FOREWORD

This report was prepared by Armour Research Foundation under USAF Contract No. 33(616)-7587. This contract was initiated under project no. 7360, "The Chemistry and Physics of Materials", Task No. 736003 "Interaction of High Energy Forms with Materials". The work was administered under the direction of the Physics Laboratory, Directorate of Materials and Processes, Aeronautical Systems Division, with Mr. R. E. Rondeau acting as project engineer.

This report covers work conducted from September 15, 1960 to March 14, 1962.

Major contributions to the work under this contract were made by P. Y. Feng, B. K. Krotoszynski and W. Bahmet.

ABSTRACT

This report describes a study of the role of internal energy transfer processes in radiation chemical reactions involving free radicals and other intermediate species, using a series of alkyl iodides with different carbon chain lengths as the experimental systems. It was found that, (1) with increasing size of the alkyl group in a homologous series, for example the 1-iodoalkanes, the extent of C-I bond rupture decreases regularly, whereas both the H_2 and the HI yields increase; (2) products with practically identical yields are formed in the radiolyses of two systems with similar elemental compositions, one consisting of pure $C_{16}H_{33}I$, and the other an equimolecular mixture of C_8H_{18} and $C_8H_{17}I$. Analysis of these results, together with those available in the literature, show that energy initially localized elsewhere in an alkyl iodide molecule cannot efficiently cause C-I bond breakage despite the latter's low bond strength, i.e. internal energy transfer does not play an important role in these reactions. Instead, it is concluded that the product yields are dependent on the effective electron fractions of the various groups in the irradiated system, a parameter which permits the quantitative correlation of the outcomes of the radiolytic reactions investigated in this program.

This technical documentary report has been reviewed and is approved.

Richard J. Vossler

RICHARD J. VOSSLER, Capt, USAF
Chief, Radiation Branch
Physics Laboratory
Directorate of Materials & Processes

TABLE OF CONTENTS

LIST OF FIGURES

LIST OF TABLES

I. INTRODUCTION

In spite of the tremendous advances made in the field of radiation research, the primary physical events resulting from the interaction of high energy radiation with matter are still misunderstood. Several simplifying generalizations were made which, however, provide neither a true description of these events nor an effective means of predicting the outcome of a radiation chemical system. Specifically, the details of the mechanism of energy transfer in liquid systems must still be regarded as vague, although several studies were made to elucidate these processes.

This work was undertaken to evaluate the nature and internal energy transfer processes using alkyl iodides as the model compounds. These compounds appeared suitable for this purpose since the particularly sensitive C-I bonds could serve as sensitive indicators for the energy transfer processes. In addition, existing literature information could permit the intercomparison of our results and the use of established experimental procedures.

Manuscript released by the author April 12, 1962, for publication as an ASD Technical Documentary Report.

II. TECHNICAL DETAILS

Procedures

(a) Materials

The normal 1-iodooctane and 1-iodohexadecane were Eastman White Label chemicals and the normal 1-iodododecane was Fisher technical grade chemical. The alkyl iodides were washed successively with concentrated hydrochloric acid, water, 10 percent sodium carbonate solution and water. Several washings with cold concentrated H_2SO_4 followed. The materials were then washed with water and after drying with anhydrous Na_2SO_4, they were purified further by a process of freezing and fractional melting.(1) This technique consisted of slow crystallization of the liquid followed by slow melting into a series of fractions. The apparatus needed in this work was constructed at ARF glass-shop. The purity of the products was checked through the use of gas-liquid chromatography with Silicon Gum Rubber as the liquid substrate on firebrick. Normal 1-iodooctane was found to be 99.96 mole percent pure, while the normal 1-iodododecane and 1-iodohexadecane were 99.91 and 99.93 mole percent pure.

4-Iodooctane was prepared in this laboratory by the method of Stone and Schechter.(2) Octanol-4 needed for the synthesis of the alkyl iodide was prepared from the reaction of n-butyl magnesium bromide and n-butyraldehyde via the usual Grignard synthesis of secondary alcohols.(3), (4) As the synthesis of octanol-4 gave 4-octanone in 3-4 percent yield, a lithium aluminum hydride reduction of the crude product was carried out. The alcohol was purified via fractional distillation. Three fractions were collected: (a) 34-36°C, (b) 36-117°C, and (c) 170-171°C. The fraction boiling from

170 to 171°C was used in preparation of 4-iodooctane. The alkyl iodide was purified by distillation under reduced pressure and its purity checked through the use of gas liquid chromatography with Silicon Gum Rubber as the liquid substrate on firebrick. This compound was found to be 99.1 mole percent pure.

Dry HI was prepared in this laboratory from a 55 percent aqueous solution of hydrogen iodide (Merck). The free iodine was removed with red phosphorus and the water was removed by covering the frozen solution with P_2O_5, and allowing it to melt after evacuation. The HI gas was then passed through P_2O_5 supported on glass wool, transferred into an evacuated vessel, outgassed and frozen.

Iodine, "Baker Analyzed Reagent" purchased from J. T. Baker Chemical Company was purified by sublimation.

Octane, Phillips Petroleum Company research grade, was used without further purification.

(b) Sample Preparation

Samples of 5 ml. of pure liquid alkyl iodides were introduced into annular irradiation cells equipped with break seals, outgassed by several cycles of freezing and pumping, then thawing and subsequently sealed off under vacuum. (10^{-6} mm Hg). Iodine was added to the sample prior to outgassing. The concentrations of added iodine were determined spectrophotometrically. Hydrogen iodide was measured into a cell of known volume and then transferred under vacuum into the irradiation vessel.

(c) Irradiation

The irradiations were carried out at approximately 24°C using the γ-radiation from cobalt-60. The dose rate was approximately 1.4×10^{19} ev/g-hr.

(d) Dosimetry

The irradiation dose was established using the ferrous sulfate dosimeter with ferric ion being determined by measuring the absorption of ultraviolet light at 304 millimicrons with a Beckman DU spectrophotometer. The geometry used in the dosimetry evaluation was identical to that used in the radiolysis experiments. A value of 15.5 Fe^{++} oxidized per 100 ev absorbed was assumed. In order to determine the dose rate in the alkyl iodides, the rate of absorption of energy in the aqueous $FeSO_4$ solution (1.43×10^{19} ev/g-hr) was multiplied by factors which included the contributions from Compton scattering, photoelectric and pair production effects. The calculated factors were 0.97, 0.98 and 0.99 for 1-iodooctane, 1-iodododecane and 1-iodohexadecane, respectively.

(e) Analysis of Products

The yield of non-condensable gas was measured manometrically on the vacuum line and the identity of the products was established by mass spectral analysis. (Consolidated Engineering Corp. Model 21-103 mass spectrometer).

The determination of hydrogen iodide involved extraction into water and employment of ultraviolet absorption technique. In a typical run the sample was cooled to liquid nitrogen temperature immediately after irradiation, distilled water was added to the solid sample and the sample was melted while being shaken. The hydrogen iodide was removed by successive extraction with water (total volume 45 ml). The concentrations of iodide ion was determined by ultraviolet absorption at 226 mμ. (5), (6)

For the purpose of determination of iodine production, a pyrex Beckman cell was attached to the annular irradiation vessel and the iodine analyses were carried out between successive irradiations of the sample without exposing it to air. The concentrations of iodine were determined with a Beckman DU spectrophotometer provided with a photomultiplier tube as the detector to increase the sensitivity. The optical absorption of iodine was measured at 478 mμ, 565 mμ and 625 mμ. Corresponding alkyl iodide was used in the reference cell.(7)

The analysis of the liquid hydrocarbon products was accomplished by using gas liquid chromatography. Silicon Gum Rubber column was employed in the determination of the total yield of octane and octene-1 and tricresyl phosphate column was used for determination of the ratio of alkane to alkene. Analyses were performed on the F and M Model 202 gas chromatograph.

III. RESULTS

The yields of hydrogen from the radiolysis of pure liquid 1-iodooctane were determined in eight experiments with the radiation dosage ranging from 3.21×10^{20} ev to 7.16×10^{20} ev. The results of these experiments are given in Table 1 and indicate that the amount of hydrogen produced is linear with dose; moreover, the magnitude of 100 ev yields ($G_{H_2} = 0.53 \pm 0.01$) indicates that hydrogen is an important radiolytic product. The minor non-condensable products as determined by mass spectral analysis include 1% methane and less than 0.6% propane, ethylene and acetylene.

