# THERMOLYSIS, PHOTOLYSIS AND RADIOLYSIS OF SOME ORGANOMETALLIC COMPOUNDS

A
THESIS
SUBMITTED IN PARTIAL FULFILMENT OF
THE REQUIREMENT FOR THE DEGREE OF

DOCTOR OF PHILOSOPHY
(Chemistry)

BY

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AT THE
BIRLA INSTITUTE OF TECHNOLOGY AND SCIENCE
PILANI (RAJASTHAN)

1971

BIRLA INSTITUTE OF TECHNOLOGY AND SCIENCE
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## SUPERVISOR'S CERTIFICATE

Certified that the research work described in the thesis entitled 'Thermolysis, Photolysis and Radiolysis of Some Organometallic Compounds' was done by Sri Sita Ram Garg, M.Sc., under my guidance and supervision.

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# ACKNOWLEDGEMENTS

I wish above all to acknowledge my sincere thanks to Dr. R.S. Rai, M.Sc., D.Phil., Assistant Professor, Department of Chemistry, B.I.T.S., Pilani, to whom I am indebted for inspiration and guidance and to whose unflagging interest therein its final completion is due. I owe him a special thanks for his advice and criticism throughout my work on this particular subject matter.

I am particularly grateful to Dr. R.C. Mehrotra, Senior Professor and Head of Chemistry Department, University of Rajasthan, Jaipur, for providing facilities for thermal analysis and photolysis and to Dr. H.K. Jain, Division of Genetics, Indian Agriculture Research Institute, New Delhi, for $Co^{60}$ - Y radiation facilities. Thanks are also due to Dr. R. Mahadeo Iyer, Scientist, Bhabha Atomic Research Centre, Bombay, and to Prof. M.V. George, Head, Department of Chemistry, Indian Institute of Technology, Kanpur, for gas liquid chromatographic analysis.

I wish to thank Dr. G.M. van der Want, Scientific Deputy Director, Organisch Chemisch Instituut, T.N.O., Utrecht, the Netherlands for generous supply of organolead compounds. I wish to acknowledge my sincere thanks to

Messrs. [illegible] Dhupar and A.D. Taneja of Chemistry Department B.I.T.S. and N.P. Bansal, Chemistry Department, Delhi University, for their valuable help in many ways. I express my thanks to Shri [illegible] Sharma, Glass-Blower, Shri Bhatnagar, incharge liquid air plant and Shri P.L. Mehta for typing the thesis.

It is my pleasant duty to thank Prof. S.K. Banerji, Head of Chemistry Department, B.I.T.S., Pilani, for his encouragement. Finally I record my particular appreciation to Dr. C.R. Mitra, Director, B.I.T.S., Pilani, for allocation of some funds from grant of the Fourth Five-Year Plan, U.G.C. Financial help provided to me by the Council of Scientific and Industrial Research, New Delhi, in the form of a Junior Research Fellowship during the tenure of my research work, is most gratefully acknowledged.

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# CHAPTER I

# GENERAL INTRODUCTION

## RADIATION CHEMISTRY OF BENZENE AND CYCLOHEXANE

Since benzene and cyclohexane have been selected as solvents in this study, it is necessary to give an account of its radiation chemistry. High energy radiation, on interaction with matter, either produces electronic excitation or is absorbed, and it leads to chemical processes and changes. The term high energy radiation includes all wave and corpuscular emanations associated with radioactivity, fission and cosmic radiation, alpha (high velocity helium ions) and beta (high velocity electron emanations) particles, gamma rays, fast neutrons, atom and fission recoils, neutrinos and mesons etc. It also includes all the analogues such as high energy protons, deuterons, helium ions, stripped carbon atoms, electrons, x-rays, etc., which are produced by Van de Graff generator, betatron, resonance transformer, linear accelerators and cyclotrons etc. The scientific investigations have centered around only those radiations, which are capable to produce substantial chemical effects. According to Platzman[1] low energy electrons also play an extremely important role in actual chemical events. But such studies begins in the energy range at about 100 ev. and majority of investigations have been carried out in the region beginning with 100 Kev and extends into Mev region, where big accelerators operate.

