1961. The energy absorption rate in the Fricke dosimeter was on that date found to be 0.931×10^{18} ev/ml min. The same value has been used in the present work and all periods of irradiation have been corrected to a common date — January 1, 1964. Taking into account the decay of the source, the dose rate was found to be 0.63×10^{18} ev/ml min on January 1, 1964. Dose rates were corrected for the differing values of μ , the linear absorption coefficient, for the various solutions. For pure methyl iodide and cyclohexane, values of 1.950 and 0.780 respectively have been used for $\mu(\text{sample})/\mu(\text{dosimeter})$. For the intermediate solutions, relative absorption values were obtained by assuming

an interpolation linear in volume fraction. To analyse I_2 spectrophotometrically, the position of λ_{\max} and the corresponding extinction coefficients, ϵ , as determined by Croft and Hanrahan²⁰ have been used (Table 1).

Effect of Additives on the Radiolysis of
Pure Cyclohexane

With added iodine

Measurements of iodine concentration vs dose were made during the radiolysis of several cyclohexane solutions. Some of the data were taken by W. C. Blasky of this laboratory (see footnotes, Figures 2 and 3). The results of the experiments in which iodine, varying from 0.3×10^{-3} M to 2.0×10^{-3} M, was initially added are shown by circles in Figure 2 (smooth lines are theoretical; see below). All of the curves are concave upwards, with the solutions having higher initial iodine concentration showing the most curvature.²⁵ The initial rate of iodine uptake in such experiments has been reported²⁹ to be independent of initial iodine concentration over the range 5×10^{-6} M to 5×10^{-3} M. The results in Figure 2 also confirm the above fact, which is basic to the use of iodine for measuring free radical yields. An average rate of iodine uptake of 3.08 molecules/100 ev has been found. It is to be noted that the value obtained for the initial G value of iodine uptake depends somewhat on the procedure used to interpret the concentration vs dose graphs, since the graphs are non-linear. To use the initial concentration dose increments is disadvantageous, since the first few points often show the most scatter. The

TABLE 1

PHYSICAL PROPERTIES OF CYCLOHEXANE-METHYL IODIDE SOLUTIONS AS A FUNCTION OF COMPOSITION

Vol. percent cyclohexane	Mole percent cyclohexane	Electron percent cyclohexane	$\frac{\mu(\text{sample})^a}{\mu(\text{dosimeter})}$	Extinction Coeff., for I_2	λ_{max} for I_2^c
0	0	0	1.950	1277	480
20	12.63	9.94	1.716	1210	483
40	27.83	22.98	1.482	1142	484
60	46.49	40.20	1.248	1075	488
80	69.81	64.16	1.014	1007	495
90	83.89	80.12	.897	974	502
95	91.66	89.49	.838	956	509
99.9	98.30	97.82	.782	942	522
100	100.00	100.00	.780	940	524

^aValues for intermediate solutions have been obtained by interpolation linear in volume.^b and ^cValues have been taken from ref. 20.

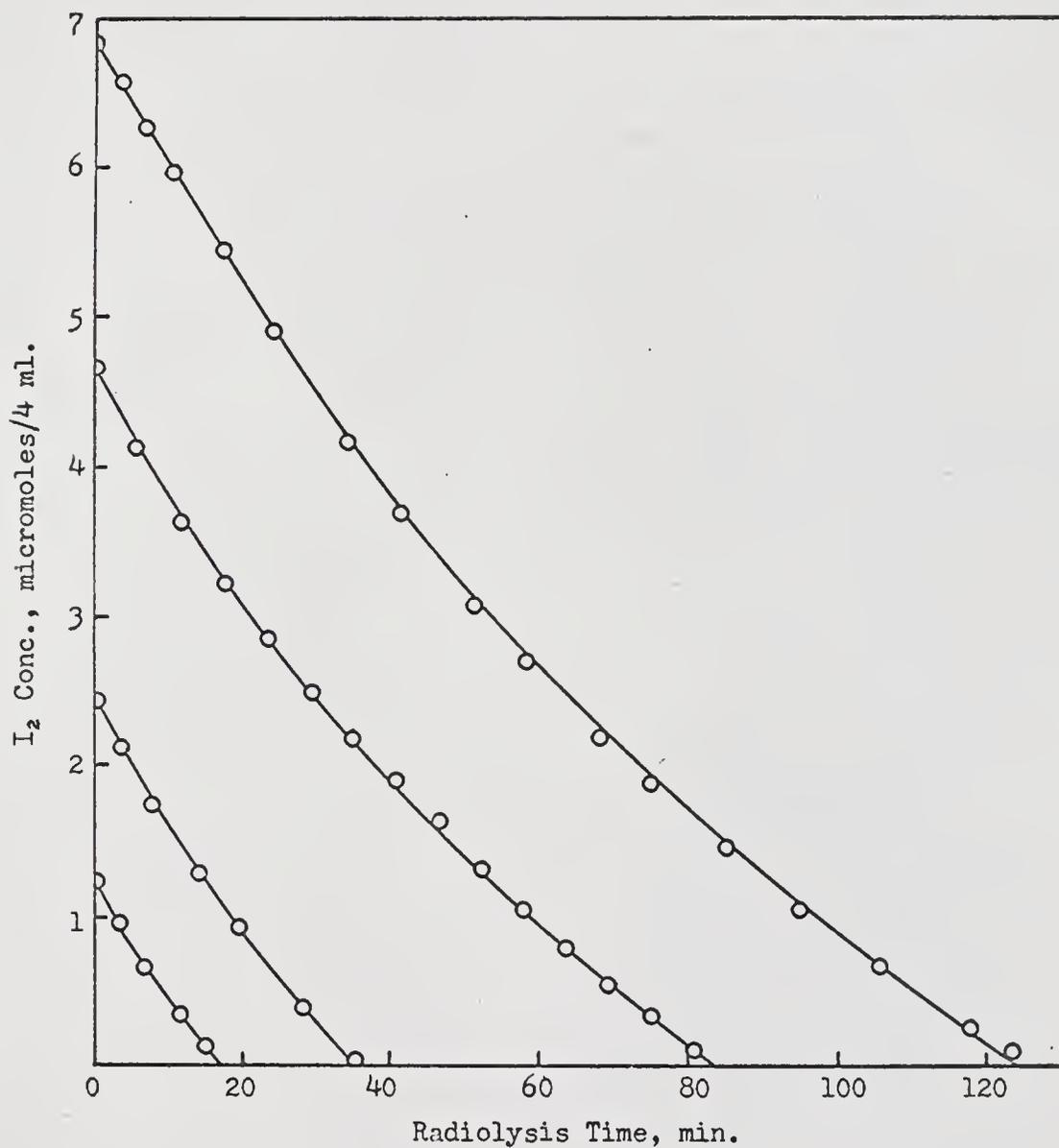


Figure 2. Iodine consumption in the radiolysis of pure cyclohexane, with added I_2 , as a function of radiation time. Circles are experimental; smooth curves are computed. Initial I_2 concentrations, reading left to right, are 0.31×10^{-3} M (W.C.Blasky), 0.61×10^{-3} M (W.C.Blasky), 1.16×10^{-3} M and 1.71×10^{-3} M.

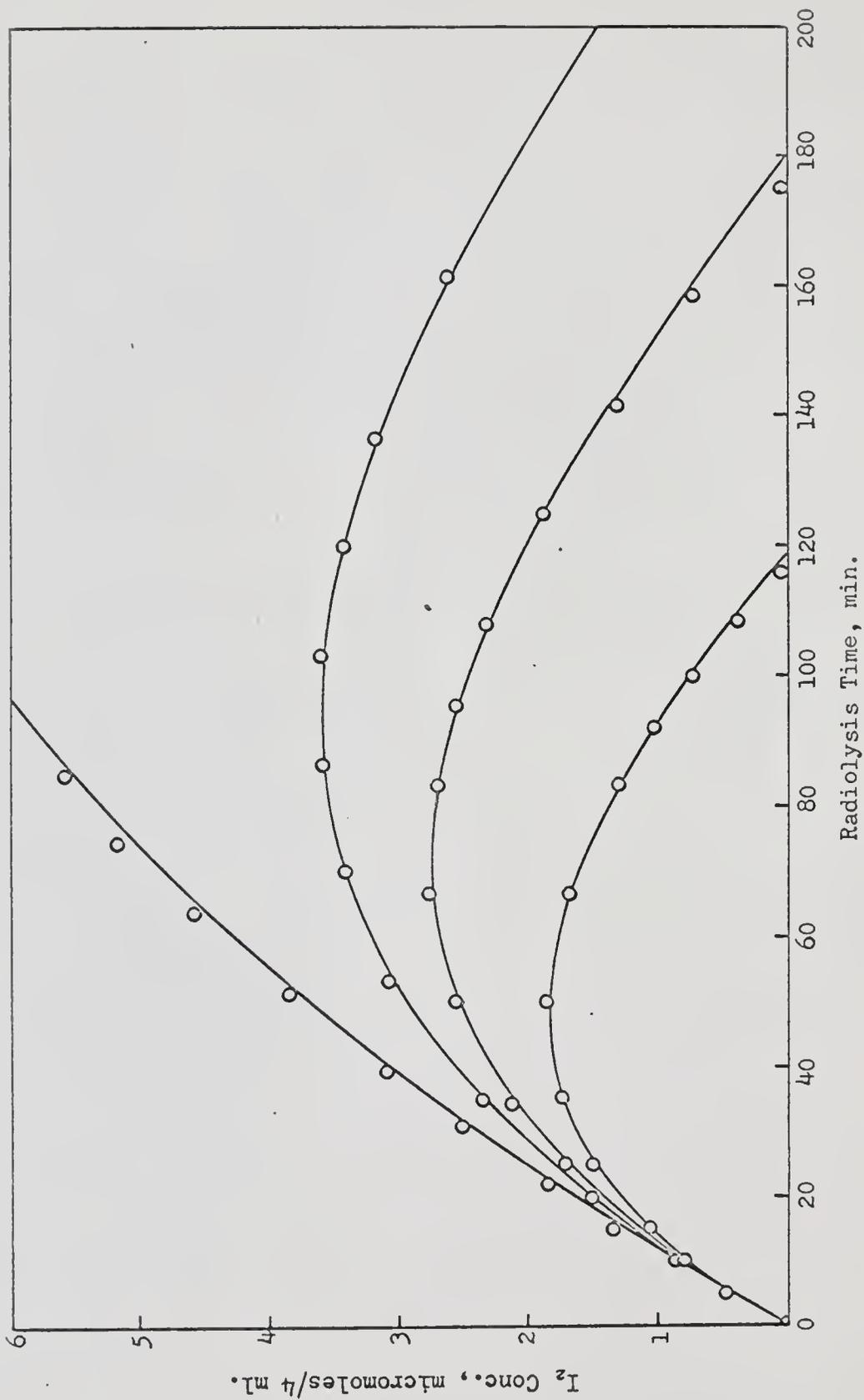


Figure 3. Iodine production in the radiolysis of pure cyclohexane, with added HI, as a function of radiation time. Circles are experimental; smooth curves are computed. Initial HI concentrations, reading downwards, are 8.88×10^{-3} M, 4.10×10^{-3} M, 3.18×10^{-3} M (W.C.Blasky) and 2.11×10^{-3} M (W.C.Blasky).

procedure adopted in this dissertation for such calculations is the following: the net change of concentration (or optical density) from time zero to each successive radiolysis time t was calculated. A graph of Δ (concentration)/ t vs t was plotted and the desired initial rate was found by extrapolating this graph to zero time.

With added hydrogen iodide

The results of the experiments in which hydrogen iodide, varying from 2×10^{-4} M to 9×10^{-3} M, was initially added are shown by circles in Figure 3. In such experiments, alkyl radicals abstract H atoms from HI and release iodine atoms which later form I_2 . Thus, iodine is initially produced rather than consumed. As the radiolysis proceeds, the iodine enters into competition with HI for free radicals so that the net rate of iodine production decreases to zero at the maximum of the curves and then becomes negative. If the experiment is continued to a sufficiently high dose, all the iodine and hydrogen iodide are finally consumed. The graphs in Figure 3 show that the positions of the iodine maxima and final "end points" of the experiments increase with increase in initial HI concentration. The initial G value of iodine production is independent of initial HI concentration. The values of $G(I_2)$ ranged from 2.8 to 3.0 and a value of 2.96, based on several consistent experiments, was used in the theoretical calculations.

In order to be consistent with notation used in connection with the radiolysis of cyclohexane-methyl iodide solutions described later, the initial rate of iodine disappearance in pure cyclohexane will be

referred to as the "Minimum Rate", and the initial rate of iodine production with added HI as the "Maximum Rate". The term "Normal Rate" which is also used in connection with cyclohexane-methyl iodide solutions is zero for pure cyclohexane.

With both iodine and hydrogen iodide added

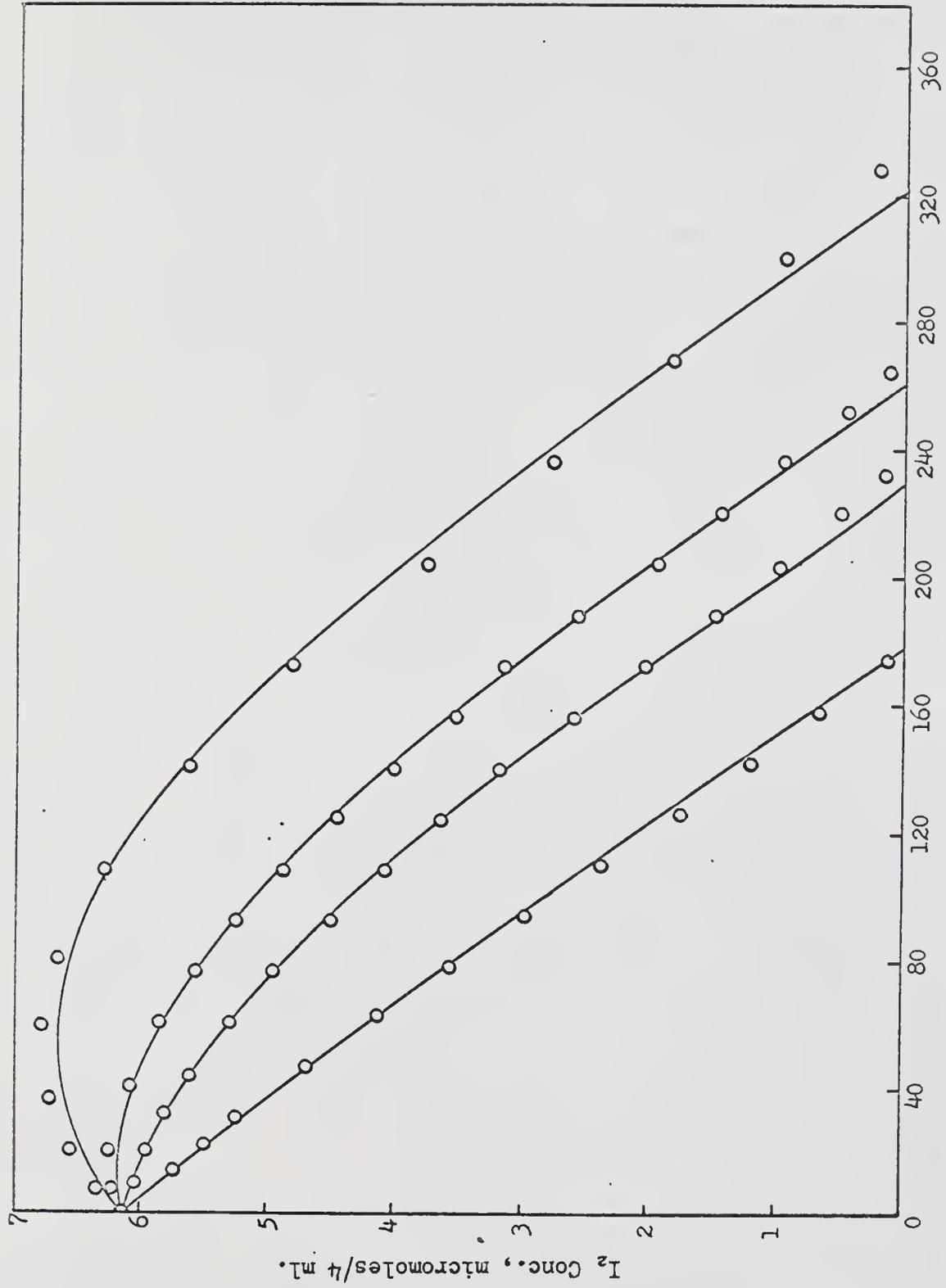
The results of similar experiments in which both I_2 and HI were initially added are shown by circles in Figure 4. In these experiments the initial iodine concentration was 1.53×10^{-3} M in all cases but the HI concentration varied from 1.08×10^{-3} M to 3.43×10^{-3} M.

Evidence of hydrogen iodide production in the radiolysis of cyclohexane-iodine solutions

If the production of hydrogen iodide during the radiolysis of cyclohexane with added iodine is considered to be responsible for the curvature of iodine vs dose graphs, then additives which prevent back-reaction of HI should linearize the curves. Such experiments with added barium oxide or water have been done previously.^{10,14,30} It was found by these workers that the addition of BaO and H_2O cause the iodine disappearance to be much less curved than in the case of a similar experiment with only iodine added.

Determination of hydrogen iodide after post-addition of iodine in irradiated cyclohexane

Four runs for the determination of HI after post-addition of iodine in irradiated cyclohexane were done. The apparent G values for HI production were found to be 0.35, 0.37, 0.35, and 0.40 for the four runs. In order to find out whether the hydrogen iodide so obtained is



Radiolysis Time, min.

Figure 4. Iodine production in the radiolysis of pure cyclohexane, with both HI and I₂ added, as a function of radiation time. Circles are experimental; smooth curves are computed. HI concentrations reading left to right, are 1.08 x 10⁻³ M, 1.91 x 10⁻³ M, 2.43 x 10⁻³ M and 3.43 x 10⁻³ M. I₂ concentration is 1.53 x 10⁻³ M in all cases.

really due to the effects of radiolysis on cyclohexane and then shaking with iodine under vacuo or just due to equilibration of iodine with water during extraction, two experiments were done under identical conditions, but without irradiating the cyclohexane. It was observed that HI was still formed and a G value of 0.35 was obtained. Any difference between this G value and some of the G values for irradiated cyclohexane experiments is probably due to experimental errors. Therefore, it is to be concluded that HI is not formed due to reaction with radiolysis products when iodine is added to cyclohexane after radiolysis.

Effect of Additives on the Radiolysis of Cyclohexane-Methyl Iodide Solutions

The theoretical deductions described later in this dissertation require a knowledge of the rates of iodine production in cyclohexane-methyl iodide solutions under three circumstances: with no additives, with added HI, and with added I_2 .

Without additives

Initial yields of iodine production in pure, degassed solutions of methyl iodide in cyclohexane without additives were reported earlier by Croft and Hanrahan.²⁰ The general character of the results reported by them is that all solutions ranging from 10 to 95 volume percent cyclohexane produced iodine nearly linearly with dose. The G value for iodine production decreased with increasing cyclohexane concentration. The slopes of the graphs of iodine concentration vs dose are designated "Normal Rates" of iodine production in the present work.

For the purpose of fitting theoretical curves to experimental iodine production data at long radiolysis times, it became important to obtain data on iodine production in cyclohexane-methyl iodide solutions at total doses larger than those used by Croft and Hanrahan.²⁰ Such experiments were performed and their results are shown in Figure 5. Iodine production rates obtained from the limiting slopes of these graphs at long radiolysis times are given in parentheses in Table 2.

With added iodine

Results of iodine production in the radiolysis of the above solutions in which iodine was present initially as a free radical scavenger are shown by circles in Figure 6. In all the experiments, the initial concentration of iodine was about 1.5×10^{-3} M. The initial iodine concentration has been subtracted from the total measured iodine concentration in plotting the ordinate points and the graph shows net iodine production or consumption. All the curves of the graph are concave upwards. In the case of solutions with 80 to 95 volume percent cyclohexane, the iodine concentration actually decreases at first and then increases. The minimum in the 95 percent curve occurs off the scale of the figure at 2400 minutes. In the case of the solution with 99.9 volume percent cyclohexane, iodine is regularly consumed until none is left after 148 minutes. The initial slopes of these curves, whether positive or negative, are designated as the "Minimum Rates". The positive values indicate that iodine is initially produced and the negative values show that iodine is initially consumed at the corresponding rates.

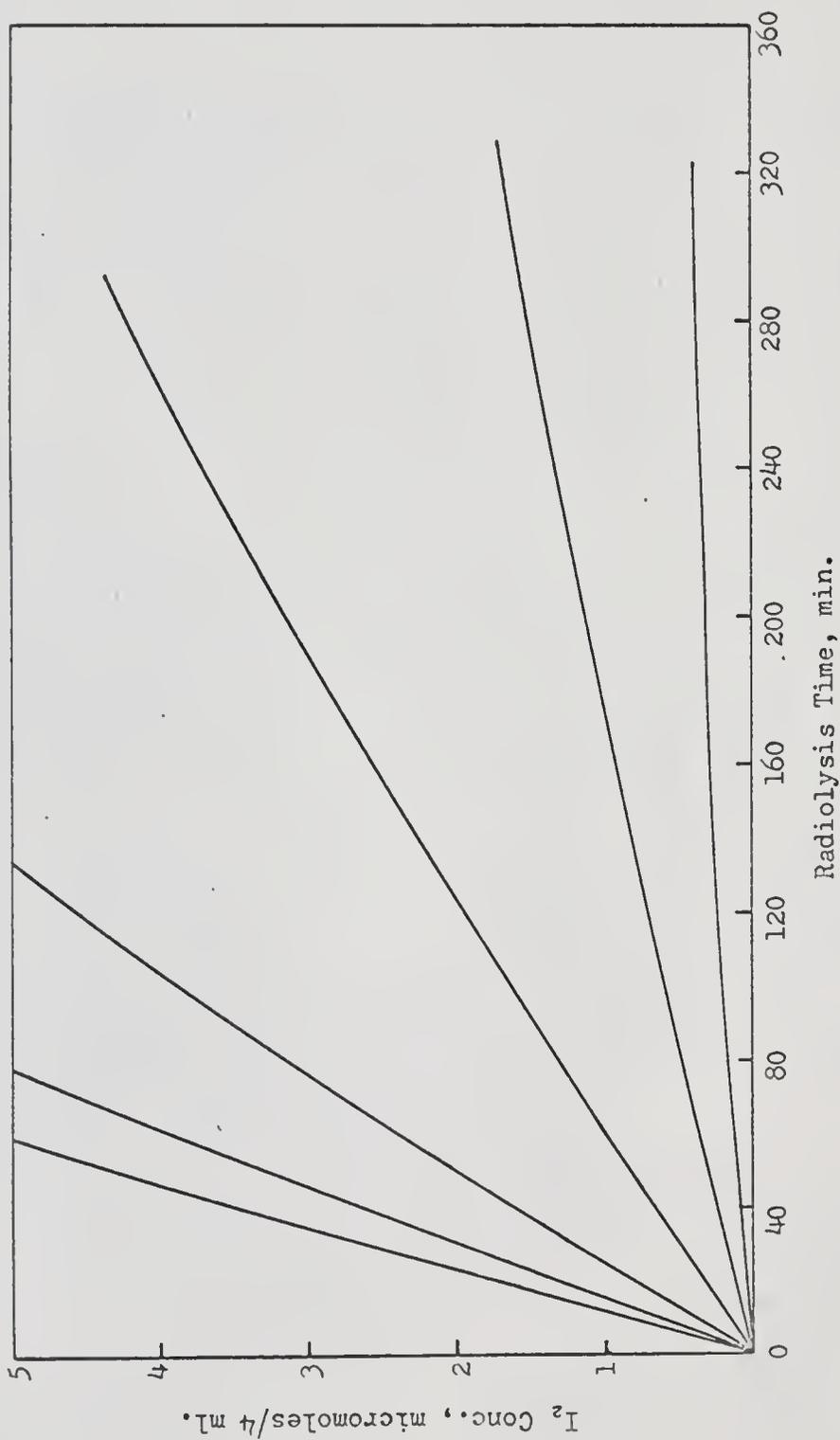


Figure 5. Iodine production in the radiolysis of cyclohexane-methyl iodide solutions, without additives, as a function of radiation time. Volume percent cyclohexane, reading downwards, is 20, 40, 60, 80, 90 and 95.