The production of hydrogen iodide as a function of radiation dosage was evaluated in seven experiments with the total dose ranging from 4.11×10^{20} ev to 7.16×10^{20} ev. The results of these experiments are also summarized in Table 1. The production of HI appears to be linear with energy input although the scattered nature of data obtained indicates the possibility of post-irradiation effects. Specifically, the 100 ev yields of hydrogen iodide obtained from samples of 1-iodooctane analyzed a few days after irradiation are lower than the corresponding values obtained from samples analyzed immediately after irradiation. These values were not considered in the calculation of the average yield of hydrogen iodide which was 0.39 ± 0.03.

The yields of iodine from the radiolysis of pure liquid 1-iodooctane as a function of radiation dosage are given in Table 2. These data indicate that the iodine production is a linear function of radiation dosage as evidenced by the constancy of the G values. The average 100 ev iodine yield determined in these experiments was 0.87 ± 0.02. It is of interest to note, that the iodine yields determined in the presence of air were found to be consistently lower than those obtained from samples analyzed in sealed vessels. These values were not considered in the calculation of the average G for iodine production.

Yields of liquid hydrocarbon products resultant from the radiolysis of pure liquid 1-iodooctane as a function of radiation dosage appear in Table 3. It may be seen that the production of octane and octene-1 appears to be linear with energy input. The average G values found were 0.98 ± 0.10 and 1.45 ± 0.06 for octane and octene-1, respectively. However, the precision of octene-1 analysis is probably low because of the possibility of decomposition of 1-iodooctane on the chromatographic column.

The pertinent experimental facts established for the radiolysis of pure liquid 1-iodooctane are now summarized. Major products are octane, octene-1, iodine, hydrogen iodide and hydrogen; minor products are methane, propane, ethylene and acetylene. The production of liquid hydrocarbons, iodine, hydrogen and hydrogen iodide is linear with dose. The material balance of all major products is indicated by their combined empirical composition $C/H/I = 8.00/17.4/0.88$.

The effect of added iodine on the production of iodine and hydrogen iodide in the radiolysis of liquid 1-iodooctane was determined in two experiments with initial iodine concentrations of 2.67×10^{-4} and 1.19×10^{-2} moles/liter. The results of these experiments are summarized in Table 4. These data indicate that the iodine production is lowered by the added iodine in the initial stage of irradiation and increases toward the G_{I_2} value for pure 1-iodooctane as the run continues. This increase is much slower in the presence of higher concentration of added iodine. The production of hydrogen iodide does not appear to be affected by the added iodine.

When hydrogen iodide was added to liquid 1-iodooctane prior to radiolysis, the effect on the production of iodine was found to be opposite to that produced by added iodine. This is illustrated by the results of two experiments summarized in Table 5. In these experiments, the concentrations of added HI ranged from 5.28×10^{-3} to 2.88×10^{-2} moles/liter. The results of these experiments show that the iodine production is increased by the added HI and falls off toward the yield for 1-iodooctane without additives in the case of lower concentration of added scavenger. This decrease is not evident, however, in the presence of higher concentration of added HI where the iodine production appears to approach a maximum rate. In both cases, the initial iodine production appears to be independent of scavenger concentration.

The effect of added iodine on hydrogen production in the radiolysis of liquid 1-iodooctane was determined in three experiments with initial concentrations of iodine ranging from 0.26×10^{-3} to 18.5×10^{-3} moles/liter. The effect of added hydrogen iodide on hydrogen yield from the radiolysis of 1-iodooctane was evaluated in two experiments with initial HI concentrations of 5.30×10^{-3} and 28.8×10^{-3} moles/liter. The results of these experiments are given in Table 6 and show that the value of G_{H_2} is not very sensitive to the iodine added; it is of interest to note, however, that the G_{HI} seems to increase with increasing concentration of added hydrogen iodide.

B. 1-Iodododecane

The results of two experiments on iodine production in the radiolysis of pure 1-iodododecane as a function of radiation dosage together with hydrogen and hydrogen iodide yields appear in Table 7. These data indicate that the yield of iodine is a linear function of energy absorbed as indicated by the constancy of the G values. The low G value of 0.47 was due to a timing error and was not considered in the calculation of the average yield. The average G value was 0.63 ± 0.03 and the 100 ev yields of hydrogen and hydrogen iodide were 0.69 and 0.68, respectively.

The effect of added iodine on the production of iodine in the radiolysis of liquid 1-iodododecane was evaluated in two experiments with initial iodine concentration ranging from 2.92×10^{-4} to 5.70×10^{-4} moles/liter. The results of these experiments are shown in Table 8 and indicate that the effect of added iodine on iodine production is similar to that observed in the radiolysis of 1-iodooctane: the initial production of iodine was lowered by the added iodine and increased toward the value for pure 1-iodododecane as the irradiation continued.

The effect of added hydrogen iodide on the production of iodine in the radiolysis of liquid 1-iodododecane was determined in two experiments. The concentrations of added HI were 1.2×10^{-2} and 2.88×10^{-2} moles/liter. The results of these experiments are given in Table 9 and indicate that the initial production was increased by the added HI and falls off toward the value for pure 1-iodododecane as the run continued. This decrease was much slower in the presence of higher concentration of added HI.

The effect of added hydrogen iodide on the production of hydrogen in the radiolysis of liquid 1-iodododecane was evaluated in two experiments with initial scavenger concentrations of 1.2×10^{-2} and 2.9×10^{-2} moles/liter. The results of these experiments together with those of experiments on the effect of added iodine on the production of hydrogen are given in Table 10. These data show that in both cases, the hydrogen yield was practically not affected by both scavengers at concentrations used in these experiments.

C. 1-Iodohexadecane

The production of iodine in the radiolysis of pure liquid 1-iodohexadecane as a function of radiation dosage was determined in two experiments with the total dose ranging from 1.02×10^{20} ev to 4.78×10^{20} ev. The results of these experiments together with hydrogen yields are given in Table 11. The constancy of G_{I_2} values obtained indicates a linear dependence of iodine yields on radiation dosage. The average G_{I_2} was 0.41 ± 0.01. The lowest G value of 0.35 was not included in the average G_{I_2} since a timing error was made. The G_{H_2} was 0.84.

Attempts were made to investigate the effect of added scavengers on the production of iodine in the radiolysis of liquid 1-iodohexadecane. The effect of added iodine was studied in two experiments with initial iodine concentrations ranging from 2.2×10^{-3} to 4.0×10^{-3} moles/liter. In a series of experiments on the effect of added HI, the concentrations of this scavenger were 1.02×10^{-2} and 2.4×10^{-2} moles/liter. The effect of additives on the production of iodine in the radiolysis of 1-iodohexadecane was found to be a very peculiar one. In contrast to the effects of iodine on the radiolysis of other alkyl iodides studied, the presence of added iodine did not decrease the initial rate of iodine production in irradiated 1-iodohexadecane. Moreover, the incorporated iodine prior to radiolysis seemed to enhance this rate to the value significantly greater than that for the pure alkyl iodide.

Even more peculiar effects were produced by the added hydrogen iodide. At first, the radiation behavior of the 1-iodohexadecane and hydrogen iodide mixture observed in the experiment with lower initial HI concentration appeared to be normal: the initial iodine production reached a value several times greater than that for the pure alkyl iodide. However, in the post-irradiation period of approximately 12 hours, the concentration of iodine produced decreased to a drastically low value. The effects produced by the higher concentration of hydrogen iodide added were found to be even more puzzling. Immediately after the melting of the white solid sample, a coloration typical of iodine appeared. The light absorption measurements carried out at 478 mμ on the unirradiated sample showed the optical density to increase very rapidly with time. Therefore, this sample could not be irradiated. Proper investigation of the observed phenomena could not be carried out since this would require effort beyond that permitted by the scope of this program.

Difficulties were also encountered in the attempted determination of the yield of hydrogen iodide from the radiolysis of 1-iodohexadecane. It was impossible to obtain reproducible results due to the difficulty in separating the layers in the procedure of HI extraction.