The work on the high energy radiation started as early as 1895, 1896 and 1898 by Roentgen, Becquerel and Curie. In 1910 Lind started the study of radiation induced ion pair formation in gases and attempted to interpret his results by ion-cluster theory. It supposes that a single molecule-ion would have adherent to it one or more molecules. The orthopara conversion of hydrogen by alpha radiation and radiolysis of HBr was explained by Eyring, Hirschfelder and Taylor[4] in 1936. This theory was just a synthesis of ideas and there were no significance activities in the field until 1942, when this branch of chemistry was christened Radiation Chemistry by Milton Burton.

In radiation chemistry impacts and coulombic interactions between the energy bearer and the electronic system of the absorbent takes place prior to the absorption. There is no single and simple energy absorption process. The absorption is related to the number of electrons present or the electron density of the substance. When a gamma or X-ray interacts with matter it ejects a high energy electron (a photoelectron) more frequently in radiation chemistry a Compton electron or at energies in excess of 1 Kev, an electron pair. Such a high velocity charged particles can interact with matter and produce further ionization and excitation. A single gamma ray may produce a 1 Mev electron and a single positive ion. Such electron in turn may produce thirty to forty thousand additional of molecules excited. Since the linear combination starts, the molecules spread the excitation, because the stationary state is that of the whole system and not only of the molecules. States with various composition are found. The forces which lead to break down the packet lead to dissipation of energy by spreading. In the time the energy is there the molecule disproportionates and it might break from the wave packet. Thus the excitation energy is transferred from the excited region to some molecule or group, which possesses a mechanism for dissipation of excitation energy. This is called the 'true protection'[6]. On the other hand the highly excited states such as those formed by neutralization, internally convert to the lowest excited states allowed by multiplicity selection rules, i.e., singlet or triplet in a time of order of $10^{-13}$ second. This is confirmed by luminescene studies[7].

The energy transfer from an excited species follows several paths. Such transfer takes place by direct collision or collision of second kind, excitation migration, transfer from higher energy state to lower energy state or luminescene. The problem now involved is that how this energy is localized and what are the phenomenon subsequent to localization. A great variety of reactive species, ions and excited molecules in their ground and excited states and electrons of fairly high energy are produced along the path of energetic photons. A fair approximation is that half of the absorbed energy is spent in production of ions and half in production of excited molecules. These species may interact with themselves and with the substrate in the close proximity of the tracks to produce more ions and secondary electrons of low energy on their way and may diffuse away to the main body. All these processes occur in a time of $10^{-12}$ seconds, before equilibrium is reached[8]. Meanwhile dissociation of ions and excited molecules results in free atoms or molecular products and radicals. On the whole the processes can be several. The excited molecules can undergo collisional deactivation and if the energy is not available for luminiscene, it is called quenching, otherwise it is emitted as luminiscence. The processes also involved radical, ion-molecule reactions[9], reactions of hot atoms and hot radicals, reactions involving electrons of thermal energy[10] and reactions involving excited molecules (known as Stern-Volmer reactions) particularly in the neighbourhood of tracks and spurs, where such excited species are highly concentrated in the earlier stage of the entire event[11].