TABLE 2
EXPERIMENTAL G VALUES FOR THE RADIOLYSIS OF CYCLOHEXANE-METHYL IODIDE SOLUTIONS

Cyclohexane percent by volume	G(I ₂)		
	Normal ^a	Maximum (with HI added)	Minimum (with I ₂ added)
0	1.41	6.51	1.20
20	1.23(1.11)	6.18	.84
40	1.10(.85)	6.25	.56
60	0.79(.60)	6.18	.09
80	0.45(.25)	5.24	-.28
90	0.18(.053)	4.37	-.64
95	0.05(.004)	4.09	-.94
99.9	0	3.45	-2.62
100	0	2.96	-3.08

^aFor solutions without adding HI or I₂ prior to irradiation. These values have been taken from reference 20. The values in the parentheses are obtained after extended periods of irradiation.

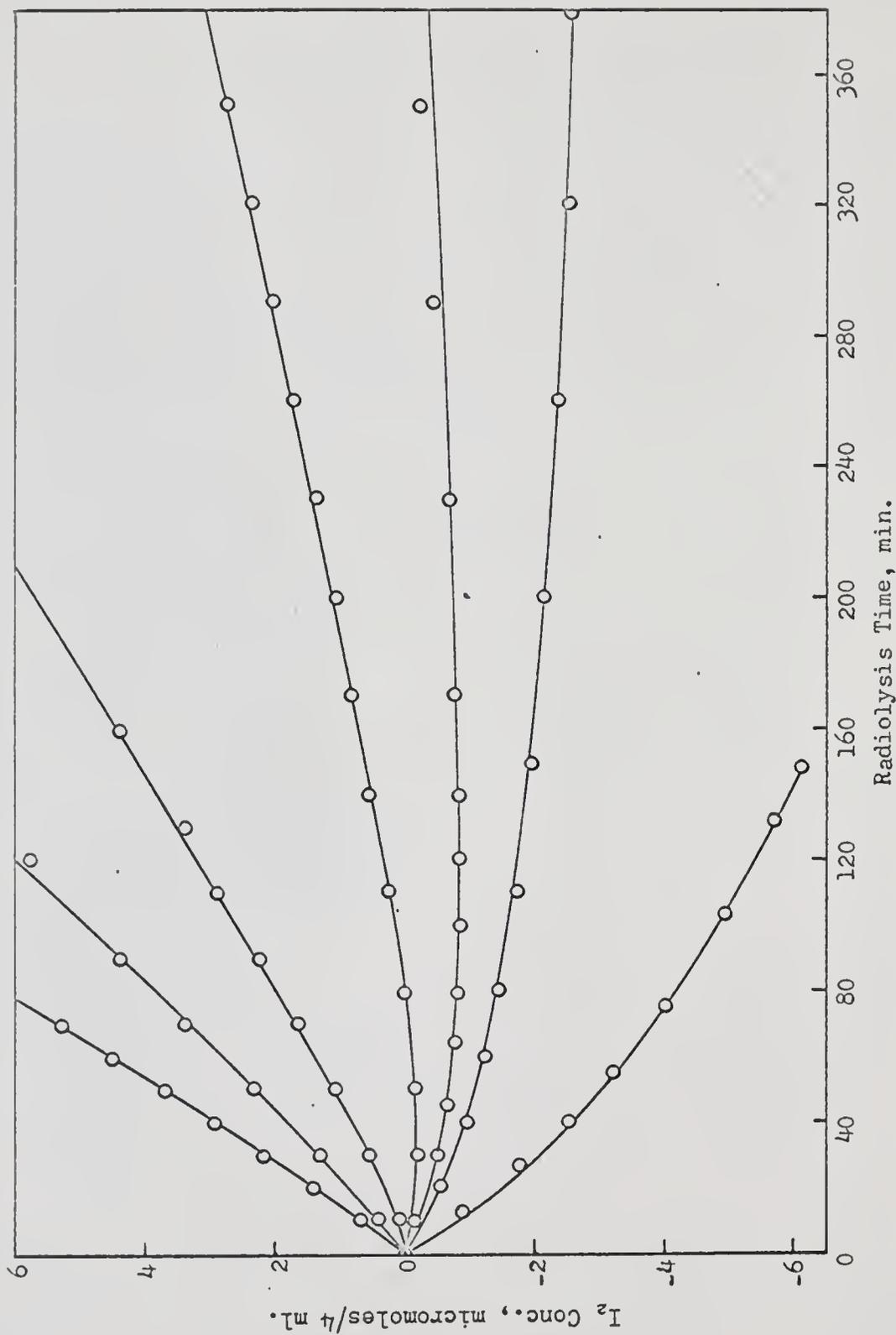


Figure 6. Net iodine production or consumption in the radiolysis of cyclohexane-methyl iodide solutions, with added I_2 , as a function of radiation time. Circles are experimental; smooth curves are computed. Volume percent cyclohexane, reading downwards, is 20, 40, 60, 80, 90, 95 and 99.9.

With added hydrogen iodide

Results of iodine production in the radiolysis of various cyclohexane-methyl iodide solutions with added hydrogen iodide are shown by circles in Figure 7. The HI concentration in all the cases was about 6×10^{-3} M. All the curves of the graph are concave downwards. For 99.9 volume percent cyclohexane solution, only a portion of the graph has been shown. The complete graph is given in Figure 8. The iodine concentration first increases, becomes maximum at about one millimolar iodine concentration after 100 minutes, and then decreases until after 314 minutes it is totally consumed. The initial slopes of the curves in Figure 7 are designated as the "Maximum Rates".

The G values for the normal rate of iodine production without additives, the maximum rate with added HI, and the minimum rate with added iodine are listed in Table 2.

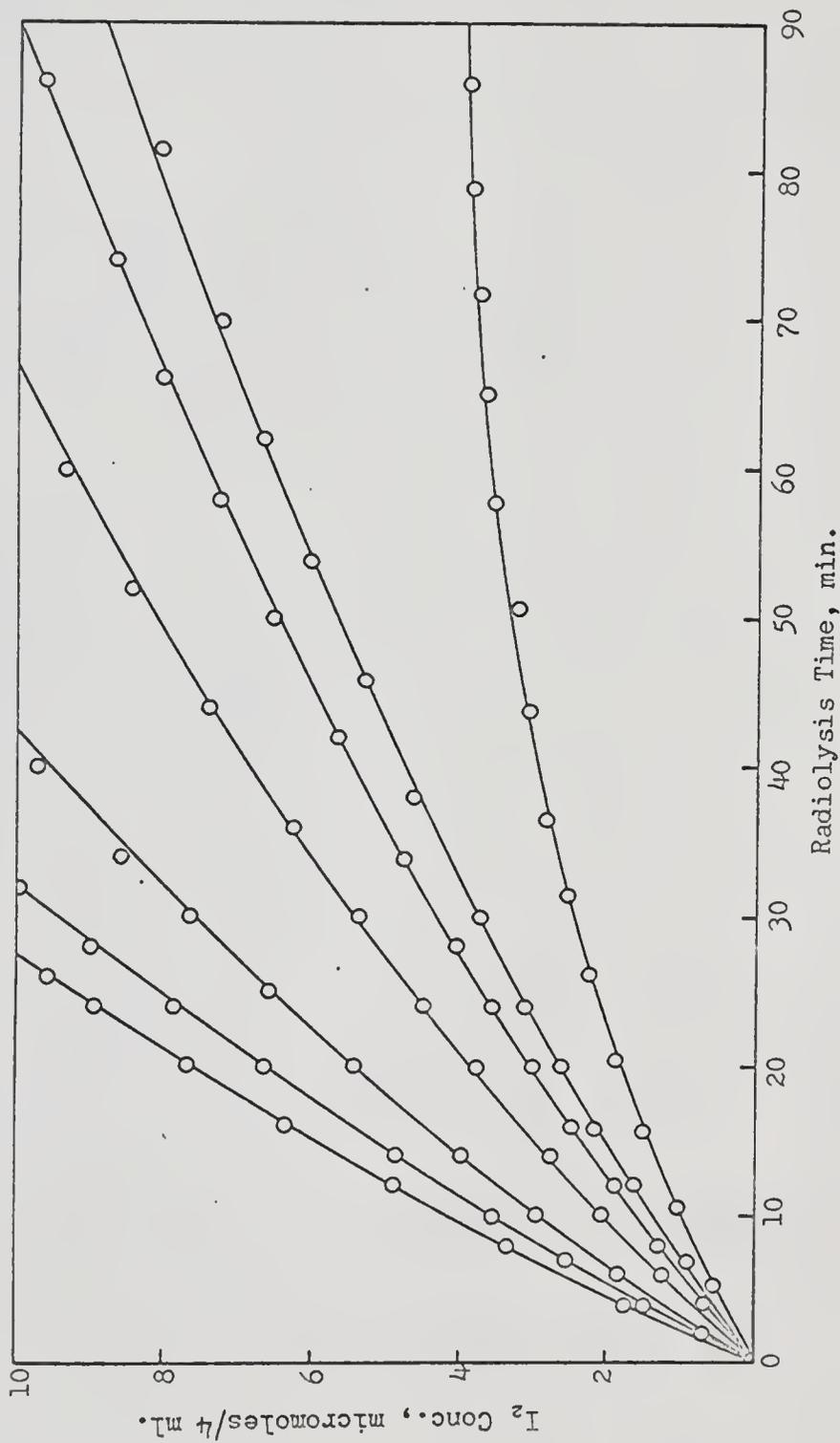


Figure 7. Iodine production in the radiolysis of cyclohexane-methyl iodide solutions, with added HI, as a function of radiation time. Circles are experimental; smooth curves are computed. Volume percent cyclohexane, reading downwards, is 20, 40, 60, 80, 90, 95 and 99.9. Initial HI concentration is 6.1×10^{-3} M.

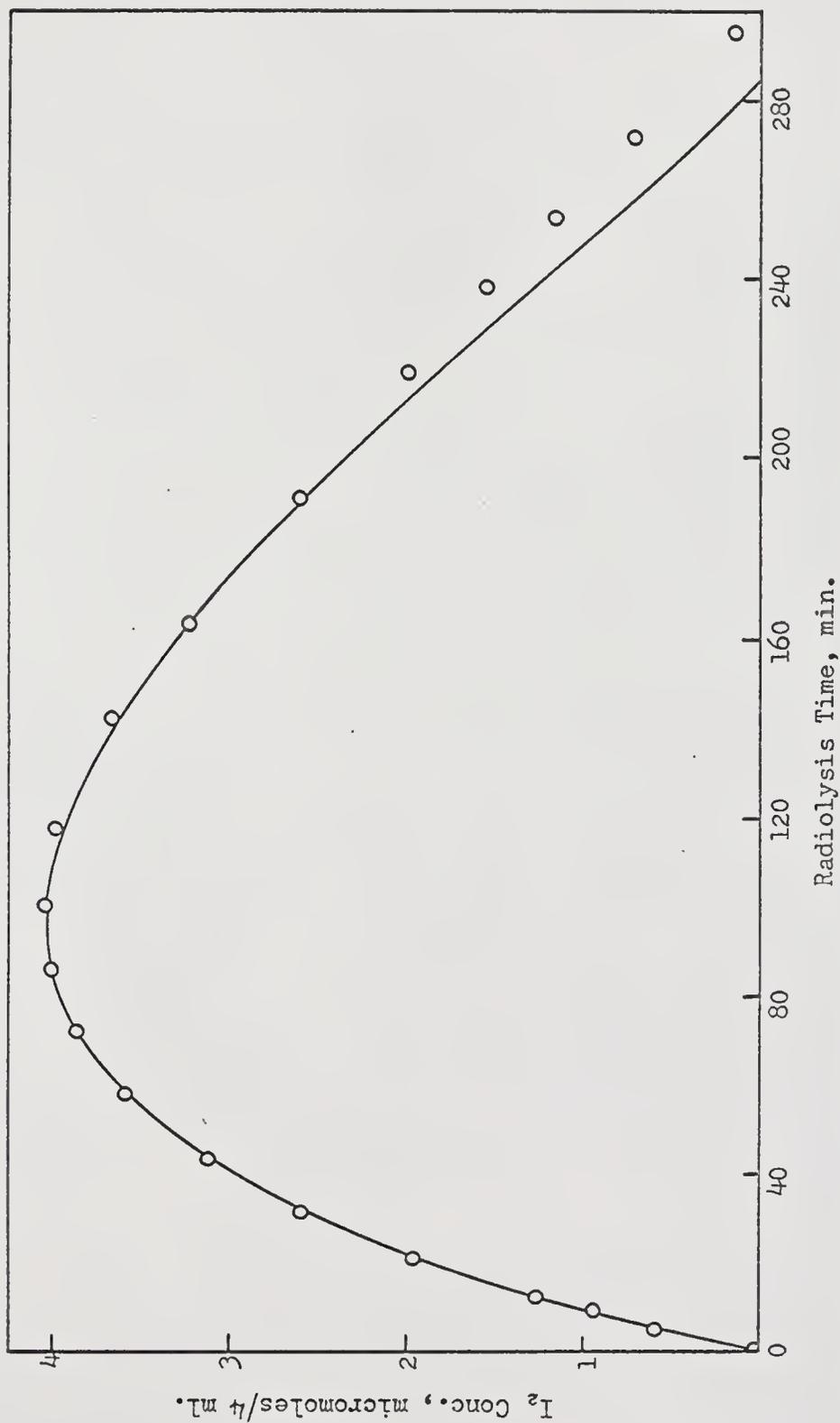


Figure 8. Iodine production in the radiolysis of cyclohexane-methyl iodide solution, for 99.9 volume percent cyclohexane, with added HI, as a function of radiation time. Circles are experimental; smooth curves are computed. Initial HI concentration is 3.4×10^{-3} M.

SECTION IV

DISCUSSION AND INTERPRETATION

Mechanism of the Gamma Radiolysis of Cyclohexane and Cyclohexane-Methyl Iodide Solutions

General

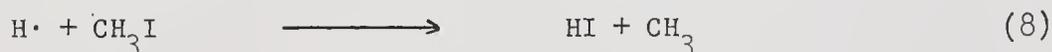
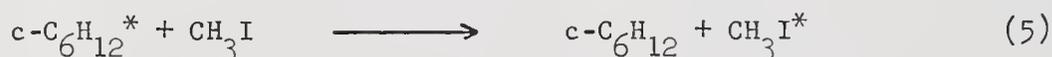
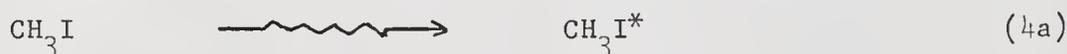
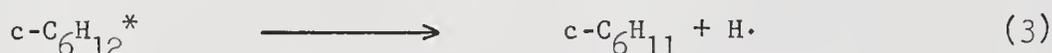
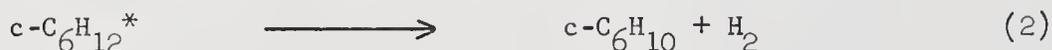
A great variety of conflicting viewpoints have been expressed on the mechanism of cyclohexane radiolysis by numerous workers who have attempted to interpret it. However, essentially all the investigators have agreed that cyclohexyl radicals, $c\text{-C}_6\text{H}_{11}\cdot$, are involved in the mechanism.^{5,9,12,15,31-34} The role of hydrogen atoms is far more obscure.

While discussing the isotopic composition of hydrogen produced in the radiolysis of $\text{C}_6\text{D}_{12}\text{-C}_6\text{H}_{12}$ mixtures, Dyne and Jenkinson¹⁵ have postulated the presence of "precursors or reactive intermediates" which provide hydrogen atoms but which may or may not actually be hydrogen atoms. During the reinvestigation of radiolysis products of pure cyclohexane system, Ho and Freeman³⁴ have found that cyclohexyl radicals are involved in the production of cyclohexene, bicyclohexyl and cyclohexylhexene.

To interpret the present experimental results, attempts have been made to provide an internally consistent free radical mechanism. A simplified mechanism, which assumes the presence of hydrogen atoms with an effective hydrogen atom yield dependent on the total concentration

of scavengers present, has been adopted. At lower concentrations, it is assumed that the hydrogen atoms are replaced by a complementary yield of cyclohexyl radicals. At sufficiently high concentrations, both HI and I₂ may become involved in electron capture or energy transfer processes.^{12,35} However, the highest concentration of scavengers used in the present experiments is about 10⁻² M, and most of these experiments were done at millimolar scavenger concentrations.¹² It is justified to assume that HI and I₂ behave predominantly as free radical scavengers at these concentrations. A simplified mechanism is given below:

Reactions in spurs



Steady-state radical reactions

Asterisks represent electronically excited species. Several steps, especially 5 and 7, represent net processes rather than actual mechanisms. This scheme allows for production of hydrogen atoms, alkyl radicals, cyclohexene, and molecular hydrogen from cyclohexane as well as methyl radicals, stable hydrocarbons, e.g., C_2H_6 , and iodine from methyl iodide. The distinction between atomic and molecular iodine indicated in equations 6 and 7a is of minor significance, since iodine atoms combine to form I_2 in any event; see equation 9. However, the important distinction between equations 6 and 7 is that 7 suggests that net iodine is produced only if the corresponding methyl radicals are stabilized as hydrocarbons. Some of the steps in the sequence are intended to represent net processes rather than actual mechanisms. In particular, energy redistribution between cyclohexane and methyl iodide in equation 5 could involve electron capture or charge exchange as well as transfer of excitation energy. Furthermore, there is evidence that net iodine production from methyl iodide (eq. 7) occurs by an ionic route. For the purposes of quantitative treatment, it is important that, for a fixed ratio of methyl iodide to cyclohexane in the solution, the rate of each of the processes listed under "Reactions in spurs" is taken as a constant, unaffected by scavengers at low concentrations. Reaction 8

is not a spur reaction in the usual sense but is included in this group because methyl iodide, which is a good radical scavenger, was present in much higher concentration than any other scavenger in most of the experiments. Under these circumstances, all hydrogen atoms are converted to HI by reaction 8.

Because of the complexity of the situation, further approximations are required before attempting mathematical analysis. In considering the steady-state radical reactions, the distinction between methyl and cyclohexyl radicals is ignored, and it is assumed that the same rate constant can represent reactions of either with a scavenger.

Modifications for pure cyclohexane

Steps 4 to 8 do not appear in the mechanism for the radiolysis of pure cyclohexane. Thus the net result of primary processes is the production of hydrogen atoms and cyclohexyl radicals which then take part in competitive reactions under steady-state conditions.

Modifications for cyclohexane-methyl iodide solutions

In cyclohexane-methyl iodide solutions with 0 to 95 volume percent cyclohexane, the concentration of methyl iodide is sufficiently high so that reaction 8 should be the predominant fate of H atoms. The net result of primary processes is then the production of I_2 , HI, and alkyl radicals which subsequently take part in competitive reactions 10 and 11 under steady-state conditions. However, in the 99.9 volume percent cyclohexane solution, some of the H atoms escape reaction 8 and enter into competitive reactions 12 and 13. It is to be noted that I_2 and HI are also formed during the radiolysis of cyclohexane-methyl iodide solutions in addition to that added as a scavenger.

Mathematical Analysis

General

The proposed reaction scheme can be treated by conventional kinetics. It is assumed that I_2 , HI, H atoms, and alkyl radicals are produced according to zero order kinetics by the radiation and that I_2 and HI then compete for alkyl radicals and H atoms according to equations 10 to 13. The rate constants for reactions 10 and 12 and for reactions 11 and 13 might be expected to be quite similar. The ratios k_{11}/k_{10} and k_{13}/k_{12} should be even more similar. During the present calculations these ratios have been assumed to be equal, which greatly simplifies the mathematical expressions involved.

To begin the calculations, steady-state assumption is applied to the alkyl radical and H atom concentrations. It is necessary to define the following quantities which represent the constant rates of various elementary processes:

- A = Rate of production of thermal alkyl radicals which escape the spurs (steps 3, 6 and 8).
- B = Rate of production of iodine in spurs (step 7a).
- C = Rate of production of hydrogen iodide in spurs or by reaction 8.
- D = Net rate of production of thermal H atoms which escape the spurs.

Then the thermal alkyl production rate is set equal to the rate of removal by reactions 10 and 11:

$$\begin{aligned}
 A &= k_{10}[R\cdot][I_2] + k_{11}[R\cdot][HI] \\
 &= [R\cdot](k_{10}[I_2] + k_{11}[HI])
 \end{aligned} \tag{14}$$

$$\text{and } [R\cdot] = A/(k_{10}[I_2] + k_{11}[HI]) \tag{15}$$

Similarly, the thermal hydrogen atom production rate is set equal to the rate of removal by reactions 12 and 13:

$$\begin{aligned}
 D &= k_{12}[H\cdot][I_2] + k_{13}[H\cdot][HI] \\
 &= [H\cdot](k_{12}[I_2] + k_{13}[HI])
 \end{aligned} \tag{16}$$

$$\text{and } [H\cdot] = D/(k_{12}[I_2] + k_{13}[HI]) \tag{17}$$

The rate of iodine production may be expressed as

$$\begin{aligned}
 d[I_2]/dt &= B - (k_{10}/2)([I_2][R\cdot]) + (k_{11}/2)([HI][R\cdot]) \\
 &\quad - (k_{12}/2)([I_2][H\cdot]) + (k_{13}/2)([HI][H\cdot])
 \end{aligned} \tag{18}$$

The factor of 1/2 is introduced because only 1/2 mole of iodine is consumed when a mole of radicals react with I_2 (reactions 9 and 10).

After substituting expressions for $[R\cdot]$ and $[H\cdot]$ from equations 15 and 17 in 18 and rearranging, this becomes

$$\begin{aligned}
 d[I_2]/dt &= B - (A/2)(k_{10}[I_2] - k_{11}[HI])/(k_{10}[I_2] + k_{11}[HI]) \\
 &\quad + (D/2)(k_{12}[I_2] - k_{13}[HI])/(k_{12}[I_2] + k_{13}[HI])
 \end{aligned} \tag{19}$$

$$\begin{aligned}
 &= B + A/2 - A[I_2]/([I_2] + [HI]k_{11}/k_{10}) \\
 &\quad + D/2 - D[I_2]/([I_2] + [HI]k_{13}/k_{12})
 \end{aligned} \tag{20}$$

After putting $k_{11}/k_{10} = k_{13}/k_{12} = k_{HI}/k_{I_2}$, this simplifies to

$$d[I_2]/dt = B + (A+D)/2 - (A+D)[I_2]/([I_2] + [HI]k_{HI}/k_{I_2}) \tag{21}$$

The rate of HI production may be expressed as

$$d[\text{HI}]/dt = C + k_{12}[\text{I}_2][\text{H}\cdot] - k_{13}[\text{HI}][\text{H}\cdot] - k_{11}[\text{HI}][\text{R}\cdot] \quad (22)$$

$$= C + [\text{H}\cdot](k_{12}[\text{I}_2] - k_{13}[\text{HI}]) - k_{11}[\text{HI}][\text{R}\cdot] \quad (23)$$

After substituting expressions for $[\text{H}\cdot]$ and $[\text{R}\cdot]$, this becomes

$$d[\text{HI}]/dt = C + D(k_{12}[\text{I}_2] - k_{13}[\text{HI}]) / (k_{12}[\text{I}_2] + k_{13}[\text{HI}]) \\ - A(k_{11}[\text{HI}]) / (k_{10}[\text{I}_2] + k_{11}[\text{HI}]) \quad (24)$$

$$d[\text{HI}]/dt = C - (A+D) + (A+2D)[\text{I}_2] / ([\text{I}_2] + [\text{HI}]k_{\text{HI}}/k_{\text{I}_2}) \quad (25)$$

The above equations are derived for the most complex case which can occur for the proposed reaction scheme. This is exemplified by the 99.9 volume percent cyclohexane solutions, in which some of the hydrogen atoms escape reaction with methyl iodide according to equation 8, and enter into competitive reactions 12 and 13. The I_2 and HI production rates in this case are given by equations 21 and 25.

In the radiolysis of pure cyclohexane and of the solutions with 5 percent or more methyl iodide, some of the terms in the rate equations are negligible. Therefore, a simplified version of the equations can be employed.