D. 4-Iodooctane

The results of two experiments on iodine production in the radiolysis of pure liquid 4-iodooctane as a function of radiation dosage together with hydrogen yields are shown in Table 12. These data indicate that the production of iodine is linear with energy input and that the average G_{I_2} 1.43 ± 0.05 is greater than the corresponding value for 1-iodooctane.

E. Liquid Octane and 1-Iodooctane Mixture

The results of one experiment on iodine and hydrogen production in the radiolysis of a 1:1 molar mixture of liquid octane and 1-iodooctane are given in Table 13. It is of interest to point out that the radiolytic behavior of this mixture is, in general, very similar to that of pure 1-iodohexadecane. The hydrogen yields are practically the same for both systems ($G_{H_2} = 0.87$ and $G_{H_2} = 0.84$ for the mixture and for 1-iodohexadecane, respectively) and the average values of iodine yields do not differ significantly ($G_{I_2} = 0.46 \pm 0.02$ and $G_{I_2} = 0.41 \pm 0.01$ for the mixture and for 1-iodohexadecane, respectively).

F. The effect of additives on the initial rate of iodine production in the radiolysis of 1-iodooctane and 1-iodododecane is shown in Table 14. In these experiments, the initial rate of iodine production in the presence of various concentrations of additives was determined graphically by plotting the average rate from time zero to time t against time of irradiation t and extrapolating to zero t. Consideration of the data summarized in Table 14 results in the following observations.

The effect of added HI on the initial rate of iodine production in the radiolysis of liquid 1-iodooctane exhibits two interesting features. (i) The initial rate is increased as compared to that in the absence of added HI. It can be seen that the initial rate with added HI is approximately four times the rate without additive. (ii) The initial rate with added HI seems to be independent of the concentration of HI added prior to radiolysis. This is evidenced by the nearly identical values for the initial rate of iodine production obtained with two different additive concentrations.

It may be seen in Table 14 that the effect of added iodine on the initial rate of iodine production in irradiated 1-iodooctane is opposite to that produced by added HI. The initial rate is approximately one half of the rate in the absence of added iodine. Moreover, it appears to be independent of the concentration of added iodine as evidenced by the fairly close values for the initial rate obtained with two different additive concentrations.

Similar effects of added iodine and hydrogen iodide on the initial rate of iodine production are observed in 1-iodododecane. It can be seen in Table 14 that the initial rate with added iodine is approximately 1.7 times less than that in the absence of added iodine. Moreover, it is independent of the concentration of added iodine at concentrations used in our experiments. The initial rate of iodine production with added HI is almost six times the rate without additives and also appears to be independent of additive concentration.

G. The literature data on the G-values for carbon-iodine bond cleavage in the radiolysis of four lower molecular weight alkyl iodides together with experimental results obtained in our investigation on 1-iodooctane and 1-iododecane are summarized in Table 15. It is of interest to note that the normal G-values for iodine atom production (determined in the absence of additives) as well as the calculated G-values for C-I bond cleavage decrease with increasing length of the carbon chain in the alkyl iodide.

IV. DISCUSSION

A. Features Common to the Radiolysis of Liquid Alkyl Iodides

(a) Lower Molecular Weight Alkyl Iodides

Experimental facts previously established which are pertinent to the radiolysis of lower molecular weight alkyl iodides are the following. The amount of iodine produced was linear with dose up to about 10^{-3} moles/liter.(8-16) The initial rate of iodine production with added iodine was significantly decreased and the initial rate of iodine production with added hydrogen iodide was several times the rate for pure alkyl iodides. Moreover, the initial rate was independent of scavenger concentrations.(11) The iodine production continued even when there was a large excess of added I_2 over HI.(11) The yield of hydrogen was insensitive to large concentrations of added iodine.(12) The $G_{1/2\ I_2}$ was found to increase as a function of the hydrogen atoms on the carbon atoms adjacent to the one containing the iodine.(13), (14), (15), (16), (17)

(b) Higher Molecular Weight Alkyl Iodides

Comparison of experimental facts established in our study with the earlier observations shows that the present work confirms these findings and advances our knowledge of the radiolysis of higher alkyl iodides. In all alkyl iodides studied, the iodine production in the radiolysis of pure compounds was found to be linear with energy input. The effects of added HI and I_2 were qualitatively similar to those on the radiolysis of lower molecular weight alkyl iodides. The initial rate of iodine production with added HI or I_2 was independent of scavenger concentrations. A striking evidence for the β-effect was provided by the results of experiments on the radiolysis of 4-iodooctane. The iodine yield obtained was significantly higher than that for 1-iodooctane. Experiments with a large excess of added iodine over hydrogen iodide showed that iodine production still continued. The yield of hydrogen was found to be insensitive to large concentrations of added iodine. Similarity of our findings with those pertinent to the radiolysis of lower molecular weight alkyl iodides suggest that the radiation behavior of these compounds exhibits several common features regardless of molecular size.

B. Features Pertinent to the Radiolysis of Higher Molecular Weight Alkyl Iodides

In spite of the great similarity in radiation behavior of alkyl iodides discussed above, there are several features pertinent to the radiolysis of higher molecular weight alkyl iodides which are distinctly different from those characteristic of lower alkyl iodides. In contrast to the radiolysis of ethyl iodide(10) where hydrogen was a minor product, our experimental results on higher alkyl iodides studied show that hydrogen is a major radiolytic product. Moreover, the yield of hydrogen increased significantly with the length of the carbon chain of the alkyl iodide, and it surpassed yield of iodine in the radiolysis of 1-iodododecane and 1-iodohexadecane. Similar behavior was observed in the production of hydrogen iodide. Another interesting observation made in our study on the radiolysis of higher alkyl iodides is the fact that the iodine yield decreased significantly with the length of the carbon chain in the alkyl iodide.

C. Possible Factors Affecting Iodine and Hydrogen Yields

The most important and characteristic observation made in extensive experimental studies on radiation behavior of lower molecular weight liquid alkyl iodides is the fact that a predominant effect of the radiolysis of these compounds is the rupture of the C-I bond. This process was shown to occur in spite of the fact that an appreciable fraction of the energy is initially absorbed in the hydrocarbon portion of the molecule. It appeared, therefore, that the absorbed energy was rapidly distributed over the whole molecule and resulted in primary chemical dissociations which were characteristic of the activated species. It was then reasonable to expect a preferential rupture of the weaker C-I bond upon localization of the energy on this site of the molecule.

Experimental findings on iodine production in the radiolysis of higher molecular weight alkyl iodides seem to contradict this expectation and suggest an important role of the length of alkyl chain in the iodide molecule. As the length of the carbon chain of the alkyl iodide increases, the number of bonds in the molecule other than the C-I bond increases. As a result of this, the rate for the C-I bond rupture might be expected to decrease. This was indeed found in our radiation study on higher alkyl iodides. This fact suggests that the distribution of initially absorbed energy over the whole molecule may be a sensitive function of the length of the carbon chain of the alkyl iodide. Therefore, localization of the absorbed energy in bonds other than the C-I bond such as for example C-H bonds should result in higher yields of other products. This expectation may be confirmed by the fact that hydrogen was found to be a major product in the radiolysis of higher alkyl iodides and that its yield increased with the length of the carbon chain of the alkyl iodides studied. The increased rate of the C-H bond rupture may be also reflected in the observed increased yield of HI as a function of the length of the alkyl chain. The hydrogen atoms produced are expected to react with alkyl iodide molecules to produce HI since the activation energy for this process is small and the probability for hydrogen atoms to react with HI or I_2 molecules is low. On the basis of the above discussion, it seems reasonable to say that the increased length of the carbon chain in the alkyl iodides studied may significantly affect the efficiency of intramolecular energy transfer processes.

D. Quantitative Examination of Experimental Results

In order to examine quantitatively our experimental results in terms of intramolecular electronic energy transfer processes, we shall use the following plan of attack on this problem. (a) In the first approach, we attempt to correlate experimental yields of iodine and hydrogen with the fraction of valence electrons of C-I and C-H bonds in the alkyl iodide molecule. (b) In the second approach, we devote our attention to a close examination of the correlation of iodine and hydrogen yields with the calculated fraction of energy initially deposited on iodine and hydrogen electrons. (c) In the last approach, we try to obtain a more intimate view on the correlation of iodine and hydrogen yields with the number of carbon atoms of the alkyl iodide.