One of the most challenging and interesting problems in the radiation chemistry of organic liquids has been the role and behaviour of aromatics. The primary events in such systems, caused by fast particles such as recoil electrons from Mev gammas, occur at intervals of about 10 Å. The secondary electrons distribute the energy of such an event in a generally spherical region or spur, 20-30 Å in diameter[4]. The positive ions are formed by simple electron removal or the electron removal accompanied or followed by rupture or rearrangement. On the other hand negative ions are formed by the electron capture or dissociation of excited neutral molecules into positive and negative ions. The ion + electron neutralization processes yield both singlet and triplet states. Theoretically it is possible that in multi-ion spurs the number of such triplet excited molecules exceeds the number of singlet excited molecules so produced. However, all upper excited states no matter how produced, internally convert within $10^{-13}$ seconds to the lowest excited states of the same multiplicity. Because internal conversion to the ground state is much slower the result is that most of the chemical changes in liquids take place from either one of the two low excited states. Luminiscence studies lead to the conclusion that such compounds as cyclohexane appears to be persist long enough after excitation and they can actually be protected against decomposition by the addition of a suitable additive. Only a small fraction of energy transferred in such a protective act appears as luminescence of the receptor molecule. Such luminiscence must always compete with other methods of energy dissipation. In addition to the primary processes mentioned above, typical secondary processes involved are: extraction addition or scavenging, recombination and disproportionation. Many experimental findings in the pure form as well as in solution are still not understood. To illustrate these features two cyclic C-6 hydrocarbons, cyclohexane and benzene are considered. The selectivity of benzene for such studies is based on the following consideration. In benzene 6π electrons are loosely bound. They are capable of having energy for a very short time and then transfer energy to other π electron system. If a hallow is formed, fluorescence is observed. If the π electrons transfer the excitation energy then energy transfer processes are involved. It has been found that lowest excited state transfers the energy.

## TABLE I

Some Physical Properties of $C_6H_6$ and $C_6H_{12}$

| | Benzene | Cyclohexane |
|---|---|---|
| C-H bond dissociation energy | 102 K.cal | 85 K.cal |
| Lowest excited state | 5 ev | 7 ev |
| Ionization Potential | 9.3 ev | 11.3 ev |
| Photochemical Quantum Yield | $2 \times 10^{-4}$ | 0.5 |
| Lifetime of persistent radiation induced excited species in pure liquid | $3.3 \times 10^{-8}$ sec. | $3 \times 10^{-10}$ sec. |

## TABLE II

Yields in Radiolysis of Benzene by $Co^{60}$ - gamma radiation at 25°C

The result of analysis by various workers is given below:

| Product | G* Value (Yield 100 ev) |
|---|---|
| $H_2$ | 0.036 to 0.38 (0.045+0.003)[12-13]<br>no dose dependence |
| $C_2H_2$ | 0.015 to 0.020 |
| $C_6H_5 \cdot C_6H_5$ | 0.05 |
| $C_6H_5 \cdot C_6H_7$ (Total Isomers) | 0.025 |
| $C_6H_5 \cdot C_6H_9$ or $C_6H_7 \cdot C_6H_7$ | 0.004 to 0.007 |
| Polymer product (Yellow residue) | 0.75 to 0.94 |

*Considerable decrease below melting point +5.5°C.

## TABLE III

Yields in Radiolysis of Cyclohexane by $Co^{60}$ - gamma radiation at 25°C

| Product | G Value* (Yield 100 ev) |
|---|---|
| $H_2$ | 5.55 to 5.85 dose dependent |
| Major gaseous products: | |
| $CH_4$ | 0.02 dose dependent |
| $C_2H_4$ | 0.14 |
| $C_2H_2$ | 0.01 |
| $C_2H_6$ | 0.02 |
| Other major products: | |
| $C_6H_{10}$ | 2.50 |
| $C_6H_{11} \cdot C_6H_{11}$ | 2.00 |
| Hexane | 0.20 |

| Product | G. Value* (Yield 100 ev) |
|---|---|
| Methylcyclopentane | 0.30 |
| Intermediate cyclohexanes | 0.30 |

*Negligible effect of temperature in the range 77° to 298°K

## TABLE IV

Comparison of Radiolysis yields of substituted $C_6H_6$ and $C_6H_{12}$

| | $G(H_2)$ | $G(D_2)$ |
|---|---|---|
| $C_6H_6$ | 0.037 | |
| $C_6D_6$ | | 0.0117 to 0.013 |
| $C_6H_{12}$ | 5.8 | |
| $C_6D_{12}$ | | 3.9 |