Modified differential equations for pure cyclohexane

Since iodine and hydrogen iodide are not produced in spurs when the radiolysis of pure cyclohexane is done, the parameters B and C are zero. Hence, the expressions for the rates of production of I_2 and HI become

$$d[\text{I}_2]/dt = (A+D)/2 - (A+D)[\text{I}_2] / ([\text{I}_2] + [\text{HI}]k_{\text{HI}}/k_{\text{I}_2}) \quad (26)$$

$$d[\text{HI}]/dt = - (A+D) + (A+2D)[\text{I}_2] / ([\text{I}_2] + [\text{HI}]k_{\text{HI}}/k_{\text{I}_2}) \quad (27)$$

Modified differential equations for cyclohexane-methyl iodide solutions

For solutions having 0 to 95 volume percent cyclohexane, all the hydrogen atoms react with methyl iodide to produce hydrogen iodide according to equation 8. Thus, the parameter D is zero. The corresponding rates become

$$d[I_2]/dt = B + A/2 - A[I_2]/([I_2] + [HI]k_{HI}/k_{I_2}) \quad (28)$$

$$d[HI]/dt = C - A + A[I_2]/([I_2] + [HI]k_{HI}/k_{I_2}) \quad (29)$$

Integration of the differential rate equations

To compare the present experimental results with the theoretical calculations, it is necessary to solve equations 21 and 25, or 26 and 27, or 28 and 29, a pair of simultaneous, first order, non-linear differential equations. Although a set of integrated rate expressions was presented earlier by Hanrahan and Willard³⁶ for a similar kinetic problem in irradiated ethyl iodide, the results are not directly applicable in the present case. The over-all stoichiometry of the radiation-induced reaction in cyclohexane-methyl iodide solutions is somewhat more complicated than in ethyl iodide. In addition, the analytical integration done for ethyl iodide radiolysis kinetics requires that the rate constant ratio for reaction of radicals with HI and I₂ respectively be unity. This is not a sufficiently good approximation in the present case. More recently, Perner and Schuler³⁷ have presented an indirect analytical solution for HI-I₂ scavenger kinetics in irradiated hydrocarbons. Again, it appears impossible to extend the mathematical treatment to hydrocarbon-alkyl iodide solutions. Their analysis applies

to a kinetic scheme which is similar to the present scheme. but they did not make any allowance for the direct participation of hydrogen atoms. They assumed that hydrogen atoms attack the substrate and are converted to alkyl radicals. In order to make the present scheme applicable not only to the radiolysis of pure hydrocarbons but also to more complicated systems of hydrocarbon-alkyl iodide solutions, the problem has been attacked by numerical integration. A published program³⁸ for the second-order Runge-Kutta method of solving simultaneous differential equations is applicable with slight modifications in the present case (see appendix). The integration has been done on the IBM 709 computer of the University of Florida Computing Center.

Assignment of Parameters

General

Before the equations for the rate expressions can be solved by the computer, it is necessary to provide values for the quantities A, B, C, and D, and for the ratio of rate constants k_{HI}/k_{I_2} . Some information about these parameters is obtained from the limiting forms of equation 21. When the concentration of hydrogen iodide greatly exceeds that of iodine, the equation reduces to the form

$$(d[I_2]/dt)_{\text{Max}} = B + (A+D)/2 \quad (30)$$

and when the concentration of iodine greatly exceeds that of hydrogen iodide, the equation becomes

$$(d[I_2]/dt)_{\text{Min}} = B - (A+D)/2 \quad (31)$$

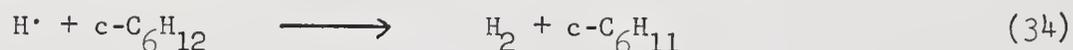
The subscripts "Max" and "Min" have been used because the first case refers to the initial, maximum value of the rate of iodine production with added HI, whereas the second refers to the initial, minimum value of the rate of iodine production or disappearance with added iodine.

Equations 30 and 31 yield

$$B = (\text{Max. Rate} + \text{Min. Rate})/2 \quad (32)$$

$$(A+D) = (\text{Max. Rate} - \text{Min. Rate}) \quad (33)$$

In order to substitute the value of $(A+2D)$ in equation 25, it is necessary to establish the value of D. Some evidence on its value is given by the experiments of Meshitsuka and Burton¹⁴ in which the initial value of the HI yield in cyclohexane with added iodine was found to be 2.1 molecules/100 ev. This can be taken as an upper limit for the hydrogen atom yield applicable to solutions with scavenger concentrations of about 2×10^{-2} M or greater. At sufficiently low scavenger concentrations of about 10^{-4} M or less, the scavengeable hydrogen yield is effectively zero because the hydrogen atoms react with the hydrocarbon substrate to form H_2 and are replaced by a corresponding yield of alkyl radicals:^{17,18,40}



At higher concentrations, iodine and other scavengers can compete with reaction 34. It has been reported by Schuler¹² that, using iodine as a scavenger, the reduction in the corresponding hydrogen yield occurs mainly in the concentration range from 10^{-3} to 10^{-2} M. According to him a concentration of 3×10^{-3} M iodine decreases the hydrogen production by 50 percent of the ultimately observed reduction. Hence, for the

purposes of the present calculations, it can be assumed that the effective G value of scavengeable hydrogen atoms varies from zero at 10^{-4} M I_2 or HI to a maximum of about 2 at ca 2×10^{-2} M scavenger concentration.

The quantity C could be found experimentally if HI yields were measured in the radiolysis of cyclohexane-methyl iodide solutions with additives. However, the HI yield is difficult to measure accurately. By an indirect method, using equations 21, 30, and 31, C can be found as follows:³⁶ the rate of iodine production expressed by equation 21 is just the Normal Rate without additives. Hence, subtracting equation 31 from equation 21 one obtains

$$\text{Norm. Rate} - \text{Min. Rate} = (A+D) - (A+D)[I_2]/([I_2] + [HI]k_{HI}/k_{I_2})$$

and subtracting equation 21 from equation 30 gives

$$\text{Max. Rate} - \text{Norm. Rate} = (A+D)[I_2]/([I_2] + [HI]k_{HI}/k_{I_2})$$

Therefore,

$$\begin{aligned} \frac{\text{Norm. Rate} - \text{Min. Rate}}{\text{Max. Rate} - \text{Norm. Rate}} &= \frac{([I_2] + [HI]k_{HI}/k_{I_2})}{[I_2]} - 1 \\ &= \frac{[HI]k_{HI}}{[I_2]k_{I_2}} \end{aligned}$$

$$\text{and } ([HI]/[I_2])_{\text{Norm}} = (k_{I_2}/k_{HI}) \left(\frac{\text{Norm. Rate} - \text{Min. Rate}}{\text{Max. Rate} - \text{Norm. Rate}} \right) \quad (35)$$

The subscript "Norm" has been used because the ratio of HI and I_2 is for the radiolysis experiment without additives.

Since HI and I₂ are produced at a constant rate

$$\left(\frac{d[\text{HI}]/dt}{d[\text{I}_2]/dt}\right)_{\text{Norm}} = \left(\frac{[\text{HI}]}{[\text{I}_2]}\right)_{\text{Norm}}$$

$$\left(\frac{d[\text{HI}]}{dt}\right)_{\text{Norm}} = \left(\frac{[\text{HI}]}{[\text{I}_2]}\right)_{\text{Norm}} \cdot \left(\frac{d[\text{I}_2]}{dt}\right)_{\text{Norm}} \quad (36)$$

Addition of equations 21 and 25 gives

$$\left(\frac{d[\text{I}_2]}{dt}\right)_{\text{Norm}} + \left(\frac{d[\text{HI}]}{dt}\right)_{\text{Norm}} = C + B - (A+D)/2 + D[\text{I}_2]/([\text{I}_2] + [\text{HI}]k_{\text{HI}}/k_{\text{I}_2}) \quad (37)$$

Substitution of equations 31 and 36 in 37 and rearrangement yields

$$C = \left(\frac{[\text{HI}]}{[\text{I}_2]}\right)_{\text{Norm}} \cdot \left(\frac{d[\text{I}_2]}{dt}\right)_{\text{Norm}} + \left(\frac{d[\text{I}_2]}{dt}\right)_{\text{Norm}} - \left(\frac{d[\text{I}_2]}{dt}\right)_{\text{Min}} - D[\text{I}_2]/([\text{I}_2] + [\text{HI}]k_{\text{HI}}/k_{\text{I}_2})$$

or $C = \left(\frac{[\text{HI}]}{[\text{I}_2]}\right)_{\text{Norm}} \cdot (\text{Norm. Rate}) + (\text{Norm. Rate} - \text{Min. Rate}) - D[\text{I}_2]/([\text{I}_2] + [\text{HI}]k_{\text{HI}}/k_{\text{I}_2}) \quad (38)$

For pure cyclohexane

The parameters needed for substitution in equations 26 and 27 for the radiolysis of pure cyclohexane with additives are A, D, and $k_{\text{HI}}/k_{\text{I}_2}$ only. As already mentioned, the effective G value of scavengable H atoms may be considered to vary from zero at 10^{-4} M I₂ or HI to a maximum of about 2 at 2×10^{-2} M scavenger concentration. However, since sufficiently detailed data on effective hydrogen atom yields at intermediate concentrations are not available, the hydrogen atom yields

in the present calculations have been obtained by using the D factor in equations 26 and 27 as an adjustable parameter for curve fitting. The sum (A + D) can be calculated from equation 33. Hence, the radical yield A can be obtained by difference. The calculated effect of varying the hydrogen atom yield in a typical experiment on the radiation-induced uptake of iodine is shown in Figure 9. It is evident from the graph that increasing $G(H\cdot)$ increases the end point of the experiment, i.e., the dose for complete removal of iodine. Figure 10 shows that increasing $G(H\cdot)$ causes a similar increase in the end point for the radiolysis experiment on pure cyclohexane with added HI. In Figures 9 and 10, the ratio of the rate constants k_{HI}/k_{I_2} was taken as 0.71, which is the value giving the best fit of experimental data.

Although there is experimental evidence suggesting that k_{HI}/k_{I_2} in non-polar solvents is of the order of unity,³⁶ there were insufficient data to assign an accurate value for the present experiments. Therefore, the ratio k_{HI}/k_{I_2} has also been treated as an adjustable parameter in the calculations. The effect of changing this ratio is shown in Figures 11 and 12. Figure 11 shows the calculated results for the radiolysis experiments on pure cyclohexane with added iodine. It is evident that changing the ratio k_{HI}/k_{I_2} modifies the curvature of a graph of iodine concentration vs radiolysis time, but does not affect the end point unless the ratio is zero. If the ratio is zero, the products at the end point would include HI as well as alkyl iodides. As long as k_{HI}/k_{I_2} has a finite value all the iodine, whether present as the chemical intermediate HI or as iodine, must ultimately appear as alkyl iodides. For all finite values of the ratio k_{HI}/k_{I_2} , the end

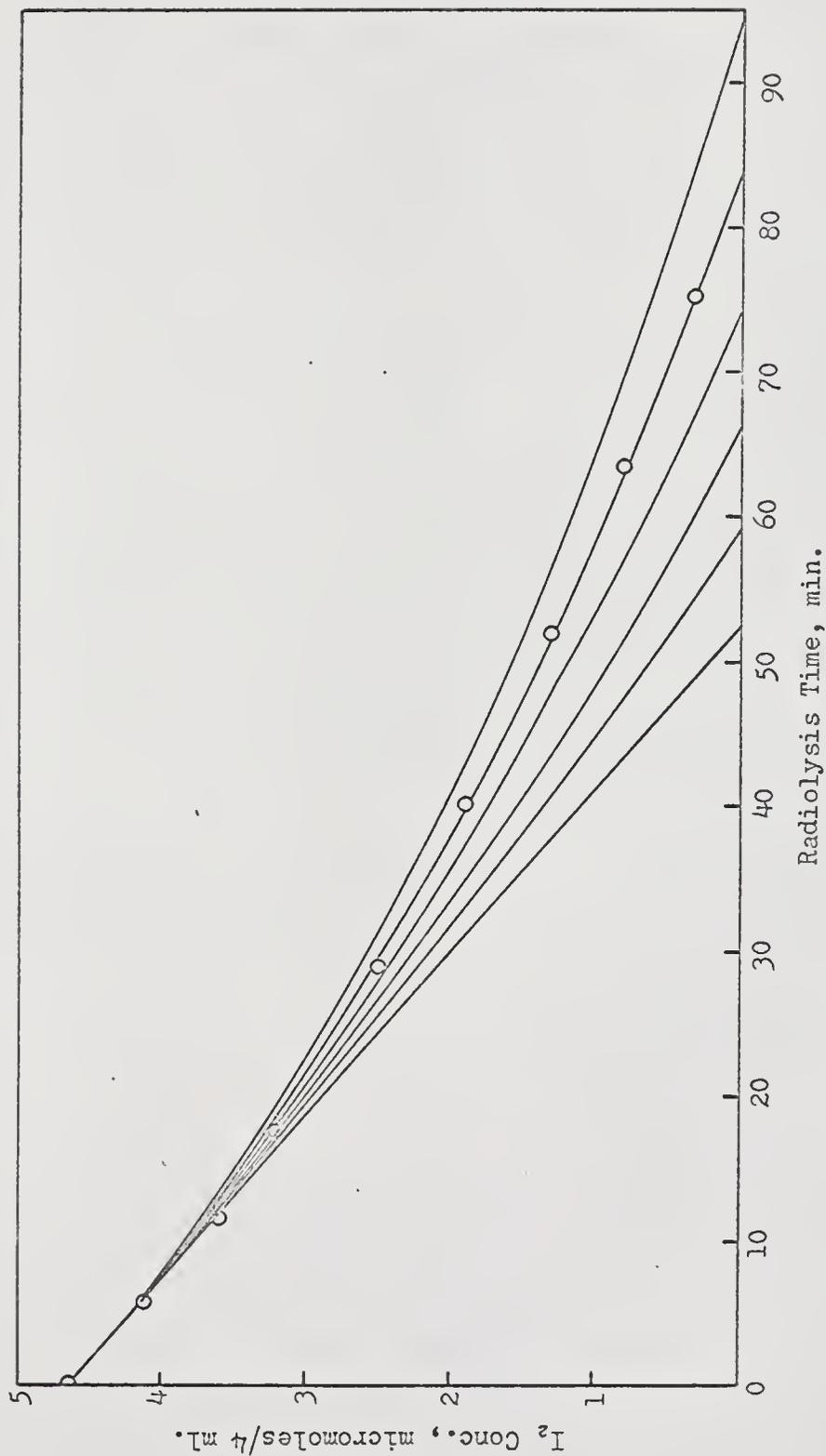


Figure 9. Role of H atom yield as an adjustable parameter: I₂ consumption in the radiolysis of pure cyclohexane, with added I₂ (1.16×10^{-3} M), as a function of radiation time. Circles are experimental; smooth curves are computed. G(H•) values, reading left to right, are 0.0, 0.35, 0.70, 1.05, 1.40 and 1.74.

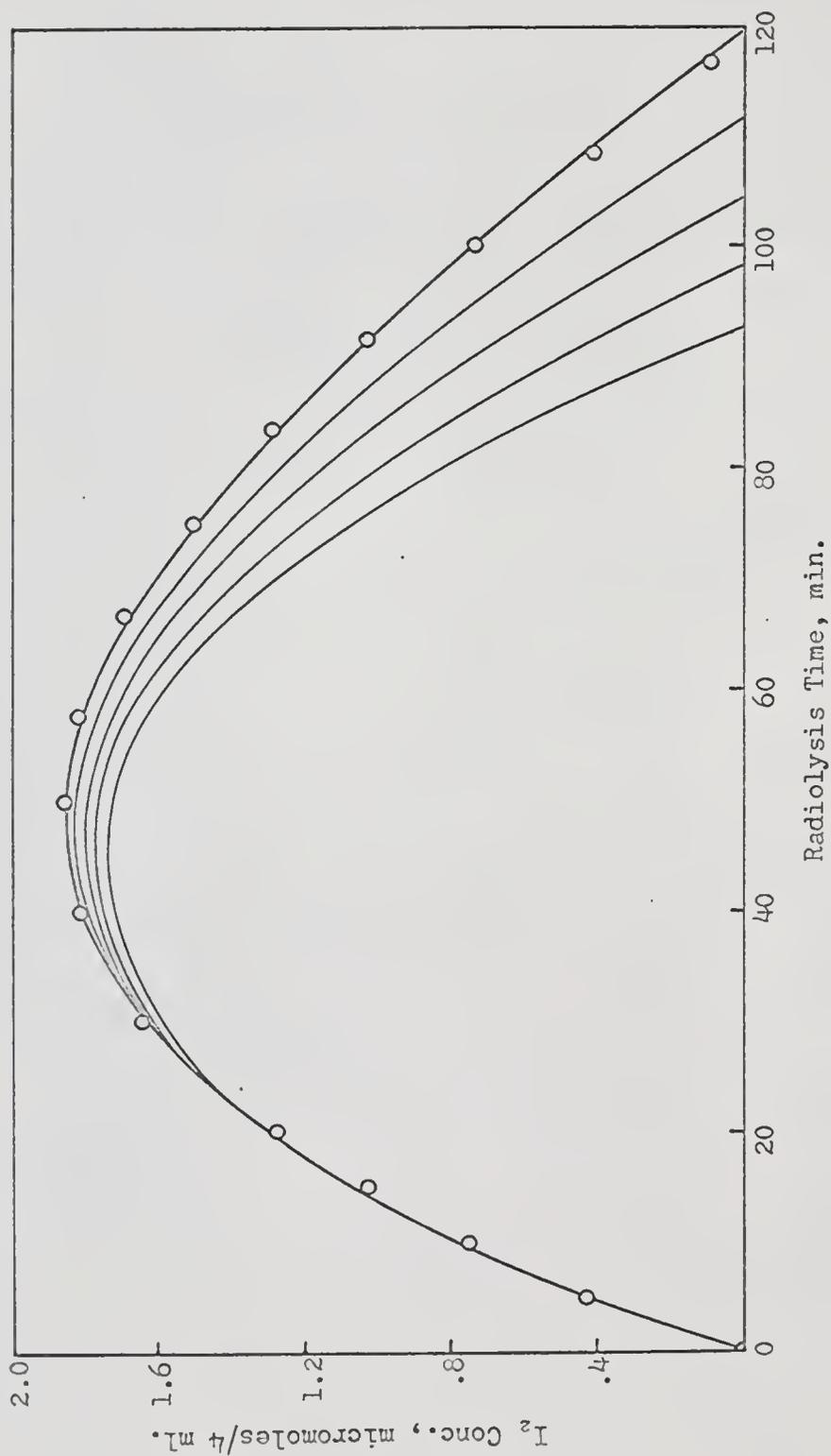


Figure 10. Role of H atom yield as an adjustable parameter: I_2 production in the radiolysis of pure cyclohexane, with added HI (2.11×10^{-3} M), as a function of radiation time. Circles are experimental; smooth curves are computed. G(H \cdot) values, reading downwards, are 1.40, 1.05, 0.70, 0.35 and 0.0.

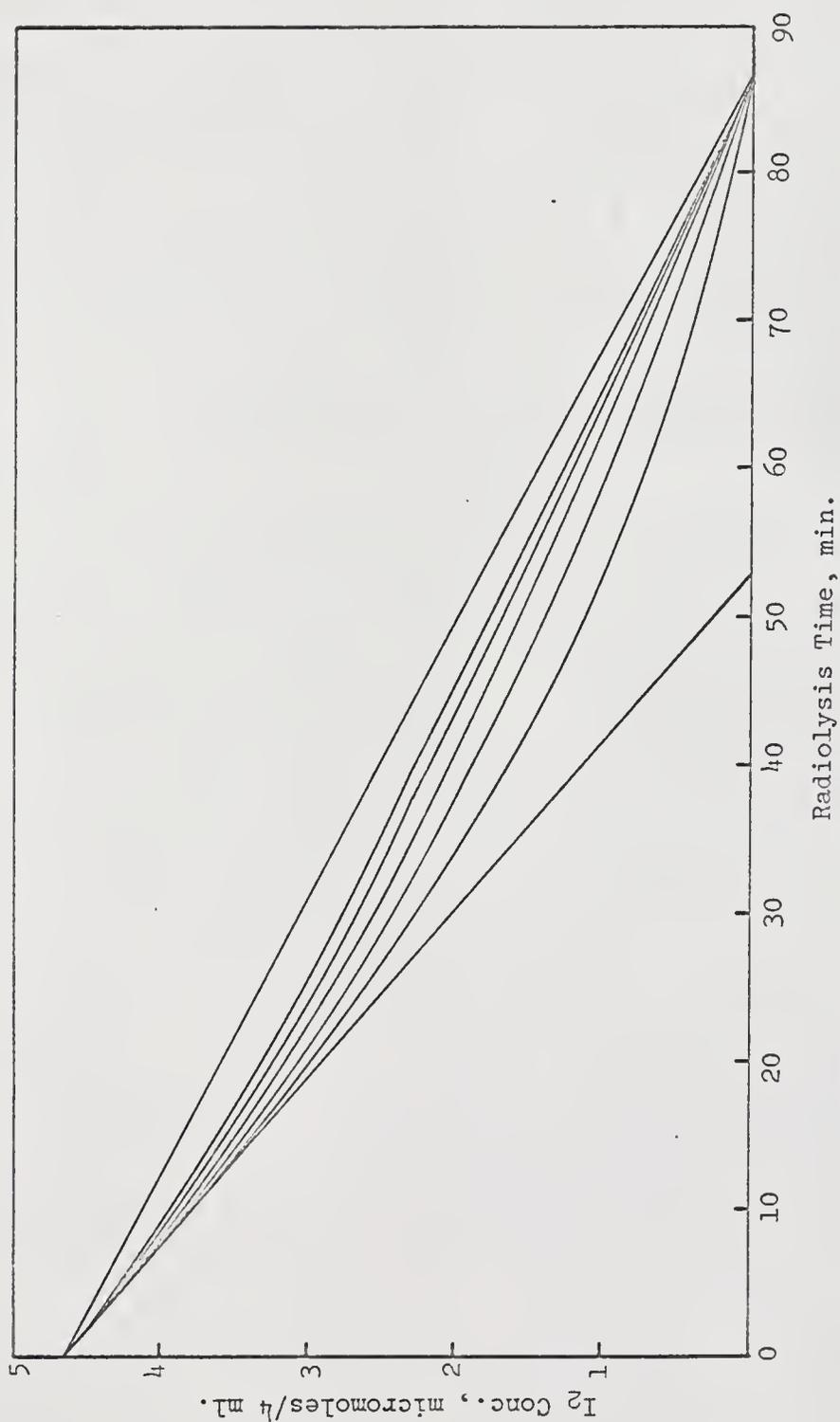


Figure 11. Role of k_{HI}/k_{I_2} as an adjustable parameter: I₂ consumption in the radiolysis of pure cyclohexane, with added I₂ (1.16×10^{-3} M), as a function of radiation time. Values of k_{HI}/k_{I_2} , reading left to right, are 0.0, 0.3, 0.6, 0.9, 1.5, 2.0 and ∞ .

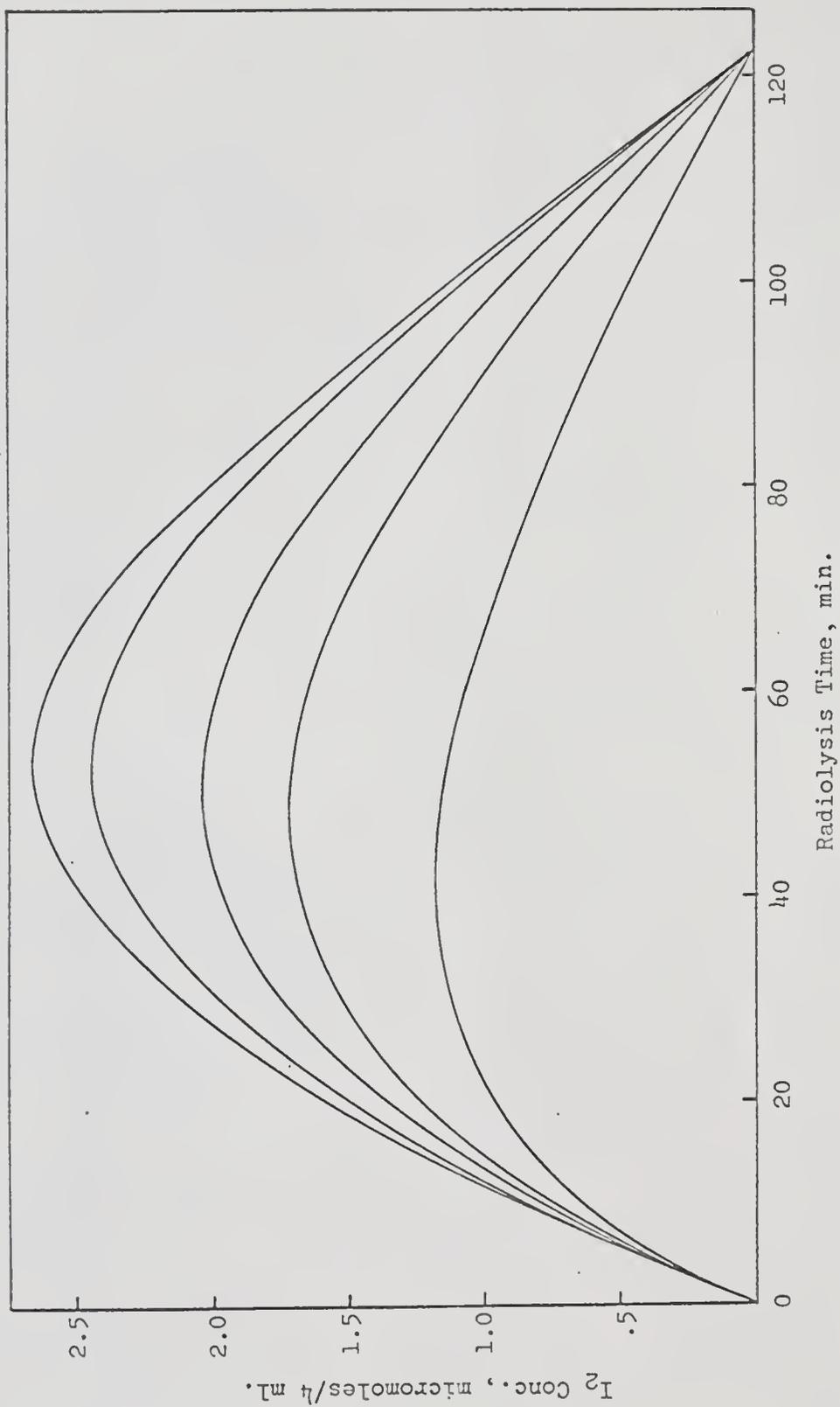


Figure 12. Role of k_{HI}/k_{I_2} as an adjustable parameter: I_2 production in the radiolysis of pure cyclohexane, with added HI (2.11×10^{-3} M), as a function of radiation time. Values of k_{HI}/k_{I_2} , reading downwards, are 2.0, 1.5, 0.9, 0.6 and 0.3.

point of the experiment is the same but the curvature increases as the ratio decreases. However, the initial slope of all the curves remains the same and approaches that for which the ratio is zero.