(a) Iodine and Hydrogen Yields as a Function of Electron Fraction

It is known that high energy gamma radiation imparts excitation energy to organic molecules by interaction with electrons. Since in organic systems the various groups constituting the molecule are held together by shared electrons, the excitation or removal of a bonding electron may disrupt the stability of the molecule, giving rise to bond cleavage and formation of unstable species. Assuming that all valence electrons have equal interaction probability, such a mode of excitation requires that each group in the molecule interacts directly with the incident beam in proportion to its fraction of valence electrons. Any greater amount of excitation that takes place should be the result of some energy transfer process.

In accordance with this view, it may be assumed that iodine and hydrogen yields should be directly related to the fraction of valence electrons of C-I and C-H bonds, as well as to the number of such bonds in the alkyl iodide molecule as shown below:

$$G_{1/2\, I_2} = K_1 X_e N_{C-I} \qquad (1)$$

$$G_{1/2\, H_2} = K_2 X_e N_{C-H} \qquad (2)$$

By using the experimental values $G_{1/2 I_2} = 4.19$ and $G_{1/2 H_2} = 0.46$ for ethyl iodide to evaluate the proportionality constants K_1 and K_2, we calculate the anticipated iodine and hydrogen yields. Comparison of these values with the corresponding experimental data (Table 16 and Table 17) results in the following observations. Except for 1-iodobutane, the experimental yields of iodine do not differ significantly from the calculated values. Moreover, they decrease at practically the same rate with the length of the alkyl iodide chain as those predicted by our approximate model. This correlation suggests that energy transfer processes do not seem to affect the yields of iodine.

When similar approach is taken in evaluating hydrogen yields, a significant discrepancy between experimental and calculated yields becomes evident (Table 17). The calculated yields are greater than the respective experimental values by a factor of approximately 2 (for higher molecular weight alkyl iodides). Consideration of this fact suggests, according to our approach, that a significant fraction of the initially absorbed energy was transferred to the C-I bond. This conclusion contradicts our previous observations on iodine yields. It is difficult to see offhand why such a disagreement between our approximate model and the observed phenomena should take place. However it seems that this choice of approach leaves something to be desired.

(b) Iodine and Hydrogen Yields as a Function of Fraction of Energy Deposited on Iodine and Hydrogen Electrons

The majority of electrons involved in the excitation processes are those with low energies. It is known that the interaction cross section of low energy charged particles is a sensitive function of the nuclear charge of the irradiated medium. Since the energy loss per centimeter for a proton and that for an electron of the same velocity, for low velocities, is approximately the same, we can either calculate the values of (-dE/dX) for low energy electrons in alkyl iodides theoretically or evaluate them from those for protons of equal velocity and use these values in our approximate model to evaluate the distribution of initial energy deposition in a molecule. The pertinent values for an alkyl iodide molecule for electrons of energy below 100 ev were found to be approximately 2.37, 1.1 and 0.26 per electron of hydrogen, carbon and iodine atom respectively.

According to this approach, it may be assumed that iodine and hydrogen yields should be proportional to the fraction of energy initially deposited on iodine or hydrogen electrons and to the number of C-I and C-H bonds per alkyl iodide molecule. Comparison of the experimental $G_{1/2\ I_2}$ values with those calculated results in a very good agreement (Table 16). This fact suggest again that energy transfer processes do not seem to affect the observed iodine yields. However, as for the first proposed model, this approach fails to explain the hydrogen behavior since a significant discrepancy is observed between the experimental and calculated values (Table 17).

(c) Iodine and Hydrogen Yields as a Function of the Number of Carbon Atoms of the Alkyl Iodide

Our experimental results as well as literature data pertinent to the radiolysis of liquid alkyl iodides showed that iodine yield decreased and hydrogen yield increased with the length of the alkyl chain. These facts suggested an important role of the size of the alkyl chain in governing the yields of these products. In order to elucidate this role, we shall examine more closely the correlation of iodine and hydrogen yields with the number of carbon atoms of the alkyl iodide by using the following approach.

(i) Iodine Production

Iodine yields can be expressed empirically by the following equation

$$G_{I_2} = G^{o}_{I_2} \frac{\beta N_{C-I}}{\beta N_{C-I} + \alpha N_{CH_2}} \qquad (3)$$

where

$G^o_{I_2}$ - yield parameter

α - relative interaction cross-section of a CH_2 group for an electron

β - relative interaction cross-section of a C-I group for an electron

N_{CH_2} - number of CH_2 groups of the alkyl iodide

$N_{C\text{-}I}$ - number of C-I groups of the alkyl iodide

Since $N_{C\text{-}I} = 1$, equation (3) can be written

$$G_{I_2} = G^o_{I_2} \frac{\beta}{\beta + \alpha N_{CH_2}} \tag{4}$$

Rearranging equation (4) to a more convenient form, we obtain

$$\frac{1}{G_{I_2}} = \frac{1}{G^o_{I_2}} + \frac{1}{G^o_{I_2}} \cdot \frac{\alpha}{\beta} \cdot N_{CH_2} \tag{5}$$

A plot of the experimental values for $\frac{1}{G_{I_2}}$ from Table 18 versus N_{CH_2} shows a straight line relationship (Fig. 1). From the slope of this line and its intercept we can evaluate the parameter $G^o_{I_2}$ and the ratio of α to β. The pertinent values are:

$$\text{intercept} = \frac{1}{G^o_{I_2}} = 0.22; \text{ slope} = \frac{1}{G^o_{I_2}} \left(\frac{\alpha}{\beta}\right) = 0.51$$

Inserting these values into the equation (5), we obtain the empirical relation (6)

$$\frac{1}{G_{I_2}} = 0.22 + 0.51\, N_{CH_2} \tag{6}$$

The fundamental point of interest emerging from this correlation is the linear decrease of iodine yield with increasing number of carbon atoms of the alkyl iodide. In an attempt to understand more clearly this behavior, we direct our attention to the following observations. With increasing number of CH_2 groups of the alkyl iodide, the probability for the incident γ-radiation to interact with the electrons of a C-I group decreases resulting in a decreased iodine yield. The linear drop of iodine yield with increasing number of CH_2 groups is somewhat similar to mass spectrometric findings of Field, Franklin and Lampe.(19) Again, energy transfer processes do not seem to affect the production of iodine.

(ii) Hydrogen Production

The hydrogen yield can be expressed by the following empirical equation

$$G_{H_2} = G^{o}_{H_2} \frac{\alpha' N_{CH_2}}{\alpha' N_{CH_2} + \beta' N_{C-I}} \qquad (7)$$

where

$G^{o}_{H_2}$ - yield parameter

α' - relative interaction cross-section of a CH_2 group for an electron

β' - relative interaction cross-section of a C-I group for an electron

N_{CH_2} - number of CH_2 groups of the alkyl iodide

N_{C-I} - number of C-I groups of the alkyl iodide

Since $N_{C-I} = 1$, equation (7) may be written

$$G_{H_2} = G^{o}_{H_2} \frac{\alpha' N_{CH_2}}{\alpha' N_{CH_2} + \beta'} \tag{8}$$

Rearranging equation (8) to a more convenient form we obtain

$$\frac{1}{G_{H_2}} = \frac{1}{G^{o}_{H_2}} + \frac{1}{G^{o}_{H_2}} \cdot \frac{\beta'}{\alpha'} \cdot \frac{1}{N_{CH_2}} \tag{9}$$

By plotting the experimental values for $\frac{1}{G_{H_2}}$ from Table 18 versus $\frac{1}{N_{CH_2}}$ (Fig. 2) we observe that all points fall on a straight line, except for the value corresponding to iodoethane. From the slope of this line and the intercept we can evaluate the appropriate constants. The pertinent values are

$$\text{slope} = \frac{1}{G^{o}_{H_2}} \left(\frac{\beta'}{\alpha'} \right) = 0.83$$

$$\text{intercept} = \frac{1}{G^{o}_{H_2}} = 0.50$$

Inserting these values into the equation (9), we obtain the empirical expression (10)

$$\frac{1}{G_{H_2}} = 0.5 + 0.83 \cdot \frac{1}{N_{CH_2}} \tag{10}$$

The most interesting and remarkable result of this approach is the linear increase of hydrogen yield with the number of carbon atoms of the alkyl iodide. This fact suggests that energy transfer processes play probably only a limited role in determining the extent of hydrogen production. Moreover, if hydrogen results from ionic processes, its linear increase with the number of carbon atoms of the alkyl chain may be also understood in terms of mass spectrometric findings of Field, Franklin and Lampe.(19)