A perusal of the yield shows that the G values of products from cyclohexane are customarily high and those obtained from henzene are lower by a factor of about 100. $G(H_2)$ is a real measure of the total number of $C_6H_{12}$ molecules decomposed. The value $G(H_2)$ between 5 and 6 is the characteristics of aliphatic hydrocarbons. $G(H_2)$ and $G(D_2)$ from benzene are significantly lower than the corresponding pertinent values for cyclohexane. The low G value shows that benzene is insensitive to high energy radiation and in the liquid state most of the energy is dissipated without decomposition. The residual $G(H_2)$ is approximately twice, the residual $G(D_2)$. This indicates a slightly greater tendency towards stabilization of $C_6D_6$ than $C_6H_6$.

It has been calculated that about 2% of the absorbed energy results in chemical decomposition and changes and the remaining 98% is dissipated in the form of heat. Benzene is known as an effective scavenger for free radicals. The low yield explained on the basis of interception of radicals by $C_6H_6$ is inadequate. The plausible explanation seems that benzene is inherently resistant to radiation induced chemical change. The benzene molecules are stable even in the excited state and lose their energy by internal conversion processes, to the ground state or by transfer of excitation to a quencher species, which may, itself, decompose or transfer to a luminescent solute. Hence benzene does not decompose appreciably.

Internal conversion is the cause of the lack of dissociation. Secondly the excited or ionized states of $C_6H_6$ are highly resonant, and hence highly stable. A long life time of the order of $8.3 \times 10^{-8}$ seconds measured for excited species of liquid benzene means an enhanced probability of collisional deactivation and quenching by surrounding molecules. The highly ordered structure of liquid or solid benzene favours 'excitation transfer', an efficient collective method of energy dissipation.

On the other hand cyclohexane is readily decomposed by high energy radiation. The G values for the products cannot be accounted for by the difference in C-H bond strength and in potential energies of the excited and ionized molecules. Mass spectrometric patterns of this molecule indicate that the $C_6H_{12}$ + ion undergoes dissociation quite readily and a variety of fragment ions are observed in abundance. The life time in the liquid has been measured as less than $3 \times 10^{-10}$ seconds[14]. Therefore the process of energy conveyance appears to be ionization transfer. The neutralization process, which thereafter occurs involves the receptor ion and the subsequent behaviour of the irradiated medium is that of the excited receptor molecule in liquid cyclohexane. Since only a fraction of the initially excited cyclohexane molecules are ions, only a fraction of them can transfer their energy in this way. The remainder decompose very quickly, in about $10^{-10}$ seconds according to the normal behaviour of irradiated cyclohexane.

Very little work has been done on the condensable products of radiolysis of benzene, although total quantity of these products is the order of the magnitude greater than the gaseous products consisting of hydrogen and acetylene. The products commonly called as 'polymer' is viscous liquid which varies in colour from light yellow to orange yellow. It is a semi-solid substance at high dose. It has aromatic odour and on exposure to air a rapid absorption of oxygen accompanied by a simultaneous increase in the refractive index and viscosity. It also forms a crystalline ozonide.

The products are complicated mixtures of high molecular weight hydrocarbons, very difficult to work with, because of the complexity and reactivity with oxygen. However, it has been clear for sometime and many investigations have pointed out that the real progress in understanding the mechanism of radiolysis of benzene could only be achieved by more complete knowledge of the nature of these condensable products. There have been some qualitative and quantitative description of the residue, but nothing extensive enough to allow anything more than a speculative formation of a mechanism.

Freeman[15] has analyzed the polymer by Mass Spectrometric analysis. A solution of polymer in a ethyl alcohol is introduced through a liquid gallium seal. Two fractions are found: (1) C-12 and (2) C-18. These compounds contain on average two or more non-aromatic double bonds per molecule. The C-12 fraction contains diphenyl and dihydrodiphenyl, phenylcyclohexane and bicyclic compounds in which neither ring is aromatic. The C-18 fraction contains hydrogenated terphenyls. It is also reported that bicyclohexadienyl, cyclohexadienyl cyclohexane and cyclohexyl cyclohexadienes are also formed. A vapour phase flow discharge of benzene is reported to have formed diphenyl and dihydrodiphenyl[16].