The calculated effect of varying the ratio k_{HI}/k_{I_2} for an experiment on the radiolysis of pure cyclohexane with added HI is shown in Figure 12. Again in this case, variation of the value of the ratio does not affect the end point of the radiolysis. Increasing the ratio increases the maximum of the graph which is the maximum concentration of iodine produced in the experiment and also increases the radiolysis time corresponding to the maximum.

For cyclohexane-methyl iodide solutions

For solutions with 0 to 95 volume percent cyclohexane, the parameters needed for substitution in equations 28 and 29 are A, B, C, and k_{HI}/k_{I_2} . Since the thermal hydrogen atom yield D is zero in these solutions, the radical yield A is given by equation 33 as

$$A = \text{Max. Rate} - \text{Min. Rate} \quad (39)$$

$$B = (\text{Max. Rate} + \text{Min. Rate})/2 \quad (32)$$

$$C = ([HI]/[I_2])_{\text{Norm}} \cdot (\text{Norm. Rate}) + (\text{Norm. Rate} - \text{Min. Rate}) \quad (40)$$

The different rates, namely Maximum, Minimum and Normal are the rates found experimentally by taking the initial slopes of the graphs. The value of $([HI]/[I_2])_{\text{Norm}}$ is found by expression 35. (Difficulties caused by fall-off of the Normal Rates are discussed below in the section entitled "Comparison with Experiments".) Substitution of the values of various rates for a particular solution in equations 32, 39,

and 40 yields values of A, B, and C for the corresponding solution.. For very dilute solutions of methyl iodide in cyclohexane, B is given directly and the sum of A and D is established by equation 33. Resolution of A and D is discussed below.

Due to lack of experimental data on the ratios k_{HI}/k_{I_2} for the series of solutions studied, k_{HI}/k_{I_2} was treated as an adjustable parameter in the calculations. The computed effect of varying the ratio k_{HI}/k_{I_2} for the various solutions with added I_2 is shown in Figures 13 to 19. For the entire range of cyclohexane-methyl iodide solutions, it is found that increasing the rate constant ratio increases the iodine concentration achieved at a given radiolysis time. This effect becomes more pronounced as the percent cyclohexane in the solution is increased. However, the initial slope of the graphs is the same in all cases and approaches that for which k_{HI}/k_{I_2} is zero. Similar effects of varying the rate constant ratio are observed for experiments with added HI and are shown in Figures 20 to 26. The effect of varying the ratio in the case of 99.9 percent solutions is quite similar to that observed for pure cyclohexane (see above).

For solutions from 0 to about 95 percent cyclohexane, that is, for all cases in which there is a non-zero Normal Rate of iodine production, the arbitrary assignment of the single parameter k_{HI}/k_{I_2} should suffice to fit the equations to experimental data. Under these circumstances A and B come directly from experimental data, and C can be calculated if k_{HI}/k_{I_2} is fixed. It has been found that adjusting only k_{HI}/k_{I_2} gave a good fit of experimental data for solutions with 20 to 90 percent cyclohexane. However, this procedure gave a rather

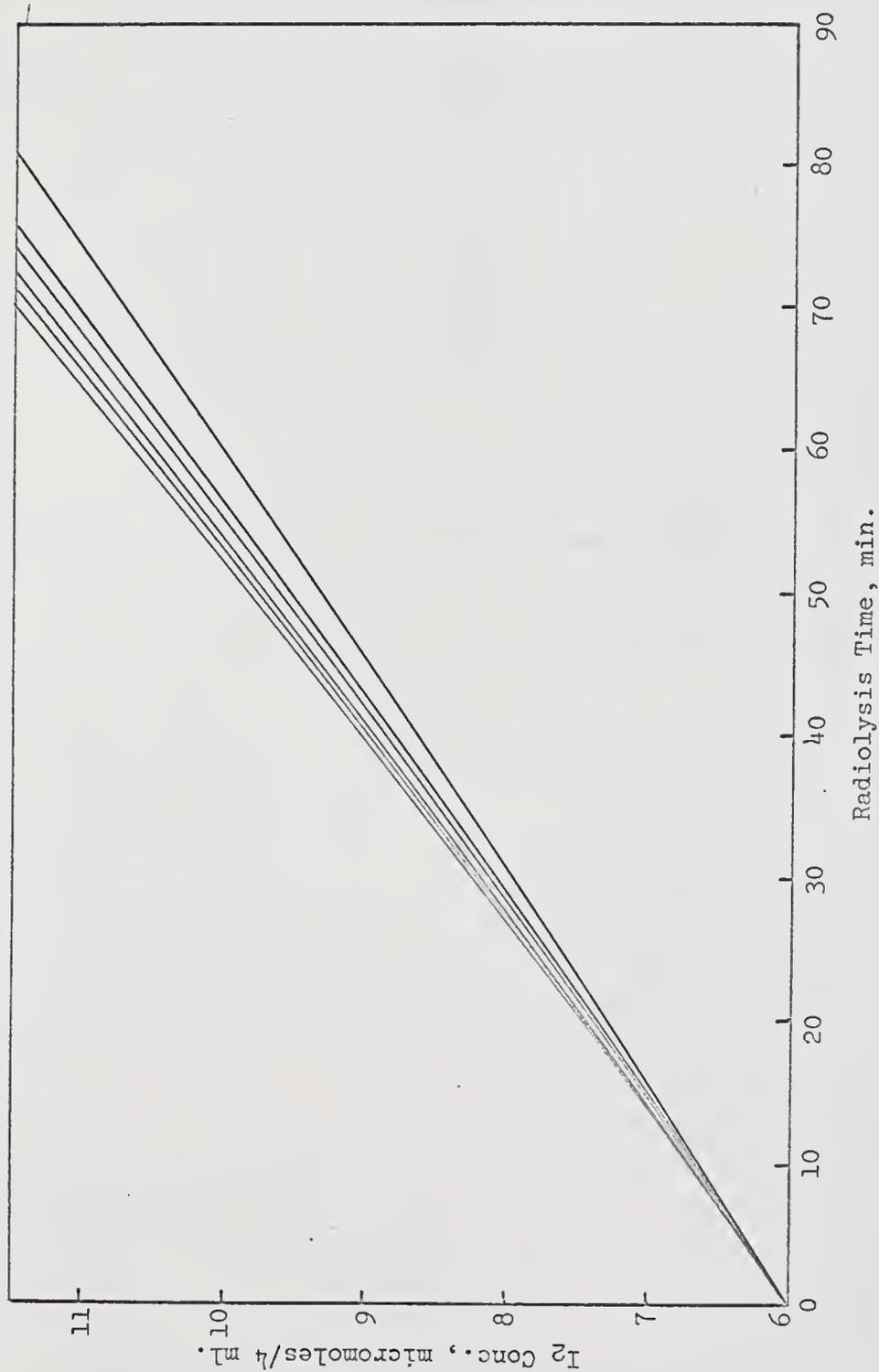


Figure 13. Role of $k_{\text{HI}}/k_{\text{I}_2}$ as an adjustable parameter: I_2 production in the radiolysis of cyclohexane-methyl iodide solution, for 20 volume percent cyclohexane with added I_2 (1.5×10^{-3} M), as a function of radiation time. Values of $k_{\text{HI}}/k_{\text{I}_2}$, reading downwards, are 2.0, 1.5, 1.0, 0.6, 0.4 and 0.01.

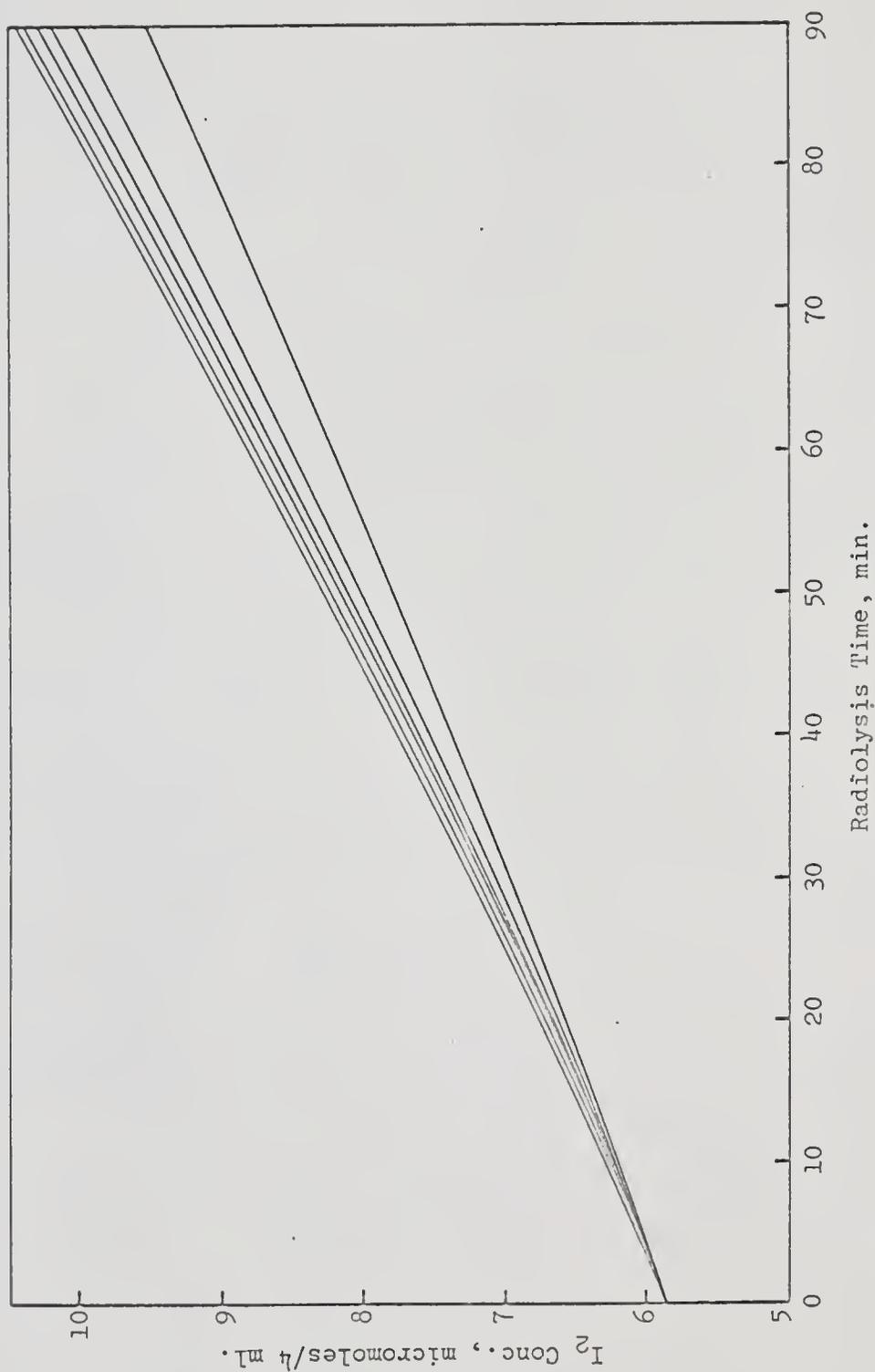


Figure 14. Role of k_{HI}/k_{I_2} as an adjustable parameter: I_2 production in the radiolysis of cyclohexane-methyl iodide solution, for 40 volume percent cyclohexane with added I_2 (1.46×10^{-3} M), as a function of radiation time. Values of k_{HI}/k_{I_2} , reading downwards, are 2.0, 1.5, 1.0, 0.7, 0.4 and 0.01.

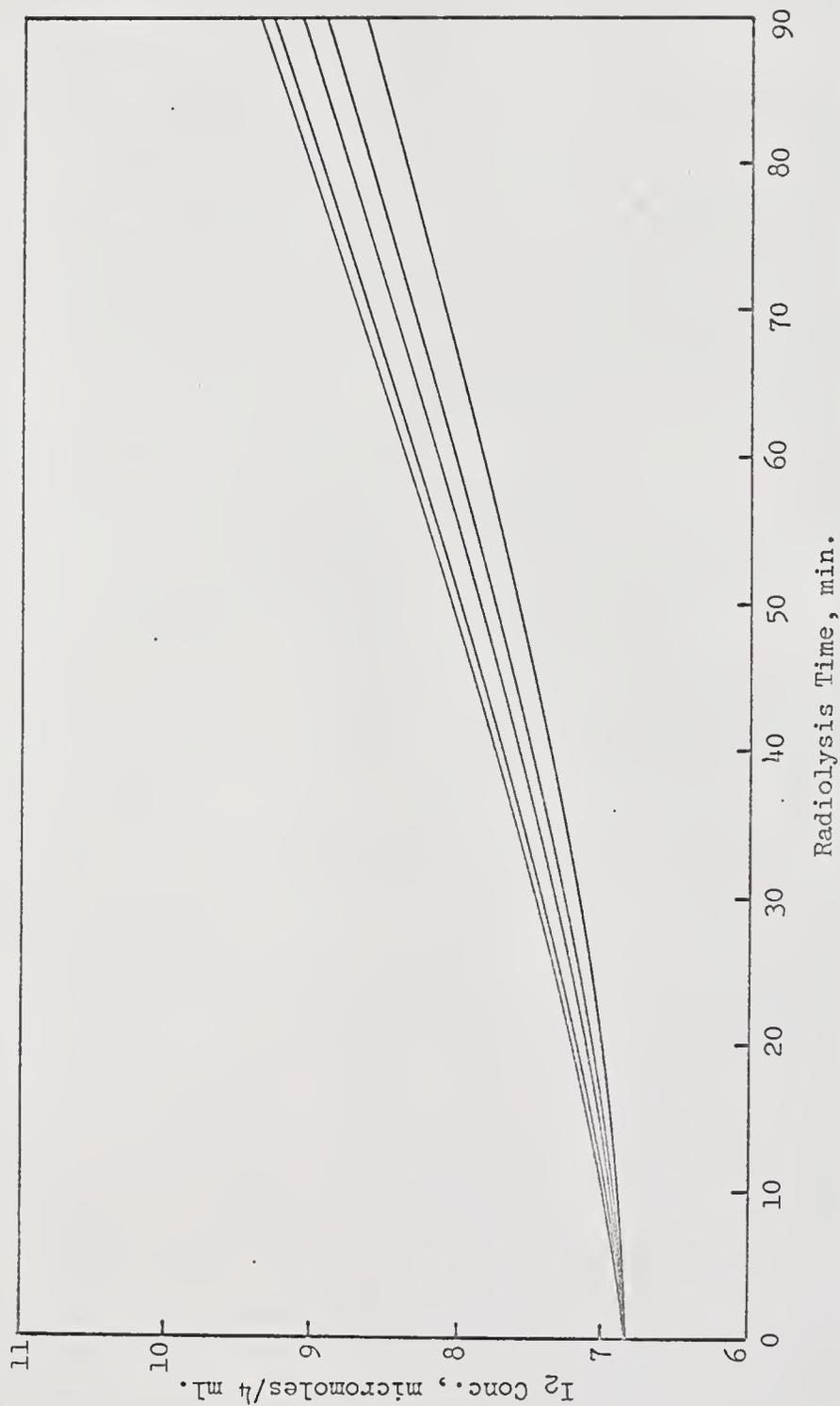


Figure 15. Role of k_{HI}/k_{I_2} as an adjustable parameter: I₂ production in the radiolysis of cyclohexane-methyl iodide solution, for 60 volume percent cyclohexane with added I₂ (1.7×10^{-3} M), as a function of radiation time. Values of k_{HI}/k_{I_2} , reading downwards, are 2.0, 1.5, 1.0, 0.7 and 0.4.

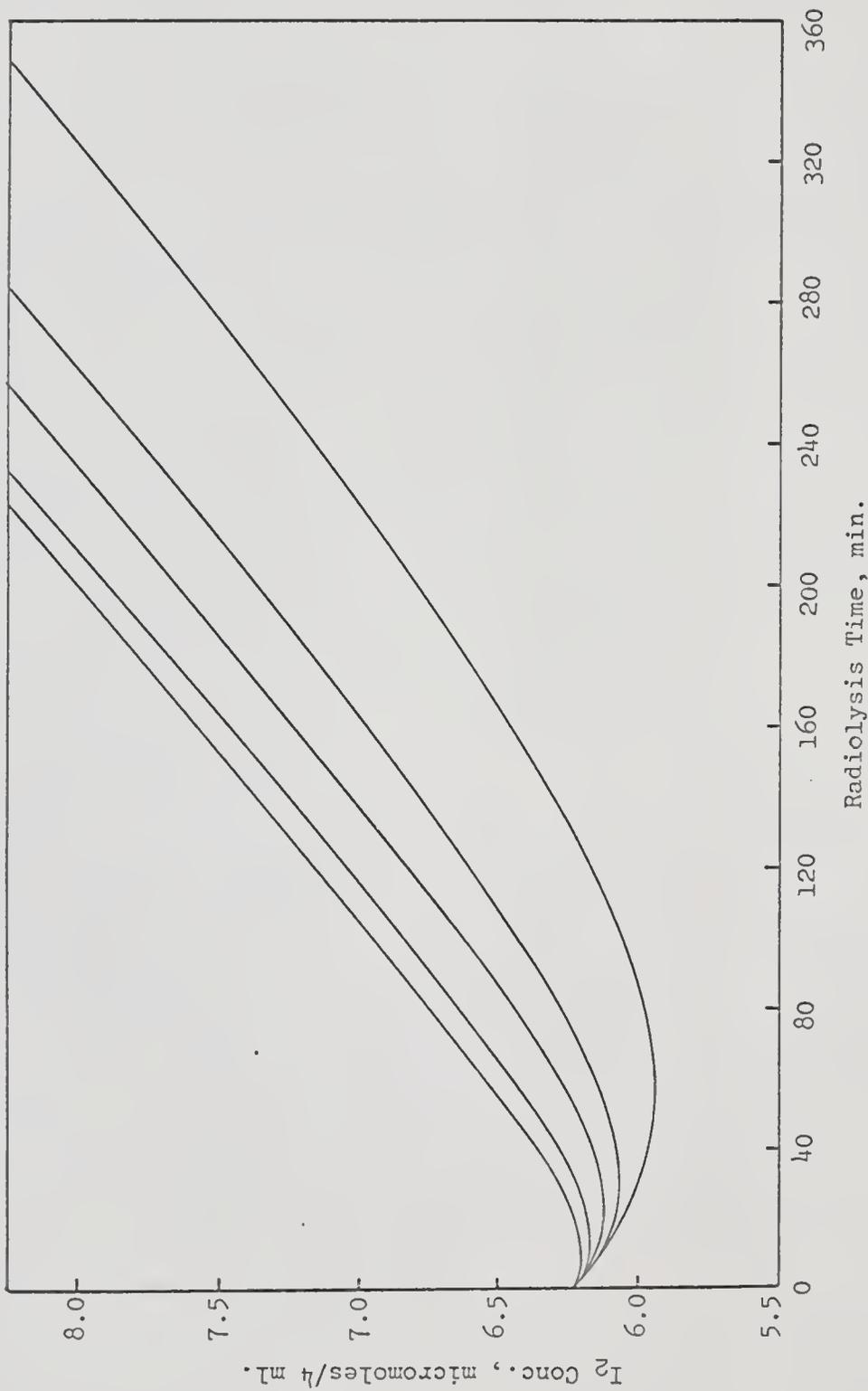


Figure 16. Role of k_{HI}/k_{I_2} as an adjustable parameter: I_2 production in the radiolysis of cyclohexane-methyl iodide solution, for 80 volume percent cyclohexane with added I_2 (1.55×10^{-3} M), as a function of radiation time. Values of k_{HI}/k_{I_2} , reading downwards, are 2.0, 1.5, 0.9, 0.6 and 0.3.

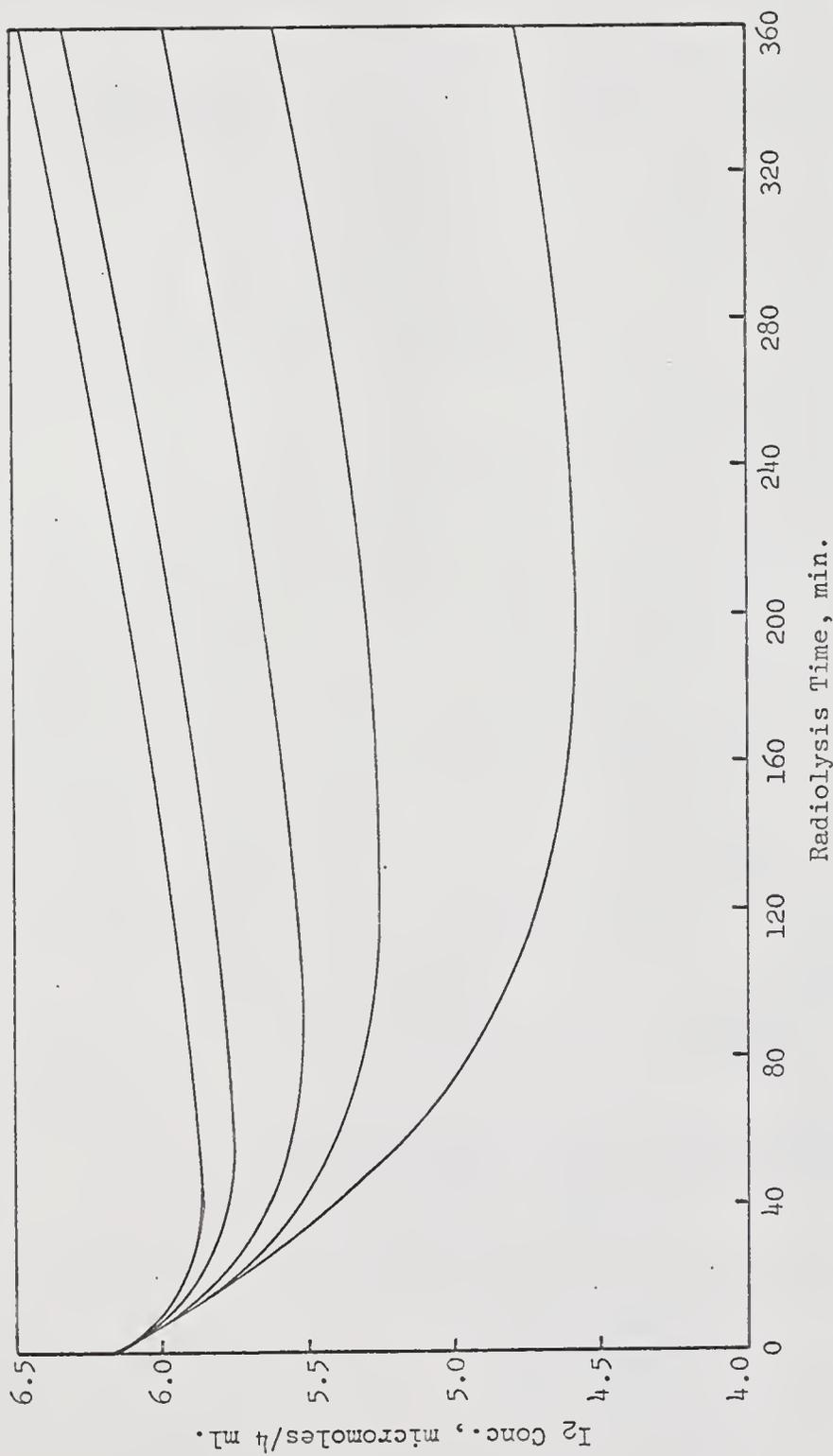


Figure 17. Role of k_{HI}/k_{I_2} as an adjustable parameter: I_2 production in the radiolysis of cyclohexane-methyl iodide solution, for 90 volume percent cyclohexane with added I_2 (1.55×10^{-3} M), as a function of radiation time. Values of k_{HI}/k_{I_2} , reading downwards, are 2.0, 1.5, 0.9, 0.6 and 0.3.