In view of the above discussion, as far as hydrogen and iodine yields are concerned, it appears reasonable to think of alkyl iodides in terms of a physical mixture of electrons residing on CH_2 and C-I groups. In other words, the linear dependence of G_{H_2} on G_{I_2} (Fig. 3) suggests that electrons of CH_2 groups compete with those of C-I groups for the incident energy in proportion to their relative concentrations. Another interesting evidence is provided by our experimental results from the radiolysis of the 1:1 molar octane and 1-iodooctane mixture. As it may be seen in Table 11 and 13, the iodine and hydrogen yields for the mixture are nearly identical to those for the pure 1-iodohexadecane. This fact is in striking agreement with our interpretation since the relative fractions of CH_2 electrons and those of C-I groups in the mixture and in the pure 1-iodohexadecane are nearly identical.

V. CONCLUSION

In spite of several similarities observed in radiation behavior of liquid alkyl iodides regardless of molecular size, there are certain features pertinent to the radiolysis of higher molecular weight alkyl iodides. In contrast to lower alkyl iodides, our experimental results showed that hydrogen is a major radiolytic product; moreover, its yield increased with the length of the alkyl chain. Similar behavior was observed in the production of hydrogen iodide. Another interesting fact established in our study concerned the iodine production. It was observed that iodine yield decreased with the length of the alkyl chain. Quantitative examination of our experimental findings results in the following conclusions. (a) The extent of hydrogen and iodine production is governed mainly by the fraction of electrons residing on CH_2 and C-I groups of the reaction system. (b) Energy transfer processes do not appear to be responsible for the production of hydrogen and iodine.

VI. REFERENCES

(1) A. R. Glasgow and G. Ross, J. Res. Natl. Bur. Standards 57, 137-42 (1956).

(2) Stone and Schechter, J. Org. Chem., 15, 491 (1950).

(3) J. Cason and H. Rapport, Laboratory Text in Organic Chemistry, Prentice-Hall, Inc., p. 309 N Y. (1954).

(4) A. I. Vogel, A Textbook of Practical Organic Chemistry Including Qualitative Organic Analysis, Longmans, Green and Co., p. 257 N. Y. (1948).

(5) H. Fronherz and W. Menschick, Z. Phys. Chem. (Leipzig) B7, 439-467.

(6) A. D. Awtrey and R. E. Connick, J. Am. Chem. Soc. 73, 1843 (1951).

(7) D. E. Schuler and R. H. Schuler, J. Am. Chem. Soc. 76, 3092 (1954).

(8) R. H. Schuler and W. H. Hamill, J. Am. Chem. Soc. 74, 6171 (1952).

(9) E. D. Hornig and J. E. Willard, J. Am. Chem. Soc. 79, 2429 (1957).

(10) R. H. Schuler and R. C. Petry, J. Am. Chem. Soc. 78, 3954 (1956).

(11) M. Lefort, P. Bonet-Maury and M. Frilley, Compt. rend. 226, 1904 (1948).

(12) P. Sue and E. Saeland, Bull. Soc. Chem. France, 437 (1949).

(13) E. L. Cochran, W. H. Hamill and R. R. Williams, Jr. J. Am. Chem. Soc. 76, 2145 (1954).

(14) C. R. Petry and R. H. Schuler, J. Am. Chem. Soc. 75, 3796 (1953).

(15) W. H. Hamill and R. H. Schuler, J. Am. Chem. Soc. 73, 3466 (1951).

(16) L. H. Gevantman and R. R. Williams, Jr. J. Phys. Chem. 56, 569 (1952).

(17) D. L Bunbury, R. R. Williams, Jr., and W. H. Hamill, J. Am. Chem. Soc. 78, 6228 (1956).

(18) H. A. Bethe and J. Ashkin, Experimental Nuclear Physics, Vol. 1, John Wiley and Sons, p. 252, 1953.

(19) F. H. Field, J. L. Franklin and F. W. Lampe, J. Am. Chem. Soc. 79, 2419 (1957).

(20) H. A. Gillis, R. R. Williams, Jr. and W. H. Hamill, J. Am. Chem. Soc. 83, 17, 1961.

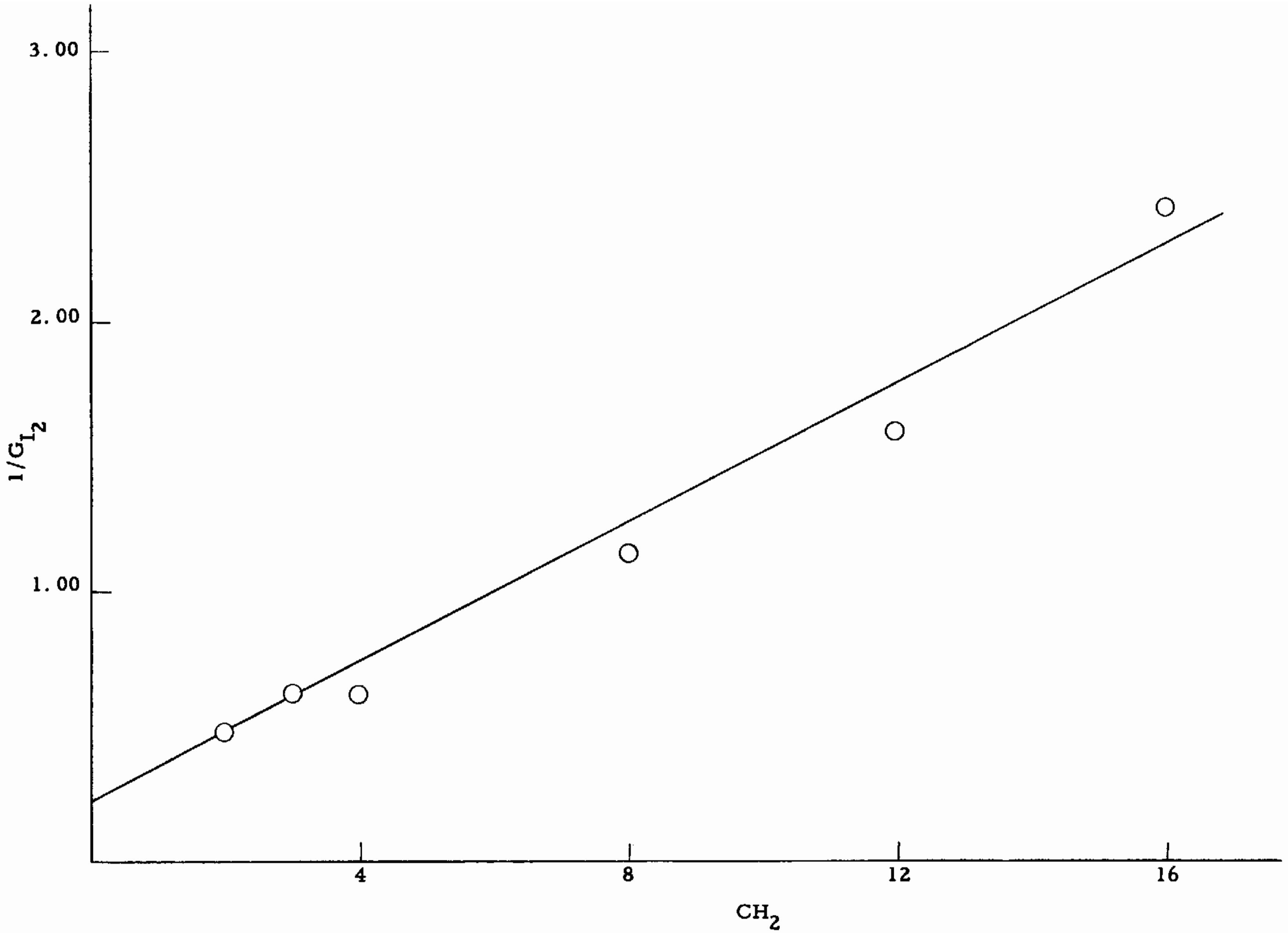

Fig. 1. IODINE YIELD AS A FUNCTION OF THE NUMBER OF CARBON ATOMS OF THE ALKYL IODIDES

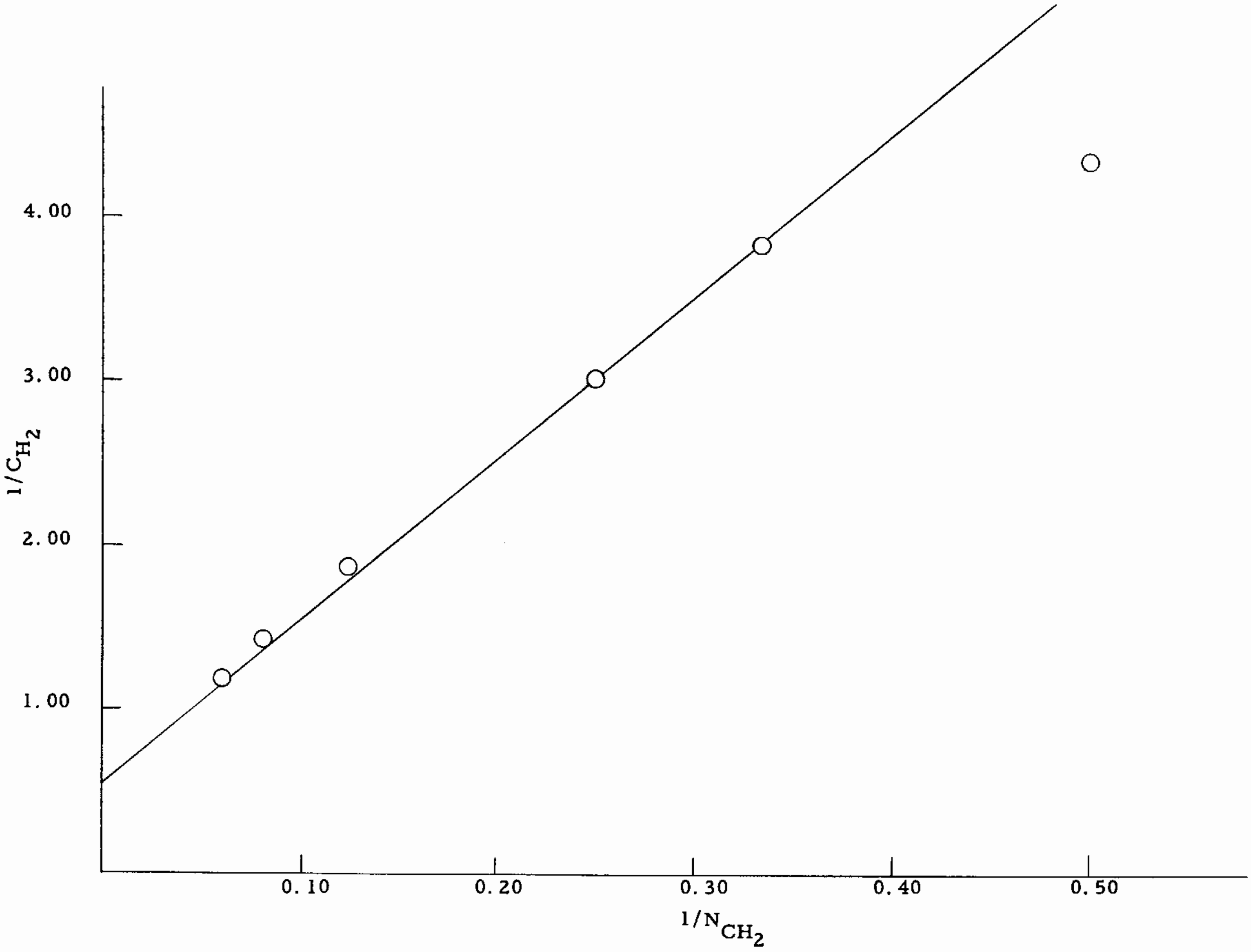

Fig. 2. HYDROGEN YIELD AS A FUNCTION OF THE NUMBER OF CARBON ATOMS OF THE ALKYL IODIDES

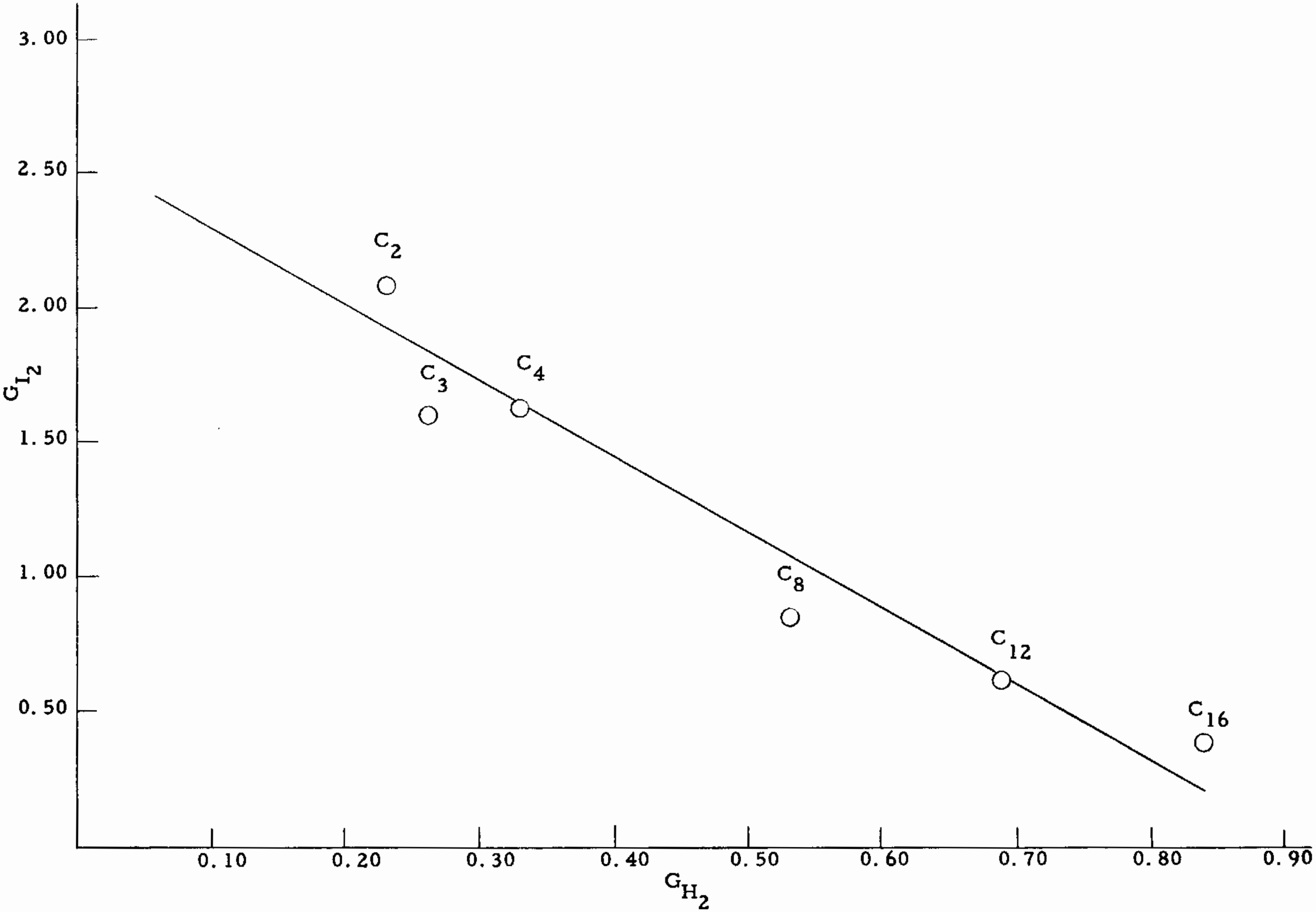

Fig. 3. IODINE YIELD AS A FUNCTION OF HYDROGEN YIELD IN THE RADIOLYSIS OF LIQUID ALKYL IODIDES

TABLE 1

YIELDS OF HYDROGEN AND HYDROGEN IODIDE FROM THE RADIOLYSIS OF PURE LIQUID 1-IODOOCTANE AS A FUNCTION OF RADIATION DOSAGE

Radiation Dosage* ev x 10-20	Moles Produced per Sample x 10^6 Hydrogen	Moles Produced per Sample x 10^6 Hydrogen Iodide	G_{H_2}	G_{HI}
3.21	2.78	**	0.52	**
4.11	3.58	2.19	0.52	0.32***
5.05	4.50	2.70	0.53	0.32***
5.18	4.72	3.68	0.55	0.43
5.18	4.70	3.52	0.54	0.41
5.34	4.68	3.64	0.52	0.41
7.06	6.20	4.27	0.53	0.36
7.16	6.16	4.27	0.52	0.36

---

* Dose rate in 1-iodooctane was 1.35 x 10^{19} ev/g-hr.