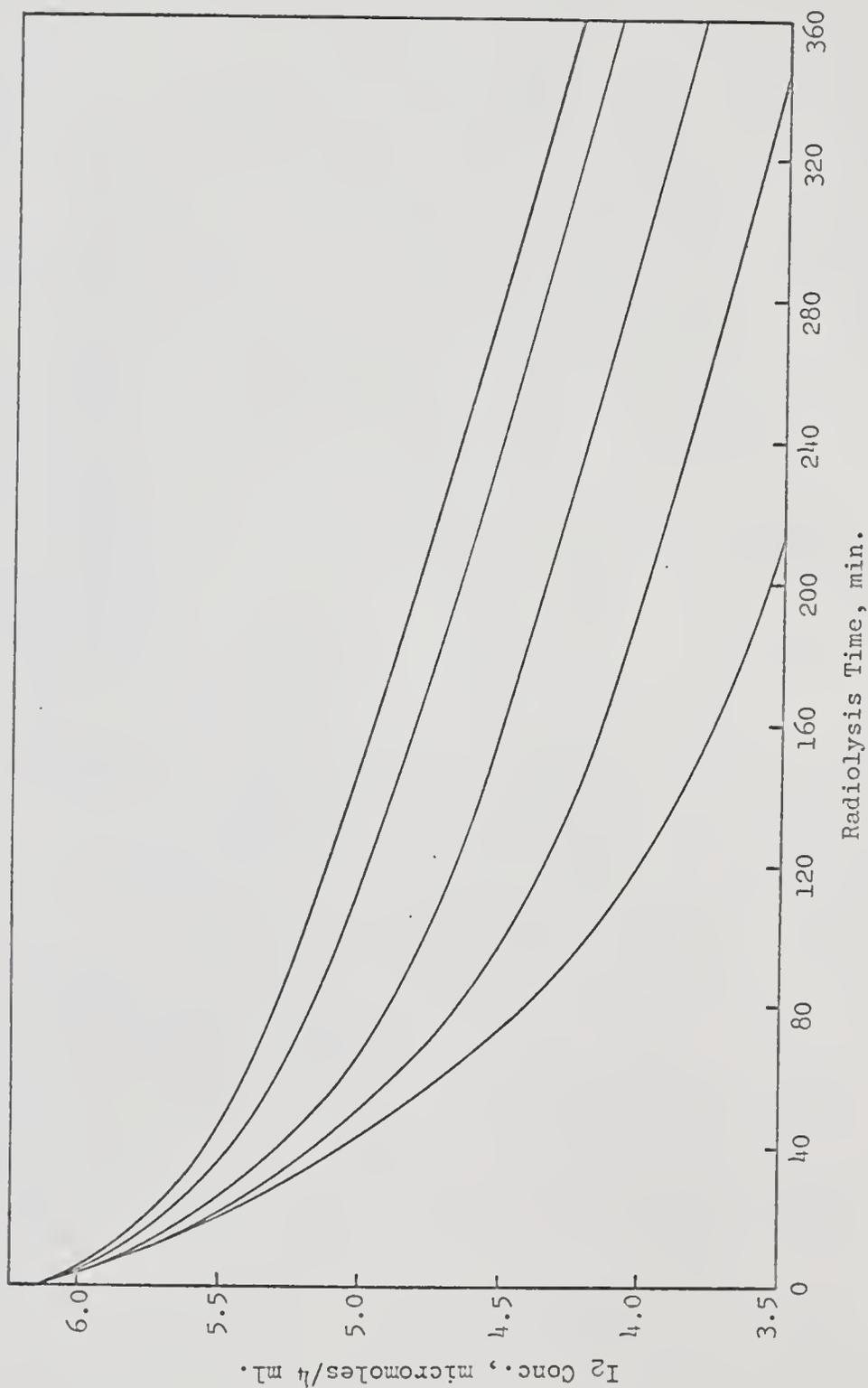


Figure 18. Role of k_{HI}/k_{I_2} as an adjustable parameter: I_2 production in the radiolysis of cyclohexane-methyl iodide solution, for 95 volume percent cyclohexane with added I_2 (1.55×10^{-3} M), as a function of radiation time. Values of k_{HI}/k_{I_2} , reading downwards, are 2.0, 1.5, 0.9, 0.6 and 0.4.

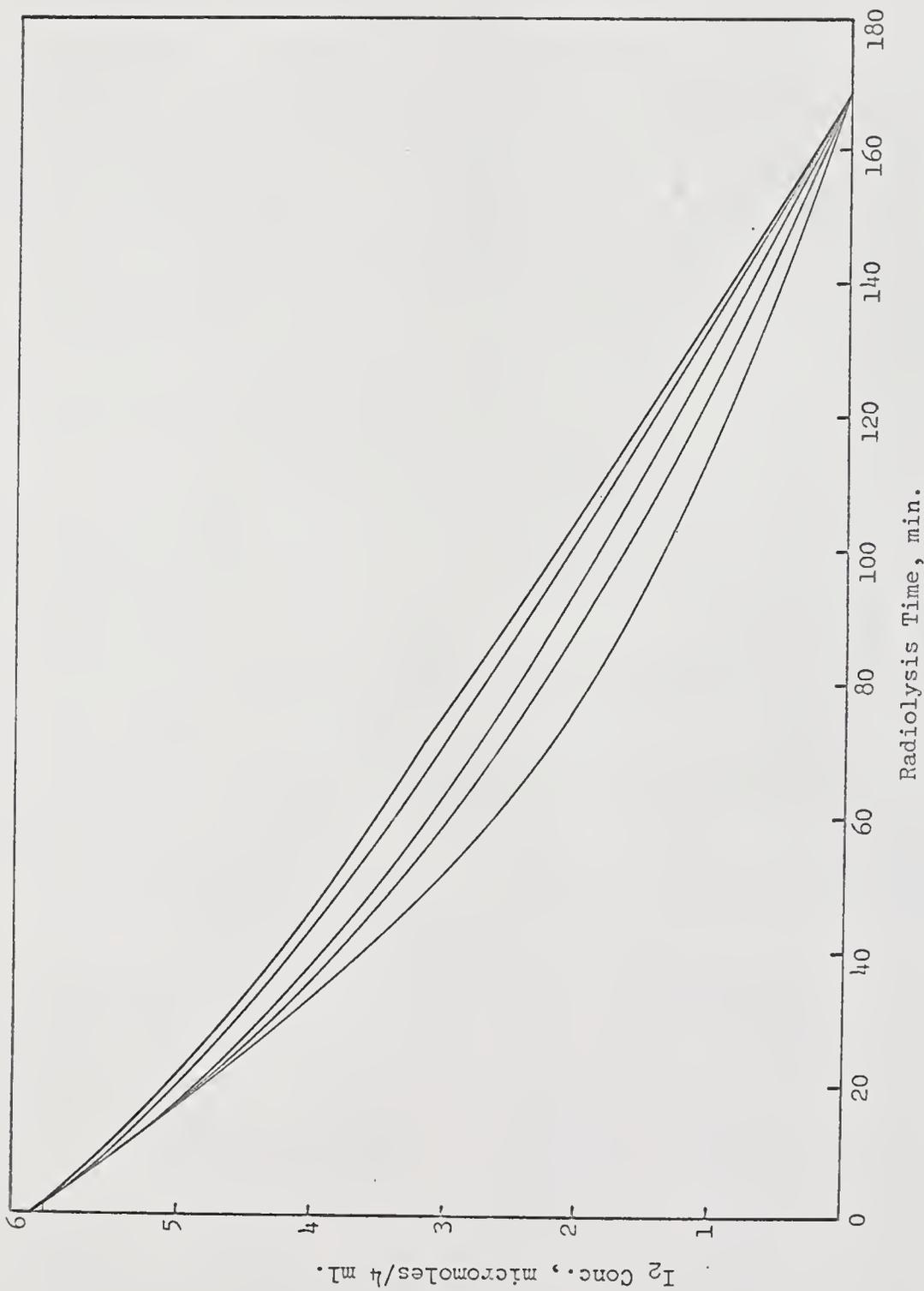


Figure 19. Role of k_{HI}/k_{I_2} as an adjustable parameter: I_2 production in the radiolysis of cyclohexane-methyl iodide solution, for 99.9 volume percent cyclohexane with added I_2 (1.5×10^{-3} M), as a function of radiation time. Values of k_{HI}/k_{I_2} , reading downwards, are 2.0, 1.5, 0.9, 0.7 and 0.4.

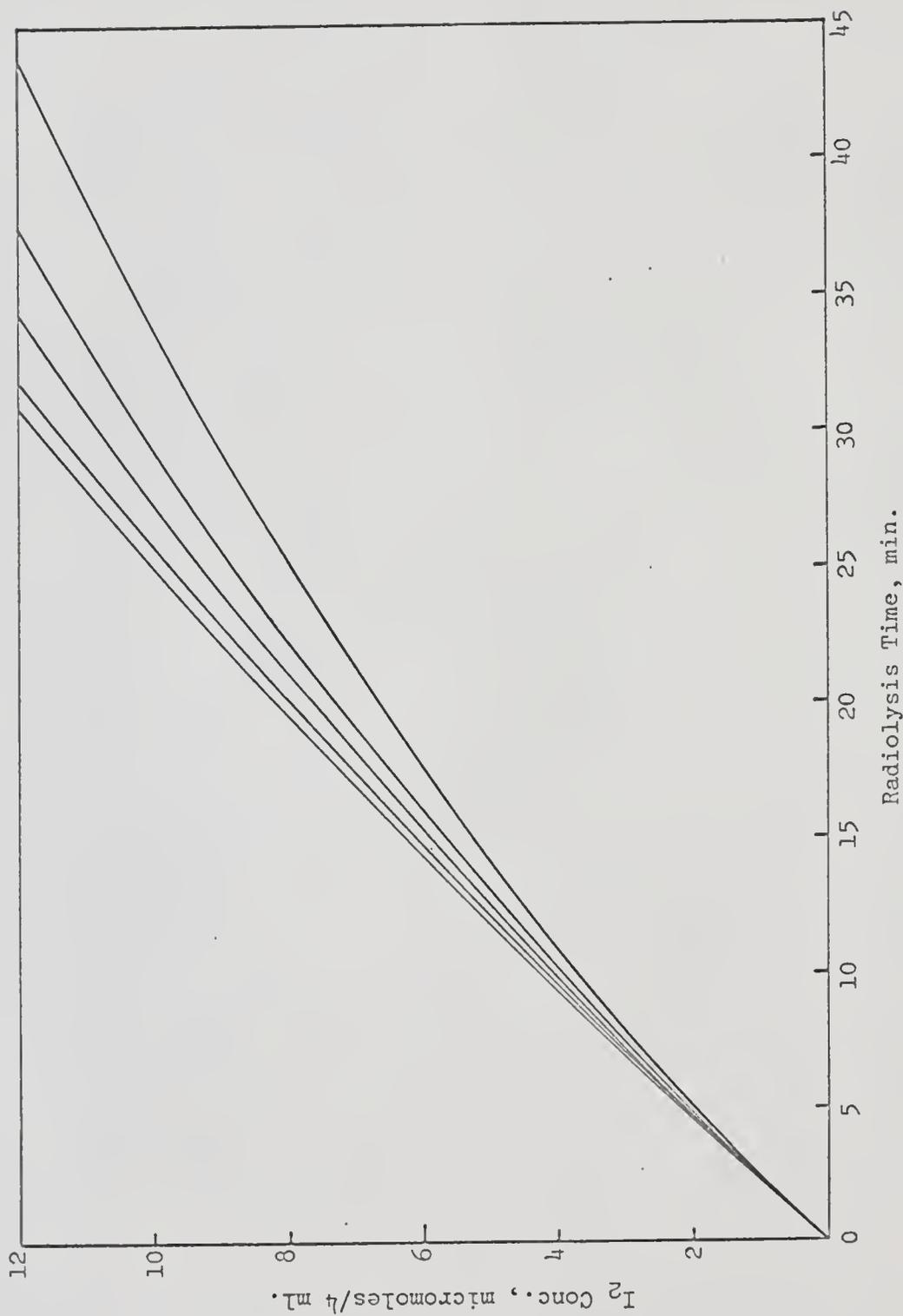


Figure 20. Role of k_{HI}/k_{I_2} as an adjustable parameter: I_2 production in the radiolysis of cyclohexane-methyl iodide solution, for 20 volume percent cyclohexane with added HI (6.1×10^{-3} M), as a function of radiation time. Values of k_{HI}/k_{I_2} , reading downwards, are 2.0, 1.5, 1.0, 0.7 and 0.4.

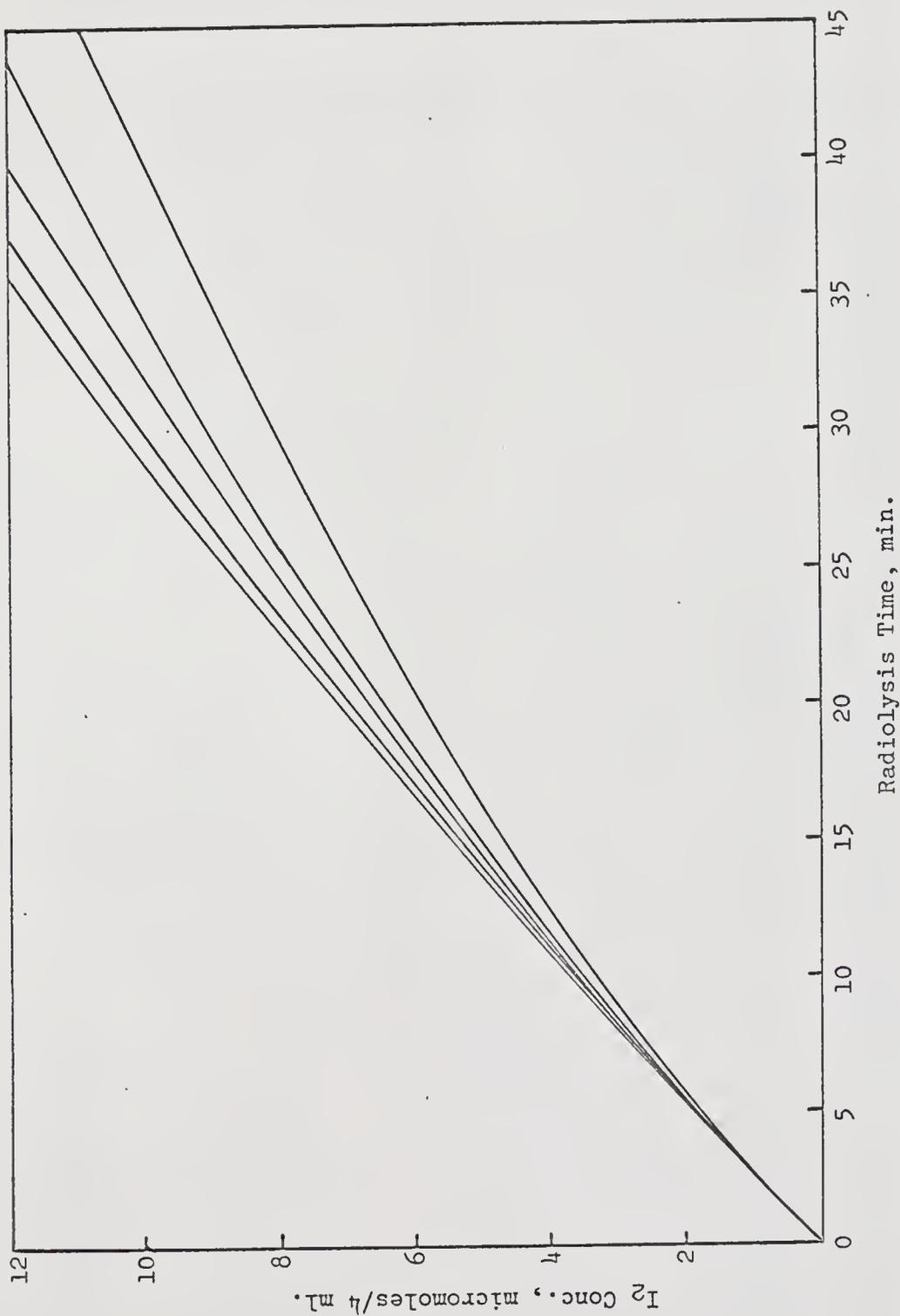


Figure 21. Role of k_{HI}/k_{I_2} as an adjustable parameter: I_2 production in the radiolysis of cyclohexane-methyl iodide solution, for 40 volume percent cyclohexane with added HI (6.1×10^{-3} M), as a function of radiation time. Values of k_{HI}/k_{I_2} , reading downwards, are 2.0, 1.5, 1.0, 0.7 and 0.4.

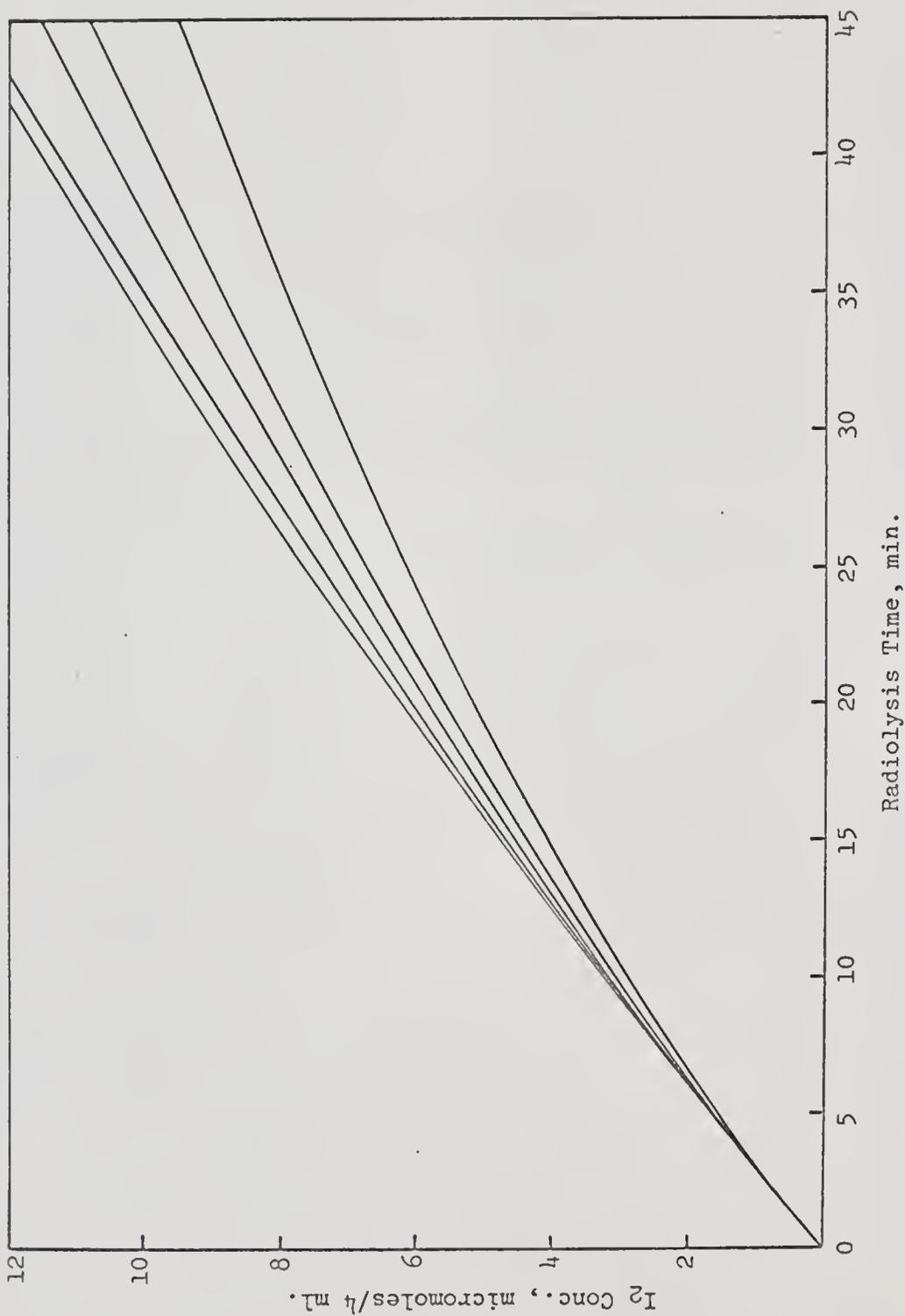


Figure 22. Role of k_{HI}/k_{I_2} as an adjustable parameter: I_2 production in the radiolysis of cyclohexane-methyl iodide solution, for 60 volume percent cyclohexane with added HI (5.2×10^{-3} M), as a function of radiation time. Values of k_{HI}/k_{I_2} , reading downwards, are 2.0, 1.5, 1.0, 0.7 and 0.4.

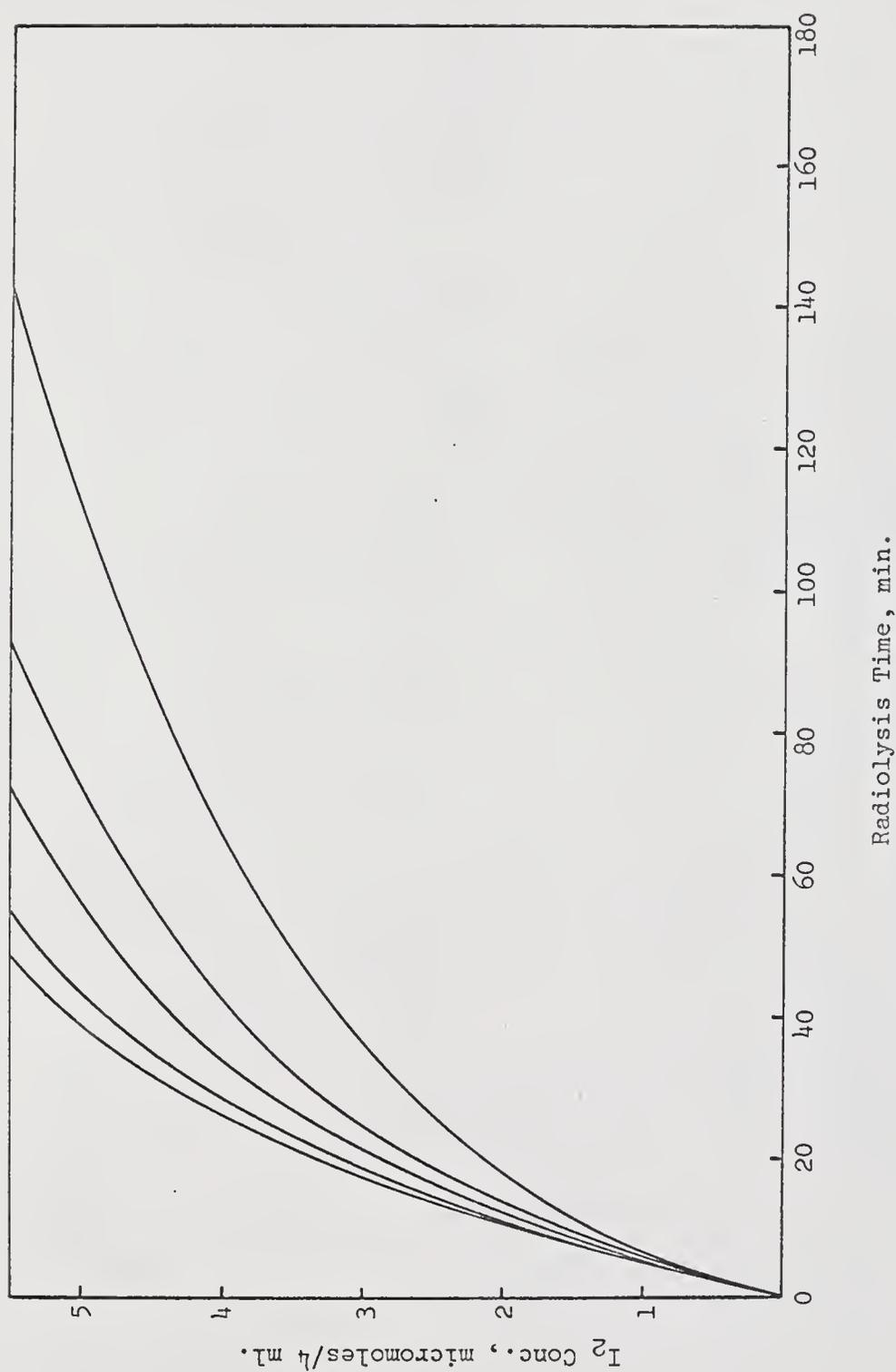


Figure 23. Role of k_{HI}/k_{I_2} as an adjustable parameter: I_2 production in the radiolysis of cyclohexane-methyl iodide solution, for 80 volume percent cyclohexane with added HI (1.5×10^{-3} M), as a function of radiation time. Values of k_{HI}/k_{I_2} , reading downwards, are 2.0, 1.5, 0.9, 0.6 and 0.3.