** Not determined.

*** Analyzed a few days after irradiation; the remaining samples analyzed immediately after irradiation.

TABLE 2

YIELDS OF IODINE FROM THE RADIOLYSIS OF PURE LIQUID 1-IODOOCTANE AS A FUNCTION OF RADIATION DOSAGE

Radiation Dosage[*] ev x 10^{-20}	Iodine Produced Moles/Liter x 10^3	G_{I_2}
0.44	0.13	0.89
0.71	0.21	0.86
1.04	0.30	0.87
1.32	0.39	0.88
5.18	1.36	0.79**
5.18	1.43	0.83
5.34	1.41	0.79**
5.37	1.52	0.85
7.16	2.15	0.90

---

[*] Dose rate in 1-iodooctane was 1.35 x 10^{19} ev/g-hr.

[**] Determined in the presence of air.

TABLE 3

YIELDS OF OCTANE AND OCTENE-1 FROM THE RADIOLYSIS OF PURE LIQUID 1-IODOOCTANE AS A FUNCTION OF RADIATION DOSAGE

Radiation Dosage* ev x 10^{-20}	Moles Produced per Sample x 10^5		G_{Octane}	$G_{Octene-1}$
	Octane	Octene-1		
4.11	0.56	0.96	0.82	1.41
5.05	0.64	1.15	0.78	1.37
5.18	0.95	1.31	1.10	1.52
5.18	0.95	1.22	1.09	1.44
5.34	1.02	1.35	1.00	1.49
7.06	1.21	1.86	1.03	1.58
7.16	1.24	1.63	1.02	1.36

---

* Dose rate in 1-iodooctane was 1.35 x 10^{19} ev/g-hr.

TABLE 4

EFFECT OF ADDED IODINE ON THE PRODUCTION OF IODINE IN THE RADIOLYSIS OF LIQUID 1-IODOOCTANE*

Total Irradiation Time, Minutes		Iodine Produced Moles/Liter x 10^4		G_{I_2}	
15**		0.45		0.58	
32		0.98		0.60	
45		1.25		0.41	
60		1.70		0.58	
90		2.59		0.57	
125		3.82		0.68	
	150***		4.0		0.51
185		6.28		0.80	
261		9.90		0.91	
	320		9.0		0.57
360		14.88		0.97	
	455		13.0		0.57
1270		60.99		0.97	
	1355		40.0		0.58

---

* Dose rate in 1-iodooctane was 1.37 x 10^{19} ev/g-hr.

** Concentration of added iodine was 2.67 x 10^{-4} moles/liter; $G_{HI} =$ 0.39.

*** Concentration of added iodine was 1.19 x 10^{-2} moles/liter.

TABLE 5

EFFECT OF ADDED HYDROGEN IODIDE ON THE PRODUCTION OF IODINE IN THE RADIOLYSIS OF LIQUID 1-IODOOCTANE*

Total Irradiation Time, Minutes		Iodine Produced Moles/Liter x 10^4		G_{I_2}	
30**		5.11		3.32	
	45***		8.34		3.61
60		9.88		3.12	
	75		14.10		3.74
90		14.33		2.89	
120		18.64		2.79	
	135		25.80		3.80
150		22.51		2.52	
180		26.22		2.42	
	195		37.43		3.77
240		33.00		2.20	
	255		48.84		3.70
300		39.12		1.99	
360	360	43.44	68.84	1.40	3.70
420		48.21		1.54	
480		52.18		1.28	

---

* Dose rate in 1-iodooctane was 1.37×10^{19} ev/g-hr.

** Concentration of added HI was 5.28×10^{-3} moles/liter.

*** Concentration of added HI was 2.88×10^{-2} moles/liter.

TABLE 6

EFFECT OF ADDED IODINE AND HYDROGEN IODIDE ON THE PRODUCTION OF HYDROGEN IN THE RADIOLYSIS OF LIQUID 1-IODOOCTANE[*]

Iodine Added Moles/Liter x 10^3	Hydrogen Iodine Added Moles/Liter x 10^3	G_{H_2} [**]
0.26	***	0.45
11.9	***	0.45
18.5	***	0.43
***	5.30	0.51
***	28.8	0.65

---

[*] Dose rate in 1-iodooctane was 1.37×10^{19} ev/g-hr.

[**] $G_{H_2} = 0.53$ in the absence of additives.

[***] Not added.

TABLE 7

IODINE PRODUCTION IN THE RADIOLYSIS OF PURE LIQUID 1-IODODODECANE AS A FUNCTION OF RADIATION DOSAGE

Radiation Dosage ev x 10^{-20}		Iodine Produced Moles/Liter x 10^{4}		G_{I_2}	
0.77*		1.20		0.47	
	1.22**		2.92		0.71
1.55		3.15		0.61	
	2.04		4.37		0.64
2.33		4.50		0.58	
	2.86		5.88		0.62
3.10		6.23		0.60	
	3.68		7.67		0.63
3.88		8.08		0.63	
	4.49		9.72		0.65
	5.31		11.82		0.67

---

* Dose rate in 1-iodododecane was 1.41 x 10^{19} ev/g-hr; $G_{H_2} = 0.69$; $G_{HI} = 0.68$

** Dose rate in 1-iodododecane was 1.34 x 10^{19} ev/g-hr; $G_{H_2} = 0.69$.

TABLE 8

EFFECT OF ADDED IODINE ON THE PRODUCTION OF IODINE IN THE RADIOLYSIS OF LIQUID 1-IODODODECANE*

Total Irradiation Time, Minutes		Iodine Produced Moles/Liter x 10^4		G_{I_2}	
15**	15***	0.28	0.26	0.41	0.38
30		0.53		0.38	
45	45	0,82	0.82	0.43	0.41
60		1.12		0.44	
	85		1.50		0.37
90		1.73		0.45	
	100		1.80		0.44
120	120	2.40	2.27	0.49	0.52
180	180	3.58	3.55	0.46	0.47
240	240	4.78	5.05	0.44	0.55
	300		6.42		0.50
360		7.48		0.50	
	420		9.40		0.55
480		10.43		0.54	

---

* Dose rate in 1-iodododecane was 1.41 x 10^{19} ev/g-hr.

** Concentration of added iodine was 2.92 x 10^{-4} moles/liter.

*** Concentration of added iodine was 5.70 x 10^{-4} moles/liter.

TABLE 9

EFFECT OF ADDED HYDROGEN IODIDE ON THE PRODUCTION OF IODINE IN THE RADIOLYSIS OF LIQUID 1-IODODODECANE*

Total Irradiation Time, Minutes		Iodine Produced Moles/Liter x 10^3		G_{I_2}	
30**	30***	0.36	0.50	2.66	3.68
60	60	0.66	0.99	2.21	3.61
90		0.91		1.84	
	120		1.99		3.68
160		1.43		1.64	
	180		2.88		3.28
	240		3.68		2.94
	300		4.41		2.68
325		2.36		1.25	
	360		5.01		2.22

---

[*] Dose rate in 1-iodododecane was 1.41 x 10^{19} ev/g-hr.

[**] Concentration of added hydrogen iodide was 1.2 x 10^{-2} moles/liter.