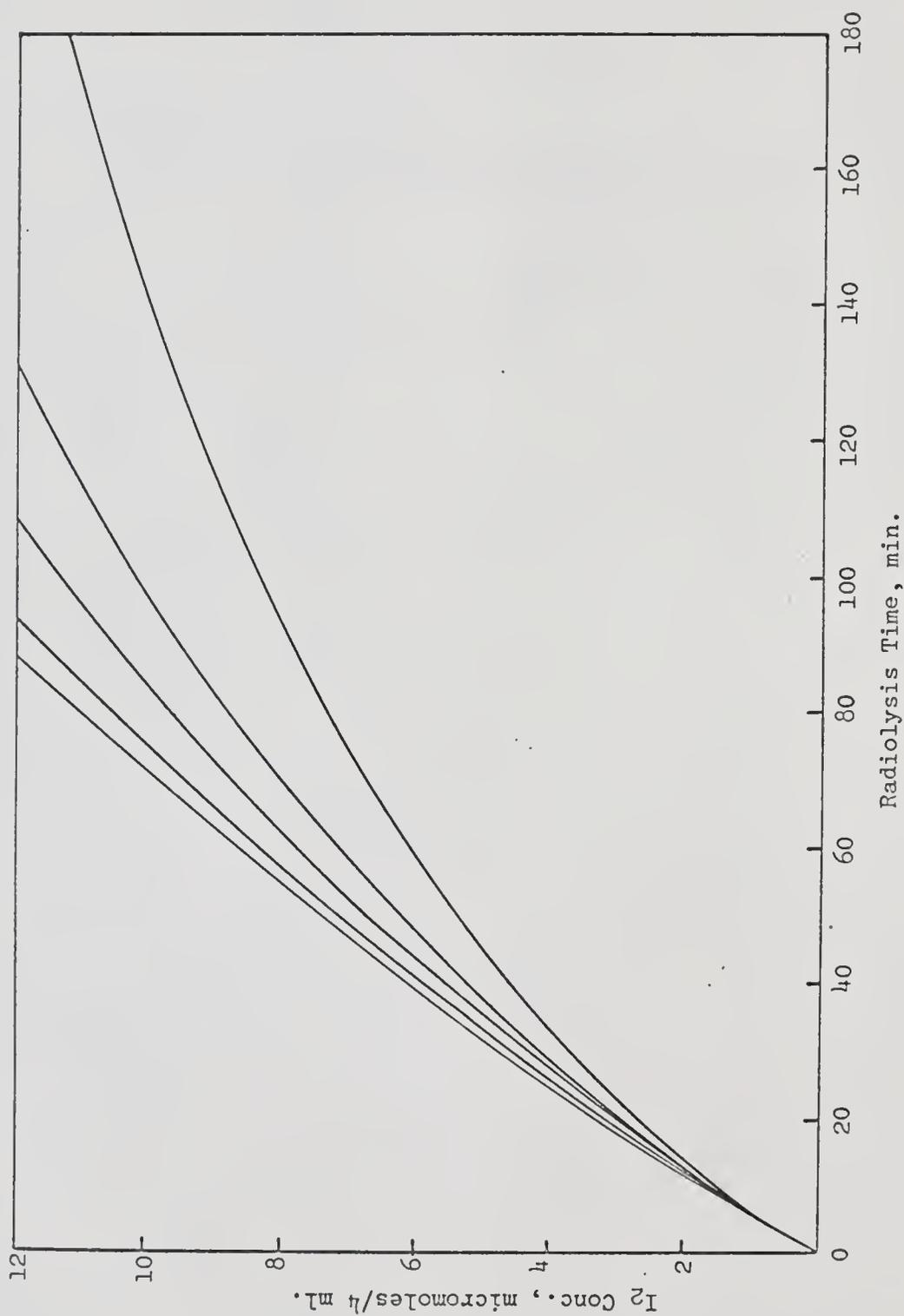


Figure 24. Role of k_{HI}/k_{I_2} as an adjustable parameter: I_2 production in the radiolysis of cyclohexane-methyl iodide solution, for 90 volume percent cyclohexane with added HI (6.1×10^{-3} M), as a function of radiation time. Values of k_{HI}/k_{I_2} , reading downwards, are 2.0, 1.5, 0.9, 0.6 and 0.3.

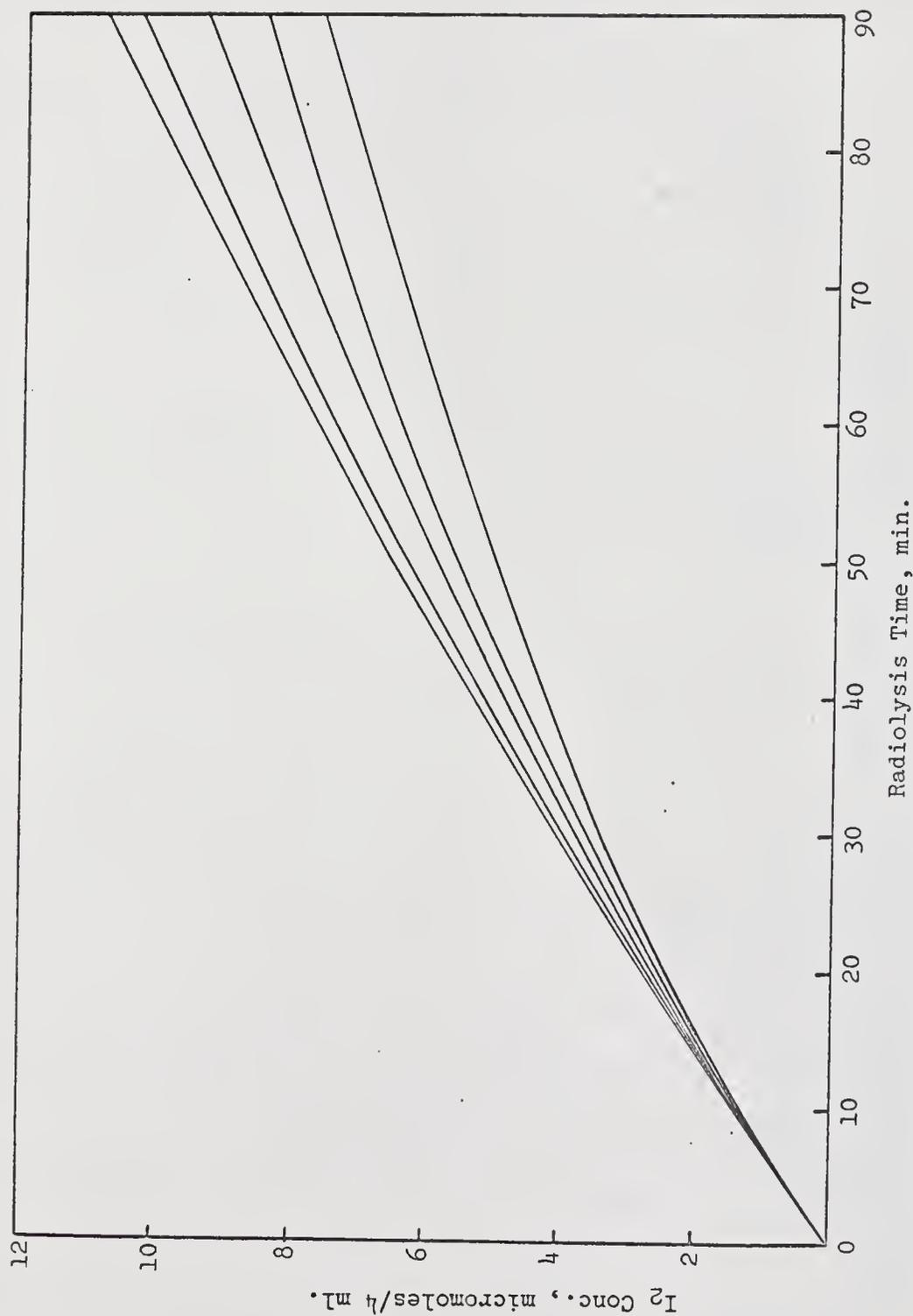


Figure 25. Role of k_{HI}/k_{I_2} as an adjustable parameter: I_2 production in the radiolysis of cyclohexane-methyl iodide solution, for 95% volume percent cyclohexane with added HI (6.1×10^{-3} M), as a function of radiation time. Values of k_{HI}/k_{I_2} , reading downwards, are 2.0, 1.5, 0.9, 0.6 and 0.4.

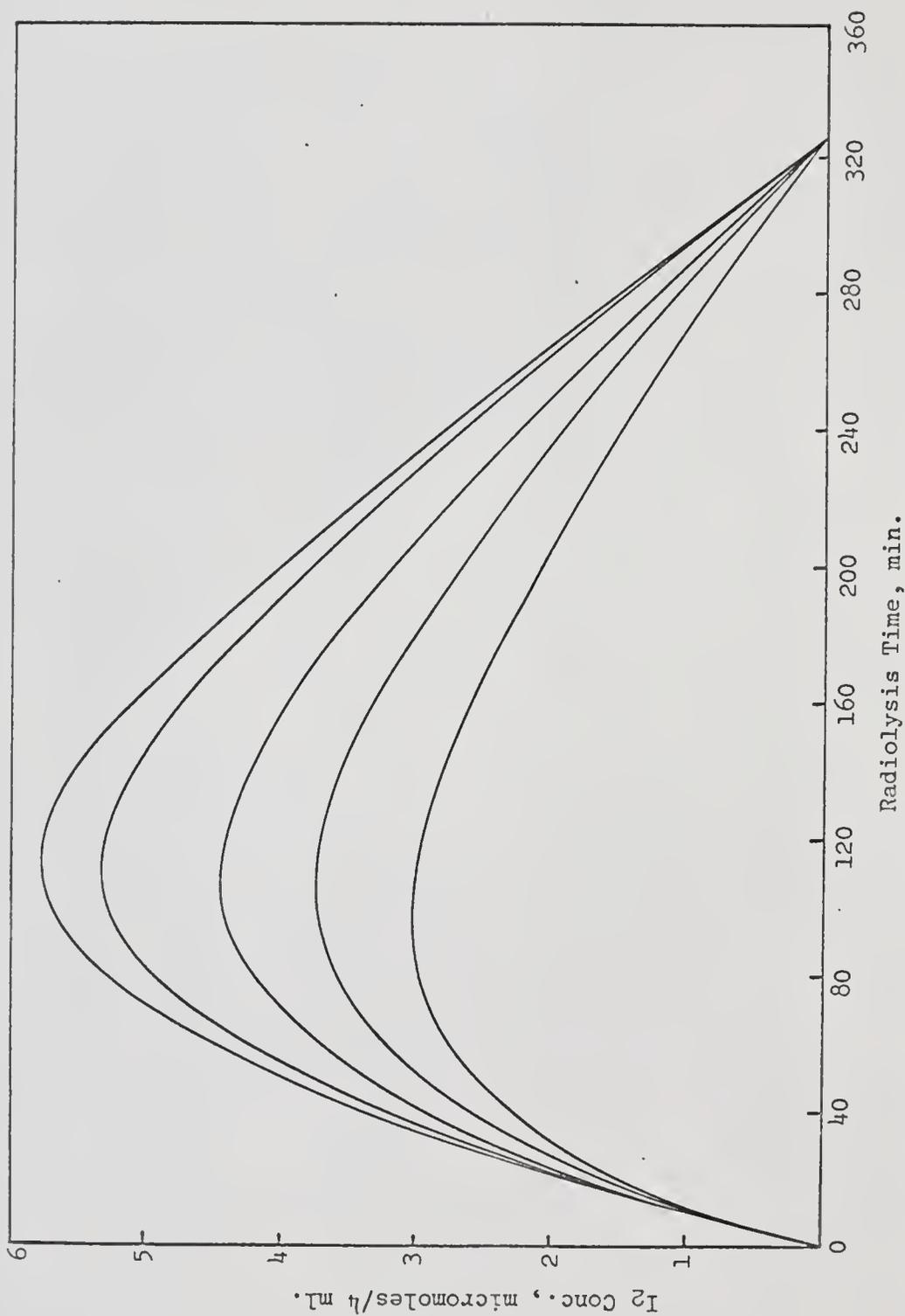


Figure 26. Role of k_{HI}/k_{I_2} as an adjustable parameter: I_2 production in the radiolysis of cyclohexane-methyl iodide solution, for 99.9 volume percent cyclohexane with added HI (3.4×10^{-3} M), as a function of radiation time. Values of k_{HI}/k_{I_2} , reading downwards, are 2.0, 1.5, 0.9, 0.6 and 0.4.

poor fit for 95 percent solution. It was found that the difficulty was due to the parameter C for HI production. Results of calculations using C as an adjustable parameter are shown in Figures 27 and 28. It can be seen that the results for experiments with added I_2 are very sensitive to this parameter. The value predicted from equations 35 and 40 is 0.033 micromoles/min; the best fit of experimental data was obtained when C was adjusted to 0.029. Since the calculation of C from equations 35 and 40 is somewhat indirect and requires several mathematical manipulations of the experimental data, the difference between 0.029 and 0.033 is within experimental error. Hence, the scheme can be considered to fit directly to all solutions through 95 percent cyclohexane.

However, determination of the various parameters for solutions with more than 95 percent cyclohexane involves some difficulties. For these solutions, the normal rate of iodine production is zero. This indicates that the yield of radicals exceeds that of iodine, but does not tell by how much. For the 0 to 95 percent concentration range, four parameters A, B, C, and k_{HI}/k_{I_2} are needed and three experimental data, Maximum, Minimum, and Normal Rates of iodine production are available. Hence, only one parameter needs to be adjusted arbitrarily. Above 95 percent cyclohexane, only two useful pieces of data, Maximum and Minimum Rates of iodine production, are available and only two of the four parameters, A and B are fixed. Hence, C as well as k_{HI}/k_{I_2} must be used as adjustable parameters. However, the situation is somewhat simplified because k_{HI}/k_{I_2} was found to have the same value of 0.71 for 90 to 95 percent solutions and for pure cyclohexane, and it can

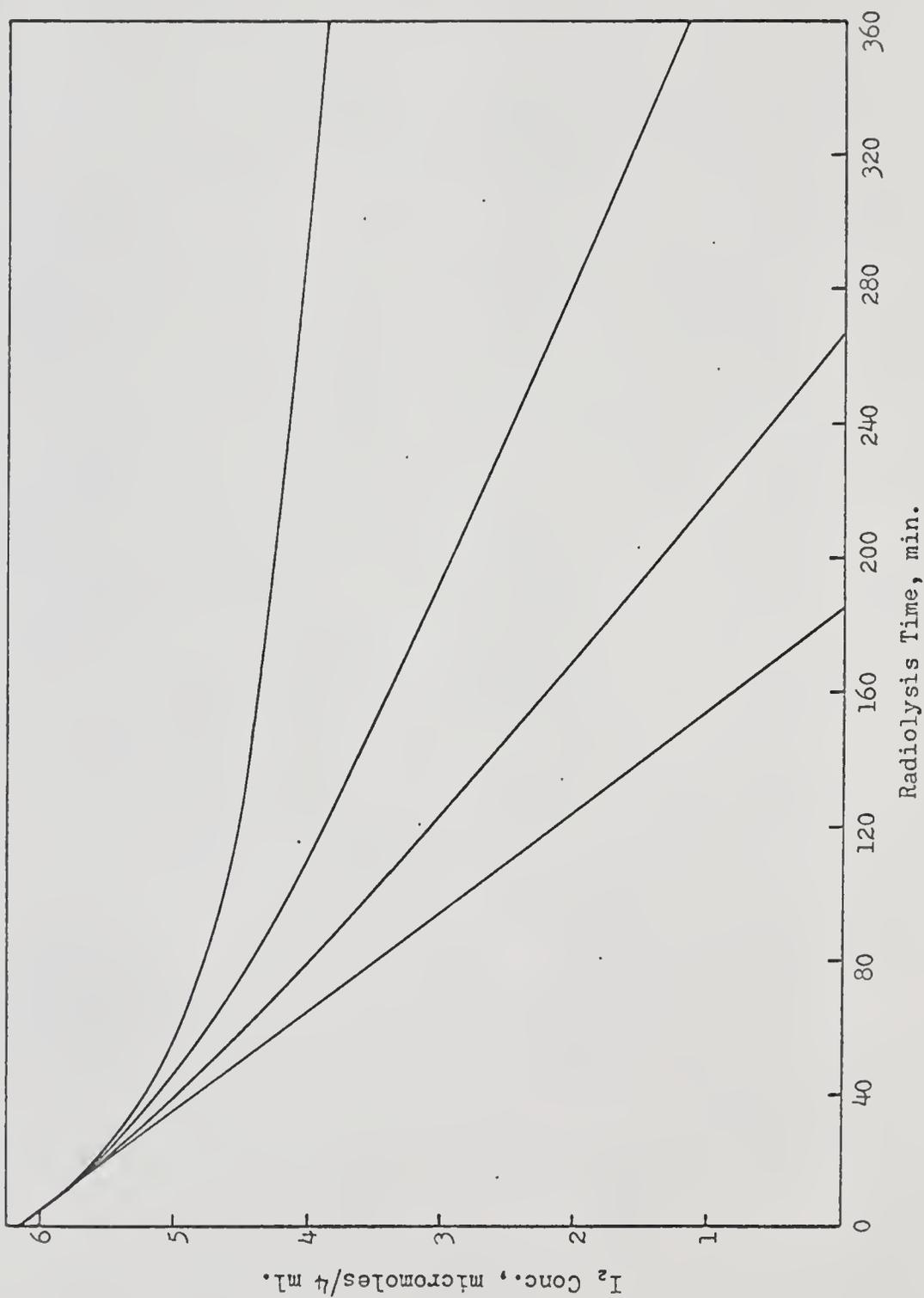


Figure 27. Role of HI production from spurs as an adjustable parameter: I₂ production in the radiolysis of cyclohexane-methyl iodide solution, for 95 volume percent cyclohexane with added I₂ (1.5×10^{-3} M), as a function of radiation time. G(HI) values, reading downwards, are 0.85, 0.57, 0.28 and 0.0.

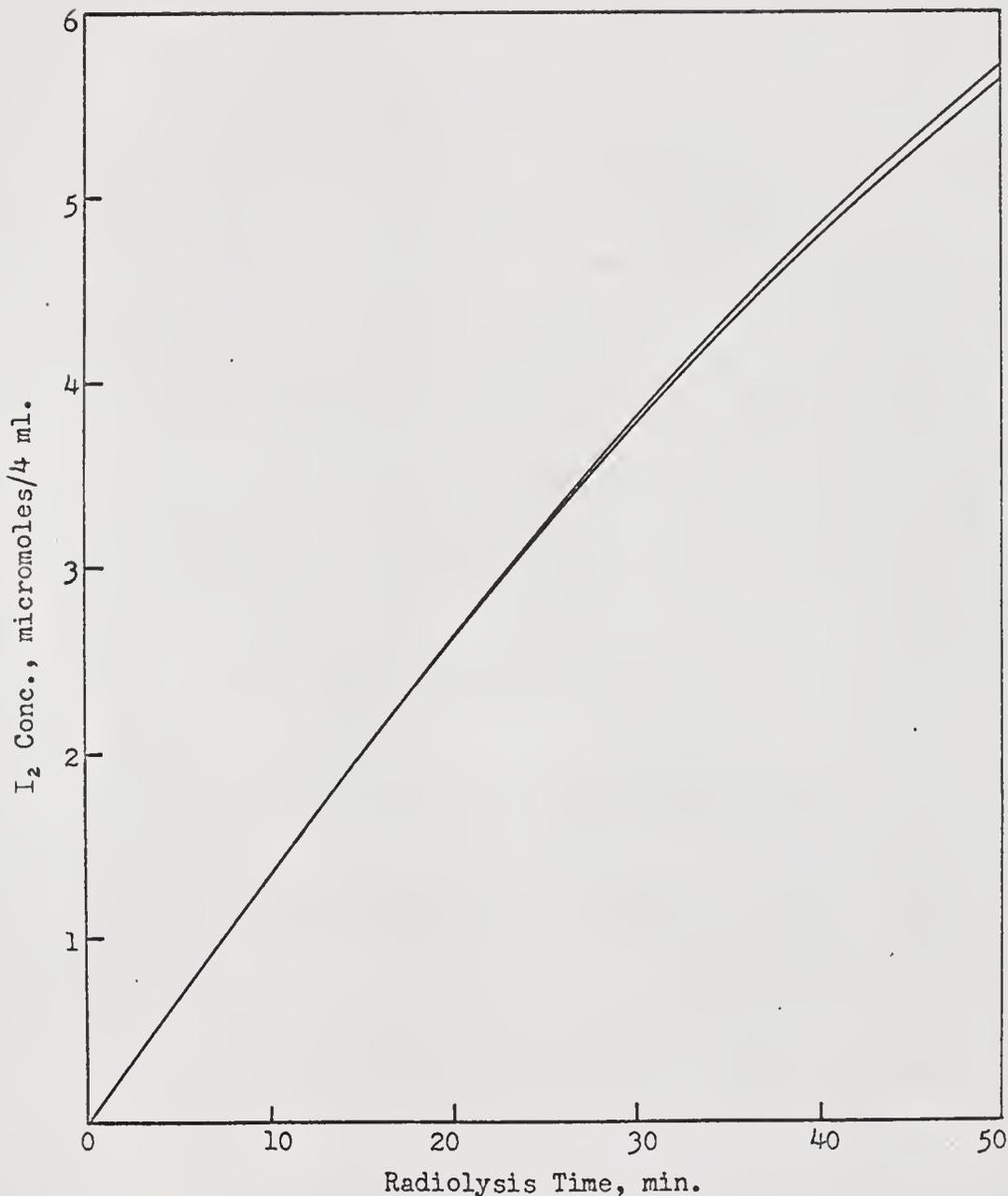


Figure 28. Role of HI production from spurs as an adjustable parameter: I₂ production in the radiolysis of cyclohexane-methyl iodide solution, for 95 volume percent cyclohexane with added HI (6.1×10^{-3} M), as a function of radiation time. G(HI) values, reading downwards, are 0.85 and 0.0.

reasonably be assumed to have the same value between 95 and 100 percent cyclohexane solutions.

Another complication develops in solutions approaching pure cyclohexane, exemplified by the 99.9 percent case. For such solutions, it can no longer be assumed that the effective yield of thermal H atoms is zero. For these solutions, B is determined from equation 32 and $k_{\text{HI}}/k_{\text{I}_2}$ can be taken as 0.71. The sum of A and D is determined from equation 33, and C is undetermined. Hence, it is necessary to vary two quantities, C and D, to fit the equations to experimental data. After several computer calculations, it has been concluded that the sum of C and D was rather well defined as 0.041 ± 0.003 micromoles/min. Considerably more variation is possible in the individual values. An adequate fit of the experimental data could be obtained with values of D in the range of 0.012 to 0.024 with C adjusted to maintain the sum of C and D as constant. The effects of varying D for experiments with added I_2 and HI are shown in Figures 29 and 30 respectively. Similar effects of varying C are shown in Figures 31 and 32. The combination $C = 0.023$ and $D = 0.020$ was used to calculate the curves for 99.9 percent solution in Figures 6 to 8. This set of values, with a rather high H atom yield and low HI yield, gave a better fit at longer radiolysis times than the reverse combination. However, this is probably somewhat fortuitous. A lower H atom yield ($G \cong 0.5$) and higher HI yield ($G \cong 0.9$) is more consistent with other work and the trends in the present data. The major difficulty for the 99.9 percent solution is probably due to the depletion of CH_3I during radiolysis; its initial concentration is only about 1.6×10^{-2} M. Complete consumption of HI (and I_2) as shown in Figure 8 required five hours of radiolysis at an

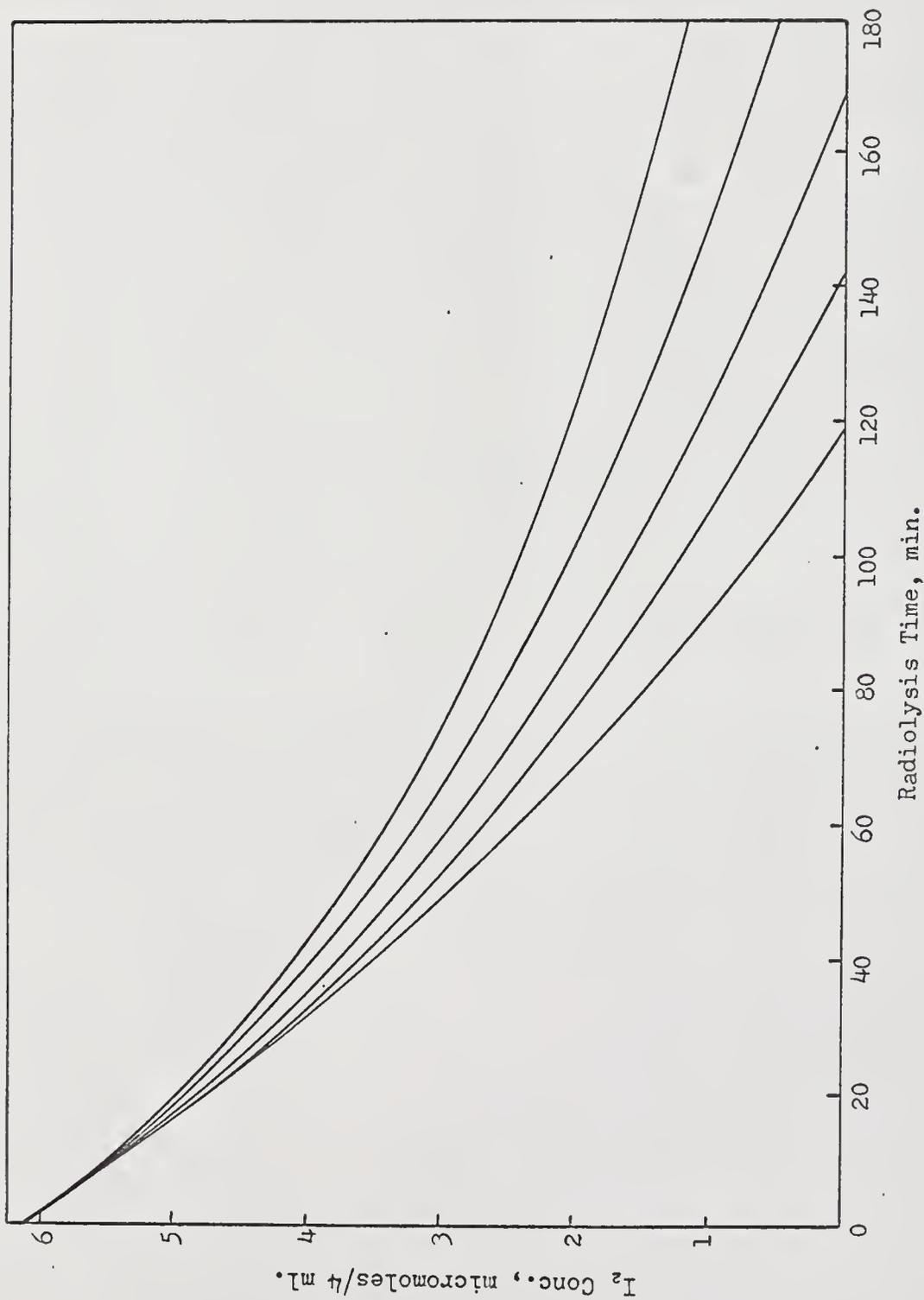


Figure 29. Role of H atom yield as an adjustable parameter: I₂ consumption in the radiolysis of cyclohexane-methyl iodide solution, for 99.9 volume percent cyclohexane with added I₂ (1.51×10^{-3} M), as a function of radiation time. G(H•) values, reading downwards, are 1.40, 1.05, 0.70, 0.35 and 0.0.

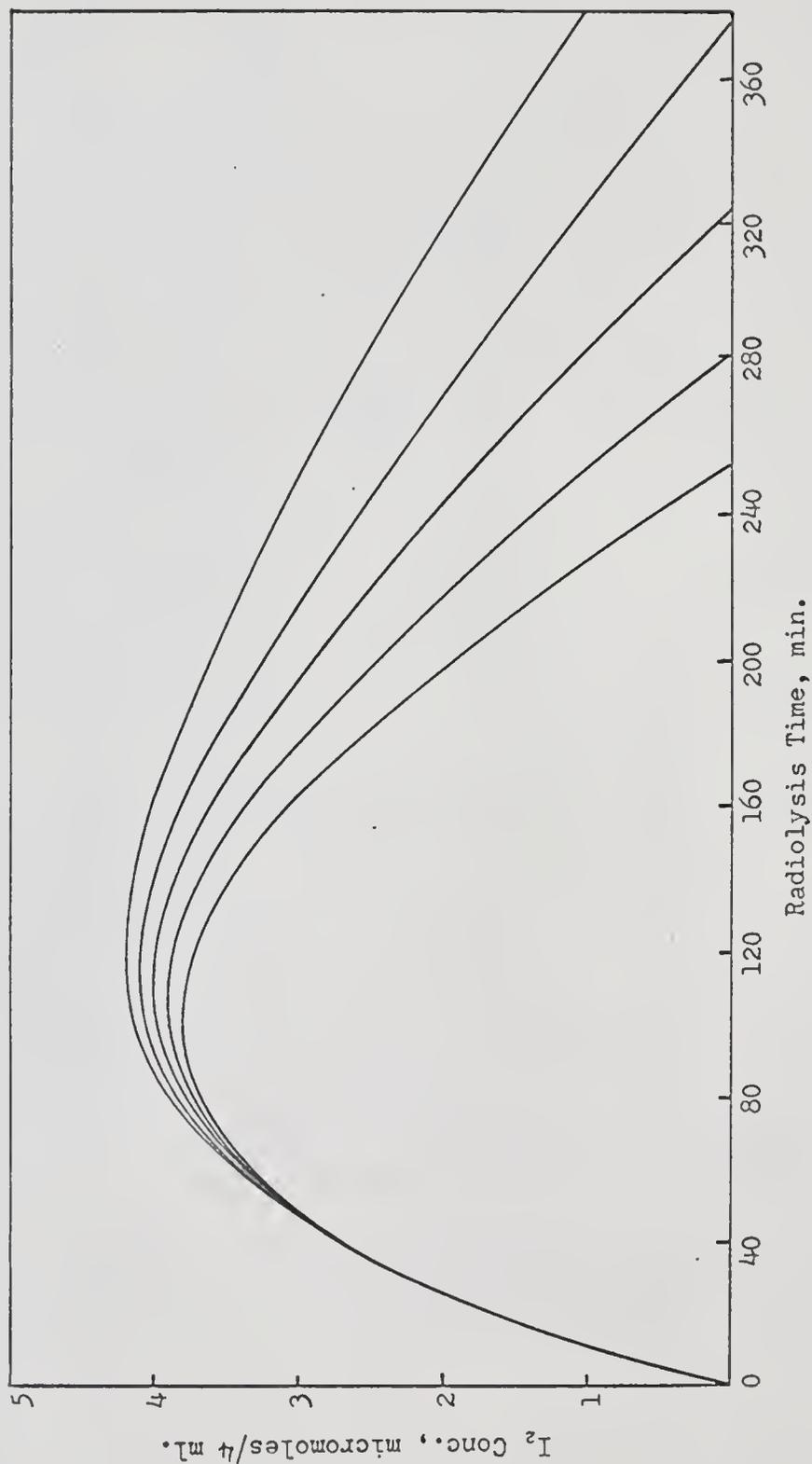


Figure 30. Role of H atom yield as an adjustable parameter: I_2 production in the radiolysis of cyclohexane-methyl iodide solution, for 99.9 volume percent cyclohexane with added HI (3.4×10^{-3} M), as a function of radiation time. $G(H\cdot)$ values, reading downwards, are 1.40, 1.05, 0.70, 0.35 and 0.0.

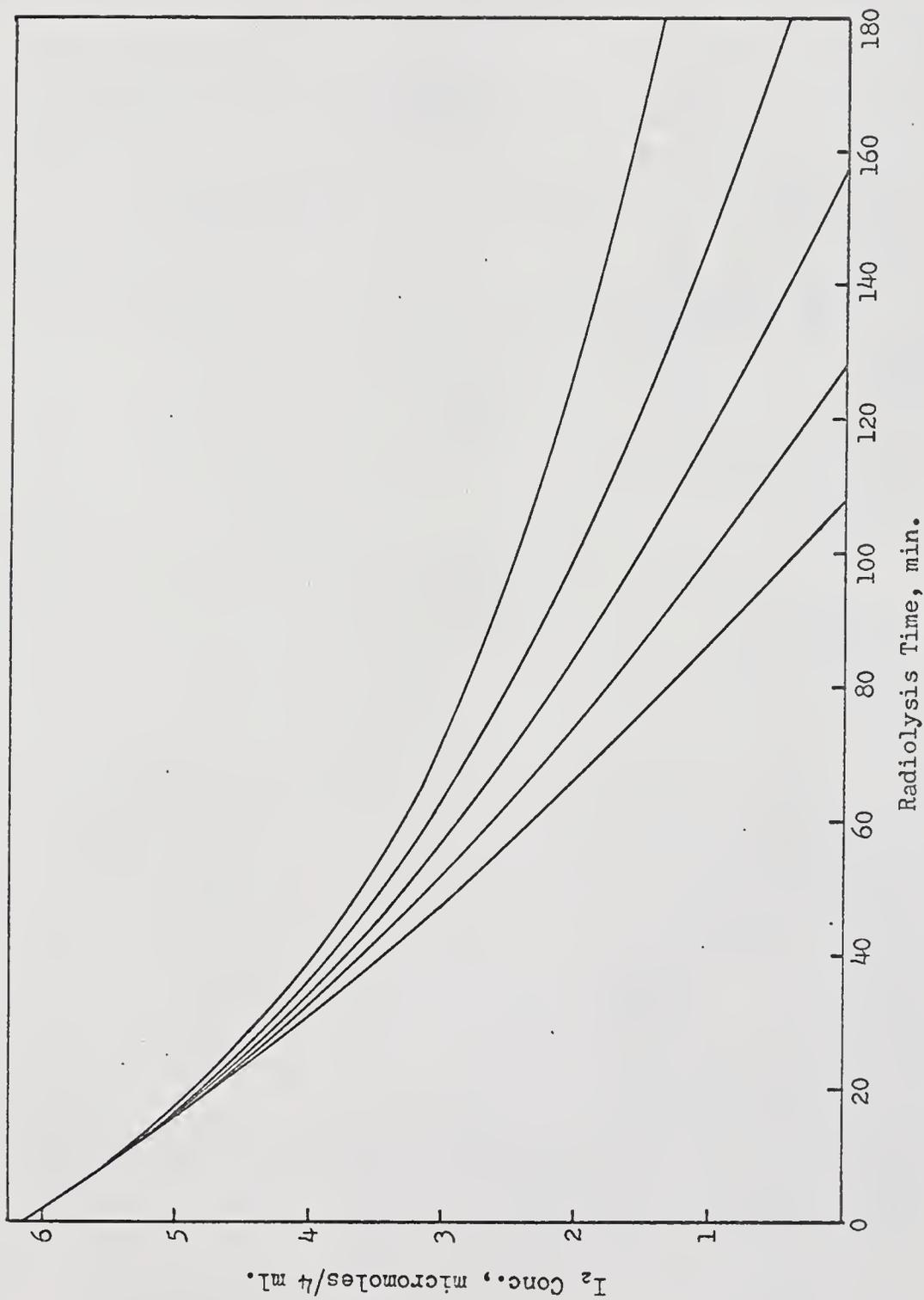


Figure 31. Role of HI production from spurs as an adjustable parameter: I_2 consumption in the radiolysis of cyclohexane-methyl iodide solution, for 99.9 volume percent cyclohexane with added I_2 (1.5×10^{-3} M), as a function of radiation time. $G(HI)$ values, reading downwards, are 1.40, 1.05, 0.70, 0.35 and 0.0.

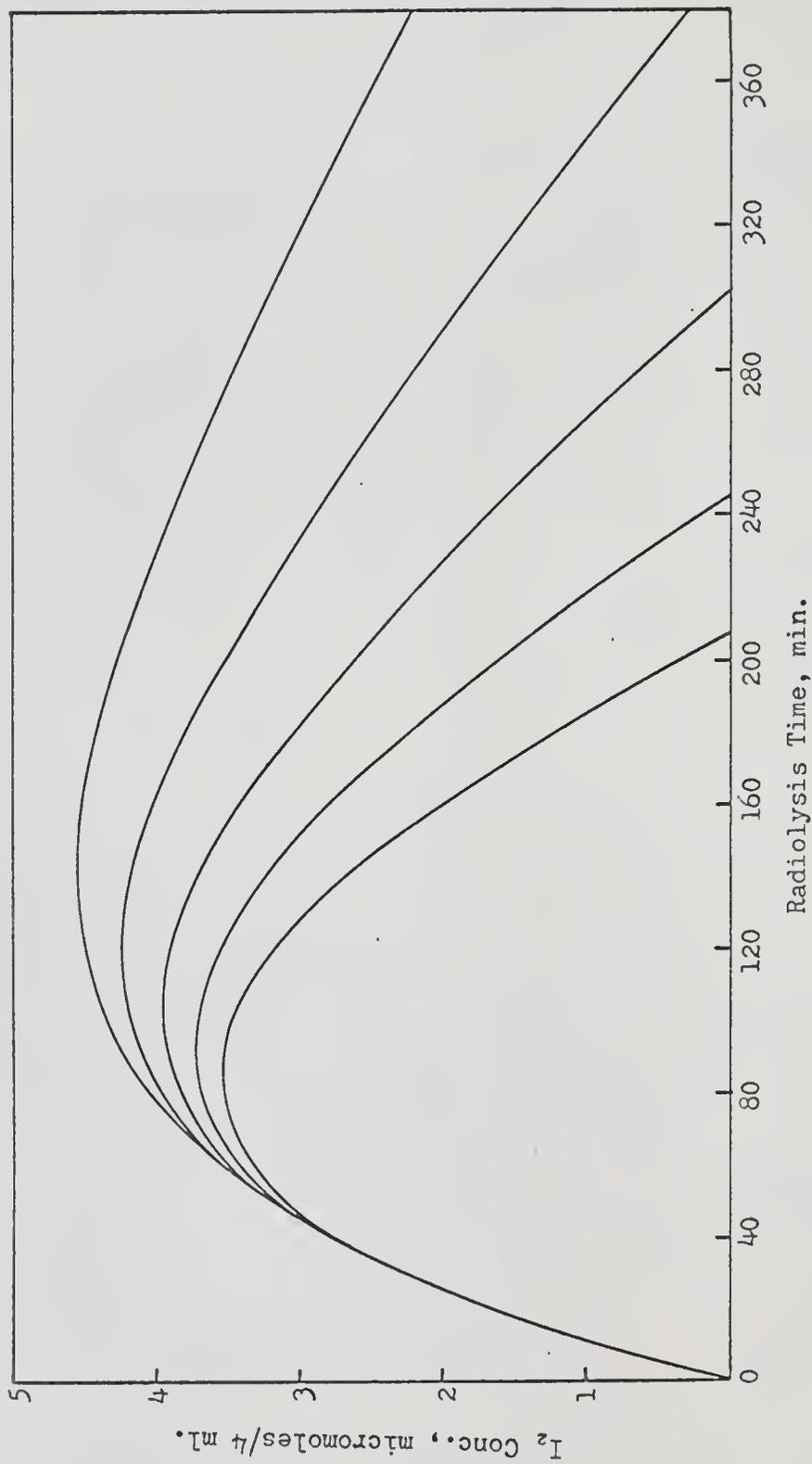


Figure 32. Role of HI production from spurs as an adjustable parameter: I_2 production in the radiolysis of cyclohexane-methyl iodide solution, for 99.9 volume percent cyclohexane with added HI (3.4×10^{-3} M), as a function of radiation time. $G(HI)$ values, reading downwards, are 1.40, 1.05, 0.70, 0.35 and 0.0.

absorbed dose rate of about 0.5 megarad/hr, which would consume 25 percent of the methyl iodide present if $G(-CH_3I) \cong 2$.

Comparison with Experiments

Pure cyclohexane

Since varying the H atom yield affects the end point but the ratio k_{HI}/k_{I_2} does not, it is fairly easy to adjust both of these quantities to give the best fit of the experimental data. The results of such calculations are shown by smooth curves in Figures 2 and 3; the circles represent experimental data. Since the radiolysis temperature ($25 \pm 2^\circ\text{C}$) was constant for all experiments and the solvent was essentially pure cyclohexane, the ratio k_{HI}/k_{I_2} should be the same in all cases.

Because of the competition between solvent cyclohexane and added scavenger for H atoms, the D factor is expected to be dependent on initial scavenger concentration. Since the scavenger concentration during each experiment decreases as the experiment progresses, it is possible to account for scavenging of hydrogen atoms only semi-quantitatively. However, the alkyl iodides produced during radiolysis are also good hydrogen atom scavengers, so the change in total scavenger concentration is never more than a factor of two.^{37,39} The effective hydrogen atom yields used in the calculations for Figures 2 and 3 are listed in Table 3. It will be noted that a greater concentration of HI than that of I_2 is required to achieve a given value of $G(H\cdot)$, implying that I_2 is a somewhat better hydrogen atom scavenger than HI.

TABLE 3

G(H·) AS A FUNCTION OF SCAVENGER CONCENTRATION

Initial I ₂ concentration	Thermal H atom yield, G(H·)	Initial HI concentration	Thermal H atom yield, G(H·)
0.31 x 10 ⁻³ M	0.70	2.11 x 10 ⁻³ M	1.40
0.61 x 10 ⁻³ M	0.80	3.18 x 10 ⁻³ M	1.46
1.16 x 10 ⁻³ M	1.40	4.10 x 10 ⁻³ M	1.57
1.71 x 10 ⁻³ M	1.43	8.88 x 10 ⁻³ M	1.74

As a further test of the proposed kinetic scheme, a series of experiments, with both HI and I₂ added initially, have been performed. Iodine concentration in all the cases was 1.53×10^{-3} M but HI concentration varied from 1.08×10^{-3} to 3.43×10^{-3} M. The experimental results and the corresponding theoretical curves are shown in Figure 4. As in the previous cases, the value of k_{HI}/k_{I_2} was taken as 0.71 and $G(H\cdot)$ as 1.50 was used for all the calculations illustrated in Figure 4.

The present kinetic analysis can be compared with the recent work of Perner and Schuler³⁷ by considering Figures 9 to 12. Starting with essentially the same mechanism, they presented a simplified kinetic scheme for radiolysis experiments for pure hydrocarbons with added HI. They integrated the rate equations analytically, although indirectly. Their analysis allows the variation of the parameter k_{HI}/k_{I_2} but does not provide for direct allowance for reaction of H atoms with I₂ producing additional HI. However, the effect of the participation of H atoms is clearly evident in their results as shown by deviations in experimental data compared with predictions of their kinetic scheme. Their analysis would give a curve identical to that for $D = 0$ in Figure 10. The error in ignoring the H atom effect is rather large for concentrations as great as 2×10^{-3} M (Figure 10). Perner and Schuler worked mainly at much lower HI concentrations which minimized such deviations. They did not treat the experiments with added I₂. For such experiments, the approximation that $G(H\cdot) = 0$ gives merely a straight line (Figures 9 and 11). Their analysis of the effect of varying k_{HI}/k_{I_2} is qualitatively similar to that given here. However, their resulting graphs differ slightly because of the allowance for the participation of H atoms in the present work.

Cyclohexane-methyl iodide solutions

Input data for a computation on a given cyclohexane-methyl iodide solution are Maximum, Minimum, and Normal Rates of iodine production. An initial concentration of I_2 or HI is given to the computer, matching an actual experiment. The ratio k_{HI}/k_{I_2} is used as an adjustable parameter. The results of such calculations are shown by smooth curves in Figures 6 to 8; circles represent experimental data. It can be seen that the theoretical curves fit the experimental points quite satisfactorily. From these curve fittings, different k_{HI}/k_{I_2} values have been obtained for the various solutions. These values are listed in Table 4. Initial I_2 concentrations in the solutions were 1.4×10^{-3} to 1.7×10^{-3} M and the initial HI concentration was 6.1×10^{-3} M in the experiments shown in Figure 7.

A difficulty which was encountered in fitting theoretical curves to iodine production and consumption data requires comment. Some of the iodine concentration vs dose graphs for radiolysis of HI or I_2 in cyclohexane-methyl iodide solutions cover several hours of radiolysis. As mentioned above, Croft and Hanrahan²⁰ reported that the rates of iodine production in cyclohexane-methyl iodide solutions without additives were nearly linear at low doses. For the longer radiolysis times used in the present work, changes in the Normal Rates, as shown in Figure 5, become significant. The decrease in $G(I_2)$ from its initial value to the value obtained after several hours of radiolysis was of the order of 0.15 to 0.25 molecules/100 ev (Table 2). This is a relatively small effect considering that total G values of I_2 production in spurs were in the range of 1.5 to 3.5 (Table 4). This fall-off cannot be due to

TABLE 4

CALCULATED $G(R\cdot)$, $G(I_2)$, $G(HI)$, AND RATE CONSTANT RATIOS

(1) Cyclohexane percent by volume	(2) G for thermal free radical production ^a	(3) G for I_2 production ^b in spurs	(4) G for HI production in spurs ^c	(5) $\frac{k_{HI}}{k_{I_2}}$ ^d
0	5.31	3.855	0.27	-
20	5.34	3.510	0.31	.98
40	5.69	3.405	0.37	.94
60	6.09	3.135	0.55	.90
80	5.52	2.48	0.59	.55
90	5.01	1.87	0.69	.71
95	5.03	1.57	0.94 ^e	.71
99.9	6.07	0.41	0.81	.71
100	6.04	-	-	.71

^a(Max. Rate - Min. Rate).^b(Max. Rate + Min. Rate)/2.^cCalculated from equation 40.^dValues obtained by adjusting k_{HI}/k_{I_2} as a parameter for curve fitting.^eThis value is predicted by equation 40. As explained in the text, a slightly lower value gives the best fit of theoretical curves to experimental data, but the difference is within experimental error.

HI-I₂ competition kinetics as described above. Equations 21 and 25 unambiguously predict constant rates of formation of I₂ and HI for the radiolysis with no additives, provided only that the yields of primary processes (A, B, C, and D) are constant. It is probable that HI and I₂ are actually formed at constant rates but react with olefin produced during extended periods of radiolysis.

Although the fall-off in Normal Rates was not considered decisive in interpreting the role of HI-I₂ competition kinetics in cyclohexane-methyl iodide solutions, it did pose problems in several respects. If the true initial values of the Normal Rates of Iodine production are used in equations 21 and 25, then the equations will predict rates for solutions with added HI and I₂ which will approach these values at large doses. In the actual radiolyzed solutions, however, lower rates are found at large doses, as in the case of radiolysis with no additives. As a result, the predicted yields from the integrated equations could not match the experimental results. It was possible to avoid this difficulty by utilizing the large-dose values of the Normal Rates in the equations, rather than the initial values.