[***] Concentration of added hydrogen iodide was 2.88 x 10^{-2} moles/liter.

TABLE 10

EFFECT OF ADDED HYDROGEN IODIDE AND IODINE ON THE PRODUCTION OF HYDROGEN IN THE RADIOLYSIS OF LIQUID 1-IODODODECANE

Hydrogen Iodide Added Moles/Liter x 10^2	Iodine Added Moles/Liter x 10^4	G_{H_2} **
1.2	*	0.67
2.9	*	0.66
*	2.92	0.65
*	5.70	0.63

---

* Not added.

** Dose rate in 1-iodododecane was 1.4×10^{19} ev/g-hr; $G_{H_2} = 0.69$ in the absence of additives.

TABLE 11

IODINE PRODUCTION IN THE RADIOLYSIS OF PURE LIQUID 1-IODOHEXADECANE AS A FUNCTION OF RADIATION DOSAGE

Radiation Dosage ev x 10^{-20}		Iodine Produced Moles/Liter x 10^4		G_{I_2}	
1.02*		1.20		0.35	
	1.59**		2.20		0.41
1.79		2.30		0.39	
	2.39		3.35		0.42
2.55		3.50		0.41	
	3.19		4.50		0.42
3.32		4.65		0.42	
	3.99		5.55		0.42
4.09		5.65		0.41	
4.60		6.30		0.41	
	4.78		6.55		0.41

---

* Dose rate in 1-iodohexadecane was 1.41 x 10^{19} ev/g-hr; $G_{H_2} = 0.84$.

** Dose rate in 1-iodohexadecane was 1.49 x 10^{19} ev/g-hr; $G_{H_2} = 0.83$.

TABLE 12

IODINE PRODUCTION IN THE RADIOLYSIS OF LIQUID 4-IODOOCTANE AS A FUNCTION OF RADIATION DOSAGE[*]

Radiation Dosage ev x 10^{-20}	Iodine Produced Moles/Liter x 10^4		G_{I_2}
0.88	5.00[**]	4.16[***]	1.56 ± 0.12
1.77	8.37	7.90	1.39 ± 0.03
2.66	12.2	****	1.38
3.59	16.3	****	1.38
4.43	20.2	21.0	1.41 ± 0.04
5.31	25.8	25.0	1.45 ± 0.01

---

[*] Dose rate in 4-iodooctane was 1.38 x 10^{19} ev/g-hr.

[**] $G_{H_2} = 0.43$.

[***] $G_{H_2} = 0.42$.

[****] Not measured.

TABLE 13

IODINE PRODUCTION IN THE RADIOLYSIS OF LIQUID OCTANE AND 1-IODOOCTANE MIXTURE AS A FUNCTION OF RADIATION DOSAGE*

Radiation Dosage** ev x 10^{-20}	Iodine Produced Moles/Liter x 10^4	G_{I_2}
0.65	1.10	0.50
1.31	2.07	0.47
1.97	3.15	0.48
2.63	4.00	0.45
3.33	4.75	0.43
3.94	5.60	0.43

---

* $G_{H_2} = 0.87$.

** Dose rate in the mixture was 1.37×10^{19} ev/g-hr.

TABLE 14

EFFECT OF ADDITIVES ON THE INITIAL RATE OF IODINE PRODUCTION IN THE RADIOLYSIS OF LIQUID 1-IODOOCTANE AND 1-IODODODECANE

Alkyl Iodide	Iodine Added Moles/Liter x 10^3	Hydrogen Iodide Added Moles/Liter x 10^3	Rate of Iodine Production Moles/Liter/Minute x 10^6			G_{I_2}		
			Normal*	I_2 Added**	HI Added**	Normal*	I_2 Added***	HI Added***
1-Iodooctane	0.27	5.26	4.34	2.44	18.2	0.85	0.46	3.56
	11.9	28.8		2.30	18.0			
1-Iodododecane	0.29	12.0	2.80	1.65	15.2	0.63	0.36	3.50
	0.57	29.0		1.67	16.4			

---

* Average values determined in the absence of additives: 4.34 ± 0.13 and 2.80 ± 0.18.

** Initial rate determined graphically.

*** Based on the average value for the initial rate of iodine production.

TABLE 15

G-VALUES FOR CARBON-IODINE BOND CLEAVAGE IN THE RADIOLYSIS OF LIQUID ALKYL IODIDES

Alkyl Iodide	G for Iodine Atom Production Normal[a]	 Maximum[b] (HI Added)	 Minimum[b] (I_2 Added)	G for C-I Bond Cleavage $1/2\,(G_{max} + G_{min})$
Iodomethane[c]	2.54	11.74	2.16	6.96
Iodoethane[c]	4.19	10.68	2.25	6.46
1-Iodopropane[c]	3.22	9.82	1.72	5.76
1-Iodobutane[c]	3.26	9.30	1.75	5.52
1-Iodooctane	1.70	7.12	0.92	4.02
1-Iodododecane	1.26	7.00	0.72	3.86

(a) For alkyl iodides irradiated without additives.
(b) Based on the average value for the initial rate of iodine production.
(c) Literature data taken from the article by R. T. Hanrahan and T. B. Williard, J. Am. Chem. Soc. 79, 2435 1957.

TABLE 16

COMPARISON OF EXPERIMENTAL WITH CALCULATED G VALUES FOR HYDROGEN ATOM PRODUCTION IN THE RADIOLYSIS OF LIQUID ALKYL IODIDES

Compound	Fraction of Valence Electrons of C-I Bond X_e	Fraction of Energy Initially Deposited on Iodine Electrons X_E	Calculated G Values		Experimental $G_{1/2\ I_2}$
Iodoethane	0.40	0.36	4.19	4.19	4.19*
1-Iodopropane	0.31	0.27	3.25**	3.13***	3.22
1-Iodobutane	0.25	0.22	2.62	2.55	3.26
1-Iodooctane	0.14	0.13	1.47	1.51	1.70
1-Iodododecane	0.10	0.09	1.05	1.05	1.26
1-Iodohexadecane	0.08	0.07	0.84	0.81	0.82

---

* This value was used for calculation of proportionality constants K_1 and K_2.

** $G_{1/2\ I_2} = K_1 X_e N_{c-I}$

*** $G_{1/2\ I_2} = K_2 X_E N_{c-I}$

TABLE 17

COMPARISON OF EXPERIMENTAL WITH CALCULATED G VALUES FOR HYDROGEN ATOM PRODUCTION IN THE RADIOLYSIS OF LIQUID ALKYL IODIDES

Compound	Fraction of Valence Electrons of C-H Bonds X_e	Fraction of Energy Initially Deposited on Hydrogen Electrons X_E	Calculated G Values		Experimental $G_{1/2\ H_2}$
Iodoethane	0.50	0.30	0.46	0.46	0.46*
1-Iodopropane	0.54	0.33	0.68**	0.69***	0.52
1-Iodobutane	0.56	0.34	0.90	0.92	0.66
1-Iodooctane	0.61	0.37	1.86	1.88	1.06
1-Iododecane	0.62	0.39	2.79	2.92	1.38
1-Iodohexadecane	0.63	0.40	3.74	3.96	1.68

---

* This value was used for calculation of proportionality constants K_1 and K_2.

** $G_{1/2\ H_2} = K_1 X_c N_{C-H}$

*** $G_{1/2\ H_2} = K_2 X_E N_{C-H}$

TABLE 18

DATA USED IN GRAPHICAL EVALUATION OF EXPERIMENTAL RESULTS

Compound	G_{H_2}	$\frac{1}{G_{H_2}}$	$\frac{1}{N_{CH_2}}$	G_{I_2}	$\frac{1}{G_{I_2}}$	N_{CH_2}
Iodoethane	0.23*	4.35	0.50	2.09*	0.48	2
1-Iodopropane	0.26*	3.85	0.33	1.61*	0.62	3
1-Iodobutane	0.33*	3.03	0.25	1.63*	0.61	4
1-Iodooctane	0.53	1.88	0.125	0.87	1.15	8
1-Iodododecane	0.69	1.45	0.083	0.63	1.60	12
1-Iodohexadecane	0.84	1.20	0.062	0.41	2.44	16

---

* Literature data, see reference 9 and 20.