Although use of the long-term Normal Rates permitted more satisfactory fitting of curves to experimental data, it could be contended that the initial values are more significant in establishing true yields of primary processes. After careful consideration, it was decided, nevertheless, that the long-term values of the rates should be used in preparing Tables 4 and 5 to avoid inconsistencies with other parts of this dissertation. It can easily be verified that the G values for the thermal-free radical yields and for the yields of I₂ from spurs are not affected (see equations 32 and 39). However, the

TABLE 5

CYCLOHEXANE-METHYL IODIDE SOLUTIONS: COMPARISON BETWEEN OBSERVED AND CALCULATED YIELDS

(1) Cyclohexane volume %	(2) $G(I\cdot)$ Normal ^a	(3) HI reacting with free ^b radicals	(4) Net HI produced ^c	(5) Total scavenger ^d equivalents	(6) $G(R\cdot)$ ^e	(7) G for excess scav. equiv. ^f over $G(R\cdot)$
0	2.82	0.21	0.06	8.25	5.31	2.94
20	2.46(2.22)	0.27	0.04	7.64	5.34	2.30
40	2.20(1.70)	0.29	0.08	7.55	5.69	1.86
60	1.58(1.20)	0.51	0.04	7.37	6.09	1.28
80	0.90(.50)	0.53	0.06	6.14	5.52	0.62
90	0.36(.11)	0.69	0	5.12	5.01	0.11
95	0.10(.01)	0.94	0	4.78	5.03	(-0.25)
99.9	0			2.44	6.07	(-3.63)
100	0				6.04	

^aFor solutions with no I_2 or HI added prior to irradiation.^b $G(I_2)$ for the radiolysis without additives minus $G(I_2)$ with added I_2 .^c(Col. 4, Table 4 - Col. 3, Table 5).^d(2 x Col. 3, Table 4 + 2 x Col. 4, Table 4).^eG for thermal-free radical production in spurs.^f(Col. 5 - Col. 6).

yields of HI from spurs as given in Tables 4 and 5 are under-estimated by 0.1 to 0.25 molecules/100 ev for solutions with 20 to 90 volume percent cyclohexane, and the total yields of scavenger equivalents are under-estimated by about 0.2 to 0.5 molecules/100 ev.

Concentration Dependence of Primary Yields
in Cyclohexane-Methyl Iodide Solutions

For the entire range of solutions of cyclohexane-methyl iodide, the present calculations provided data for the yield of thermal alkyl radicals, I_2 , and HI from spurs. These data are listed in Table 4. As the cyclohexane concentration is increased, $G(I_2)$ decreases and $G(HI)$ increases fairly smoothly. However, $G(R\cdot)$ does not show a clear trend as a function of composition of mixtures; it is approximately constant at 5.5 ± 0.5 . The fluctuations which are observed are probably due to the fact that this is a composite quantity which includes the yields of both cyclohexyl and methyl radicals. The net yields of each of them and their sum are determined by numerous reactions, some competitive and others additive, resulting in an approximately constant combined yield.

It can be seen that the net, observed yield of iodine (col. 2, Table 5) is much less than that produced from spurs (col. 3, Table 4). The difference, of course, is due to reactions of cyclohexyl and methyl radicals with I_2 . There is also a thermal process producing I_2 , namely the reaction of radicals with HI, but this is a relatively small effect. The same situation occurs in the radiolysis of pure alkyl iodides; it has been shown previously^{21,36} that in such systems the observed I_2 yield is the sum of the excess of iodine production over alkyl radical

production in spurs plus the contribution due to the reaction of thermal-free radicals with HI.

A discussion of trends in primary yields in the radiolysis of cyclohexane-methyl iodide solutions was presented several years ago by Croft and Hanrahan.²⁰ Their remarks were of necessity hypothetical, since detailed yield data were not available at that time. They investigated the postulate that the various intermediates, reacting in a simple free radical scheme similar to that used here, might be formed in yields determined directly by the electron percent of the parent compound in the mixture. A graph was presented showing the concentration dependence of total radical yields and total iodine yields predicted by such a model. The graph predicts that net iodine production should fall to zero for solutions richer in cyclohexane than about 30 electron percent. Since their experimental results showed that net iodine production persists until methyl iodide is diluted with about 93 electron percent cyclohexane, they concluded that there was evidence of substantial sensitized decomposition of the methyl iodide. This conclusion has been confirmed during the course of the present work. Taking into account the role of HI, G values for total scavenger equivalents for the entire range of solutions have been calculated and are plotted as a function of electron percent cyclohexane; see Figure 33. It will be noted that the yields of HI and I_2 from methyl iodide in the mixture are markedly greater than would be predicted by an "ideal solution" law. There is only a small gradual diminution in the total scavenger yields up to about 80 electron percent solutions; the yields fall sharply in solutions richer in cyclohexane than 80 electron percent.

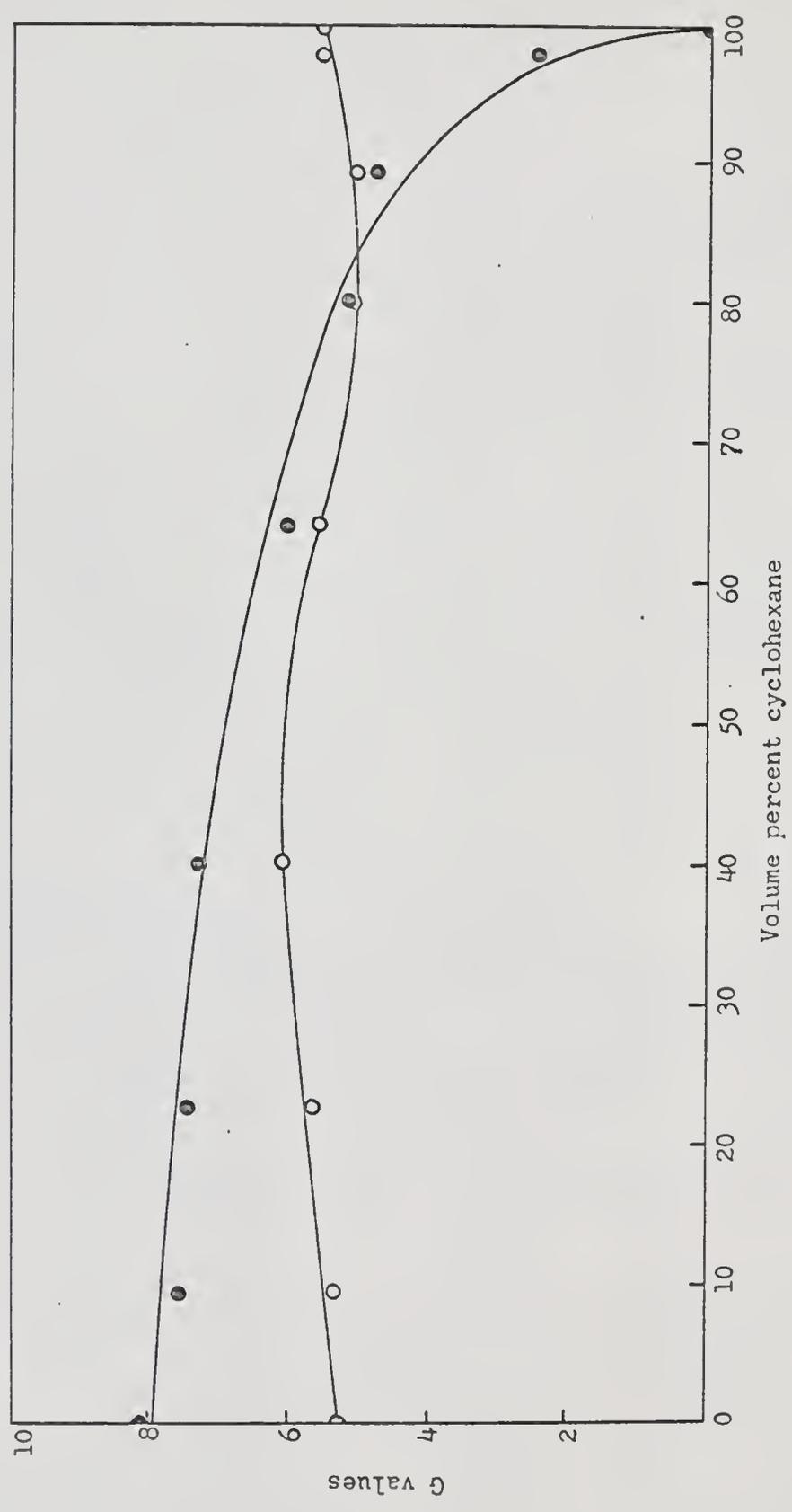


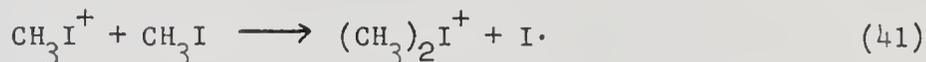
Figure 33. G values as a function of composition for cyclohexane-methyl iodide solutions: ● total scavenger yield in equivalents; ○ thermal free radical production.

Although the figure indicates that there should be no net iodine production for solutions with more than 85 electron percent cyclohexane, difference between this value and the experimentally observed value is probably due to small errors in determining the various parameters.

In considering the relationship of the various HI rates given in Tables 4 and 5, it should be recalled that the HI which is produced from spurs has two possible fates. Most of it reacts with alkyl radicals giving a complementary yield of iodine atoms. Therefore, the rate at which HI plays the role of a scavenger for $R\cdot$ is given by (Norm. Rate - Min. Rate), where Norm. and Min. Rates are the rates of iodine production without additives and with I_2 added respectively. These values are listed in column 3, Table 5. The remaining HI appears as net HI accumulating in the solutions; see column 4, Table 5. The sum of these figures is the total rate of HI production, given in column 4, Table 4.

Since, on reaction with alkyl radicals, HI furnishes a hydrogen atom to the radical and releases an iodine atom, the activity of HI is equal to two scavenger equivalents. Hence, the total scavenger activity in equivalents is the $I\cdot$ produced from spurs plus twice the HI that reacts with alkyl radicals. Column 5 shows the total scavenger activity in equivalents. Column 7 shows the scavenger equivalents which are in excess of the free radicals produced, and is obtained by subtracting column 6 from column 5. The figures given are just the sum of the I_2 yield, which is measurable, and the HI yield, which is inferred. The negative values for total scavenger yields for 95 and 99.9 volume percent cyclohexane solutions simply indicate that there is no net HI or I_2 present in the irradiated solutions over this concentration range.

It has been proposed by Gillis, Williams and Hamill²¹ that the production of iodine in the radiolysis of pure CH_3I is due to the ion-molecule mechanism



The product ion, upon neutralization, gives a net yield of C_2H_6 and I_2 . Croft and Hanrahan suggested that the efficient production of iodine in dilute solutions in cyclohexane is due to the same mechanism and that it is able to occur with considerable efficiency because of charge transfer from cyclohexane:



The present calculations confirm these observations. The postulate that charge exchange process 42 occurs appears necessary to account for net iodine production in solutions in which methyl iodide is the minor constituent. However, the possibility that electron capture also occurs, as suggested by Forrestal and Hamill,¹⁰ cannot be excluded. It is likely that electron capture and charge exchange both take place in solutions with more than 90 electron percent cyclohexane.

Conclusion

The kinetic analysis given here accounts for competitive reactions of radicals with I_2 and HI in the radiolysis of pure cyclohexane and cyclohexane-methyl iodide solutions over the whole concentration range. A simplified model, involving an internally consistent free radical mechanism, has been provided. The experimental quantities are the initial rates of iodine production under three conditions:

with added I_2 , with added HI, and with no additives. The rate constant ratio k_{HI}/k_{I_2} has been used as an adjustable parameter in all cases. For very dilute solutions of methyl iodide in cyclohexane, H atom yields and HI production in spurs are also treated as adjustable parameters.

This scheme successfully approximates the complete shape of the experimental curves by utilizing the three experimental rates, namely Normal Rate with no additives, Minimum Rate with added I_2 , and Maximum Rate with added HI. However, the necessity of using large-dose Normal Rates has already been discussed. Analysis of experimental data according to this scheme provides values for the rates of production of thermal radicals, I_2 and HI from spurs. Trends in these yields corroborate the conclusion that there is extensive energy or charge transfer from cyclohexane to methyl iodide in the mixtures studied. This conclusion had been inferred earlier from data on iodine production alone.²⁰

The deviations of the theoretical curves from the experimental points are most pronounced towards the end of the experiments in all cases. This is perhaps expected, since there are a number of further complicating reactions intentionally ignored in the simplified scheme given. These include reactions of H atoms with alkyl iodide products in the case of pure cyclohexane, and reactions of HI, I_2 , and possibly radicals with unsaturated radiolysis products in both pure cyclohexane and the mixtures. It is possible that corrections for some further reactions such as these could be incorporated in the kinetic scheme and subsequent computer analysis. However, the scheme as given is already rather complicated, and these further refinements would tend

to obscure its value as an aid in visualizing the kinetic behavior of the system.

The type of kinetic scheme given here for HI-I₂ competition kinetics during radiolysis was first suggested several years ago for pure alkyl iodides.^{21,36} The present work shows that this approach is useful also in pure cyclohexane with HI or I₂ added as a scavenger, as well as for the intermediate situation in which cyclohexane-methyl iodide solutions are irradiated. During the course of the present work, a parallel interpretation of the kinetics in pure hydrocarbons, using an indirect analytical integration, was developed by Perner and Schuler of the Mellon Institute. It has been scheduled for publication simultaneously with the portion of the present work dealing with pure cyclohexane.^{37,43}

The present kinetic analysis obviously can be extended to the radiolysis of other hydrocarbon-alkyl iodide solutions. The original scheme was successfully applied to the photolysis of alkyl iodides by Luebbe and Willard,⁴⁴ and it would be of interest to investigate extension of the present analysis to the photolysis of hydrocarbon-alkyl iodide mixtures.

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APPENDIX

RADIOLYSIS KINETICS OF HYDROCARBON AND ALKYL IODIDE SOLUTION

C MAIN PROGRAM

```

15 READ INPUT TAPE 5,1,DT,XLAST,TIME,BII,AHI
  1 FORMAT(F4.2,5X,F6.2,4X,F4.2,4X,F10.5,5X,F10.5)
    READ INPUT TAPE 5,2,AMAX,AMIN,ANORM,RATIO
  2 FORMAT(F10.5,5X,F10.5,5X,F10.5,5X,F10.5)
    READ INPUT TAPE 5,3,CONC
  3 FORMAT(F4.1)
    WRITE OUTPUT TAPE 6,4,CONC
  4 FORMAT(F5.1,1X,35H PERCENT HYDROCARBON + ALKYL IODIDE)
    WRITE OUTPUT TAPE 6,5,AMAX,AMIN,ANORM,RATIO
  5 FORMAT(7H AMAX =,1X,F10.5,2X,6HAMIN =,1X,F10.5,2X,7HANORM =,1X,F10.5
    2X,7HRATIO =,1X,F10.5)
    A=AMAX-AMIN
    B=(AMAX+AMIN)*0.5
    RNORM=(ANORM-AMIN)/((AMAX-ANORM)*RATIO)
    C=(RNORM*ANORM)+(ANORM-AMIN)
    WRITE OUTPUT TAPE 6,6,A,B,C
  6 FORMAT(4H A =,1X,F10.5,5X,3HB =,1X,F10.5,5X,3HC =,1X,F10.5)
    WRITE OUTPUT TAPE 6,7
  7 FORMAT(3X,5H TIME,6X,6HIODINE,6X,15HHYDROGEN IODIDE)
30 IF(MODF(TIME,2.0))12,10,12

```

10 WRITE OUPUT TAPE 6,8,TIME,BII,AHI

8 FORMAT(2X,F6.2,3X,F10.5,5X,F10.5)

12 DELIIO=DT*P(A,B,RATIO,BII,AHI)

DELHIO=DT*Q(A,C,RATIO,BII,AHI)

DELIIT=DT*P(A,B,RATIO,BII+DELIIO/2.,,AHI+DELHIO/2.)

DELHIT=DT*Q(A,C,RATIO,BII+DELIIO/2.,,AHI+DELHIO/2.)

TIME=TIME+DT

BII=BII+DELIIT

AHI=AHI+DELHIT

IF(TIME-XLAST)30,30,20

20 GO TO 15

END

C P SUBPROGRAM

FUNCTION P(A,B,R,Y,Z)

$P=B+A/2.-A*Y/(Y+R*Z)$

RETURN

END

C Q SUBPROGRAM

FUNCTION Q(A,C,R,Y,Z)

$Q=C-A+A*Y/(Y+R*Z)$

RETURN

END

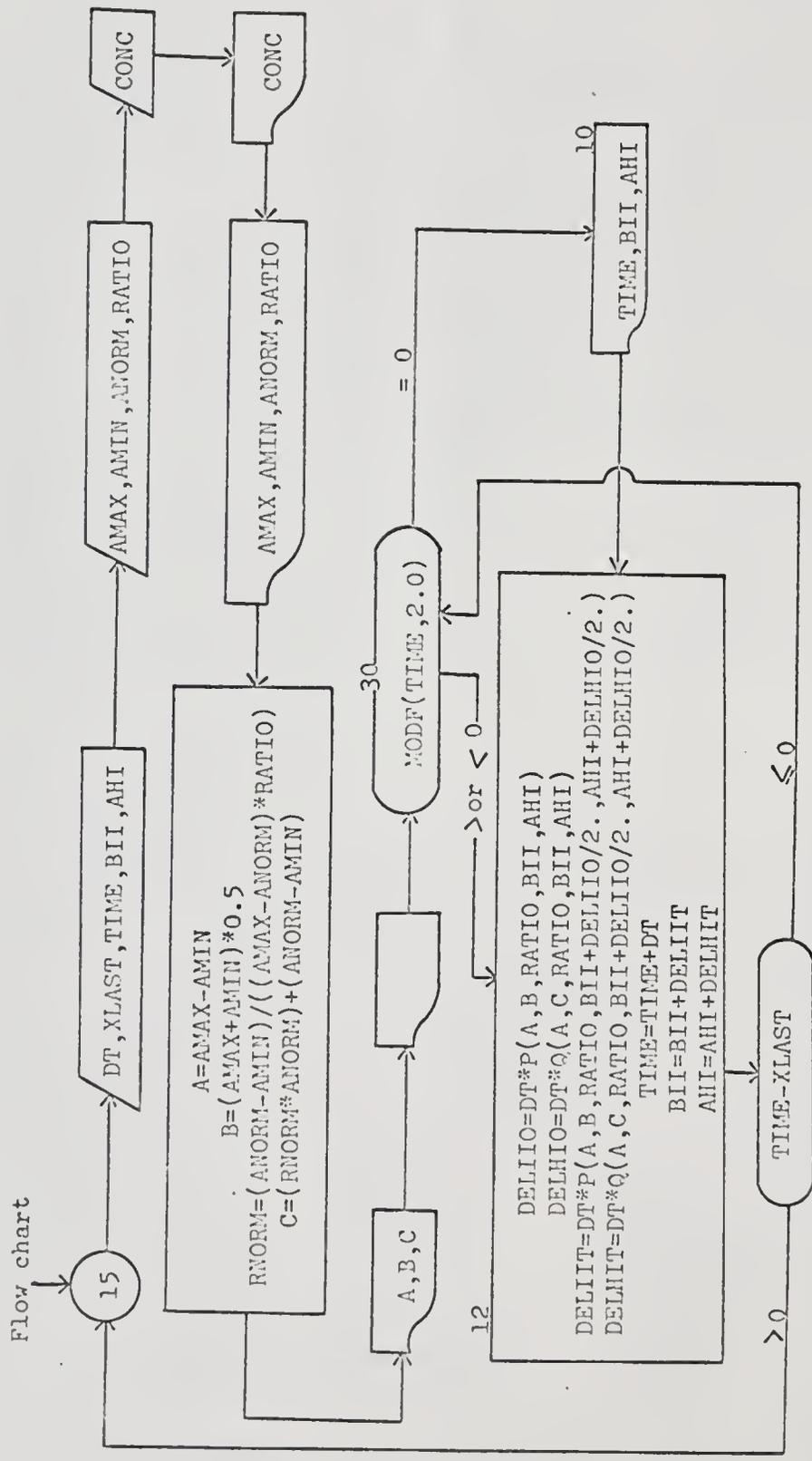


Figure 34. Flow chart for main program. ○ , Statement label; ▭ , input statement; ▭ , output statement; ▭ , substitution statement; ○ , conditional statement; → , GO TO

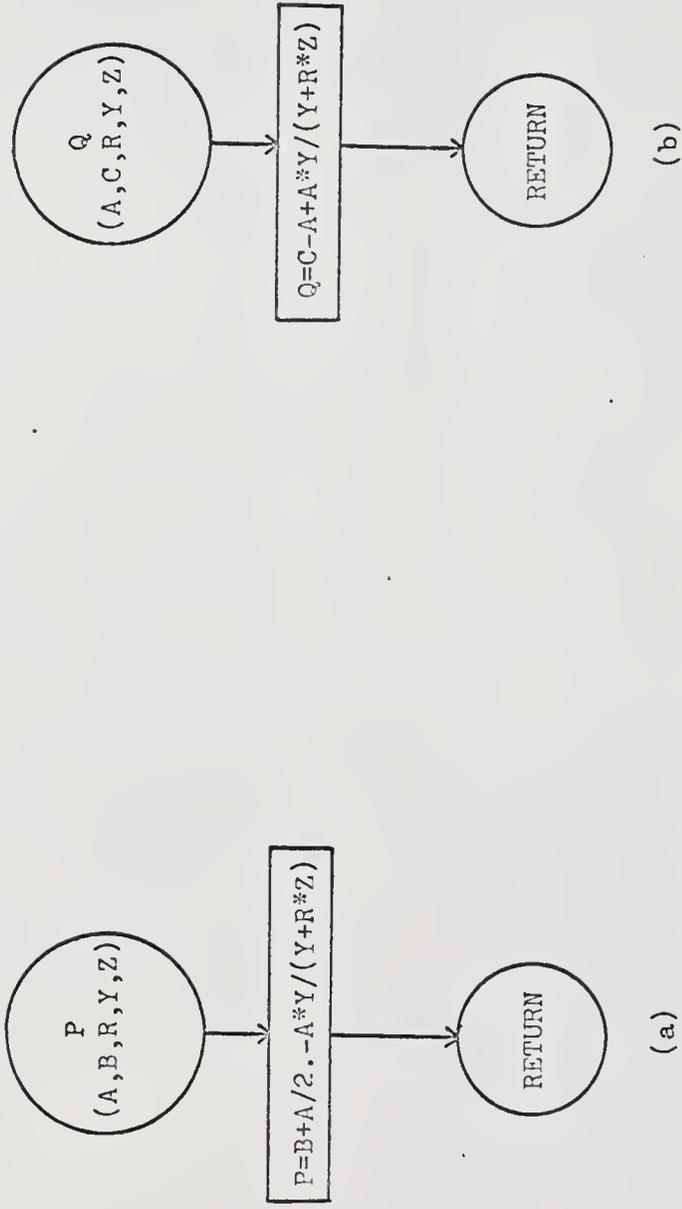


Figure 35. (a) Flow chart for function program P. (b) Flow chart for function program Q.

 , Entry to an external-function definition program;  , substitution statement;
 , exit from a function-definition program.

BIOGRAPHICAL SKETCH

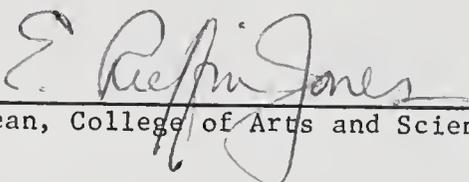
Inder Mani was born at Sardhana, district Meerut, U.P., India, on February 15, 1928. He was graduated from St. Charles' High School, Sardhana in 1941, and entered Meerut College, Meerut, U.P., affiliated to Agra University, Agra. He received his Bachelor's and Master's degrees from Agra University, Agra in 1946 and 1948, respectively.

Since 1948, he has been on the staff of Meerut College, Meerut as a lecturer in chemistry. He entered the Graduate School of the University of Florida, Gainesville, Florida, in September 1963. Since then he has served as a nuclear research assistant in the Department of Chemistry.

Inder Mani is married to Vinod Agrawal and is the father of two children, Nisha and Sanjiv.

This dissertation was prepared under the direction of the chairman of the candidate's supervisory committee and has been approved by all members of that committee. It was submitted to the Dean of the College of Arts and Sciences and to the Graduate Council, and was approved as partial fulfillment of the requirements for the degree of Doctor of Philosophy.

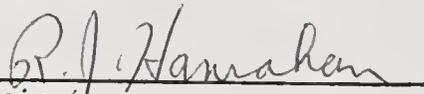
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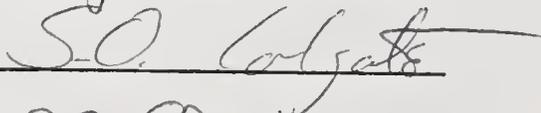
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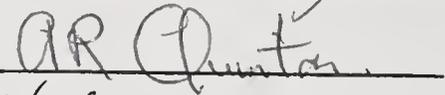
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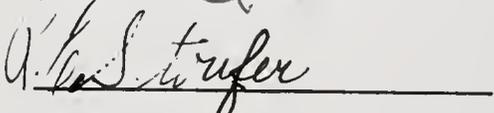
Supervisory Committee:



Chairman









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