## Mechanism for Benzene Radiolysis

The probability of dissociation of excited and ionized benzene molecule is considerably reduced due to the presence of π electrons in the orbitals in its ring system. Benzene ions show little tendency to break down into smaller fragments by fission of an aromatic ring, in a mass spectrometer. This tendency is even less likely under normal radiolytic conditions, where ions can lose their extra energy rapidly by collisional process. The radiolytic products of benzene are divided into three different groups. The bond cleavage yields gaseous products of low molecular weights. Hydrogenation, dehydrogenation and rearrangement yield, products which have molecular weight in the intermediate range. The products in the high molecular weight group are called 'Polymer', which is formed by condensation, polymerization or cross linking. The following reaction mechanism is suggested:

$$C_6H_6 \longrightarrow C_6H_6^+ + e^- \longrightarrow C_6H_6^* \qquad (1)$$

$$\longrightarrow C_6H_6^*,\ C_6H_6^{**},\ C_6H_6^{***} \qquad (2)$$

$$C_6H_6^* + C_6H_6 \longrightarrow 2\ C_6H_6 \qquad (3)$$

$$C_6H_6^{***} \text{ or } C_6H_6^{**} \longrightarrow C_2H_2 + ? + H_2 + ? \qquad (4)$$

$$C_6H_6^* \longrightarrow C_6H_5^{\bullet} + H^{\bullet} \qquad (5)$$

$$2H^{\bullet} \longrightarrow H_2 \qquad (6)$$

$$C_6H_5^{\bullet} + C_6H_6 \longrightarrow C_6H_5 \cdot C_6H_6^{\bullet} \qquad (7)$$

## Mechanism for Benzene Radiolysis

The probability of dissociation of excited and ionized benzene molecule is considerably reduced due to the presence of $\pi$ electrons in the orbitals in its ring system. Benzene ions show little tendency to break down into smaller fragments by fission of an aromatic ring, in a mass spectrometer. This tendency is even less likely under normal radiolytic conditions, where ions can lose their extra energy rapidly by collisional process. The radiolytic products of benzene are divided into three different groups. The bond cleavage yields gaseous products of low molecular weights. Hydrogenation, dehydrogenation and rearrangement yield, products which have molecular weight in the intermediate range. The products in the high molecular weight group are called 'Polymer', which is formed by condensation, polymerization or cross linking. The following reaction mechanism is suggested:

$$C_6H_6 \longrightarrow C_6H_6^{+} + e^{-} \longrightarrow C_6H_6^{*} \qquad (1)$$

$$\longrightarrow C_6H_6^{*},\ C_6H_6^{**},\ C_6H_6^{***} \qquad (2)$$

$$C_6H_6^{*} + C_6H_6 \longrightarrow 2\ C_6H_6 \qquad (3)$$

$$C_6H_6^{***} \text{ or } C_6H_6^{**} \longrightarrow C_2H_2 + ? + H_2 + ? \qquad (4)$$

$$C_6H_6^{*} \longrightarrow C_6H_5^{\cdot} + H^{\cdot} \qquad (5)$$

$$2H^{\cdot} \longrightarrow H_2 \qquad (6)$$

$$C_6H_5^{\cdot} + C_6H_6 \longrightarrow C_6H_5 \cdot C_6H_6^{\cdot} \qquad (7)$$

$$2C_6H_5.C_6H_6^{\bullet} \longrightarrow C_6H_5.C_6H_5 + C_6H_5.C_6H_7 \quad (8)$$

$$\longrightarrow C_6H_5.C_6H_6.C_6H_6.C_6H_5 \quad (9)$$

$$C_6H_5.C_6H_6^{\bullet} + H^{\bullet} \longrightarrow C_6H_5.C_6H_7 \quad (10)$$

$$C_6H_6 + H^{\bullet} \longrightarrow C_6H_7^{\bullet} \quad (11)$$

$$C_6H_7^{\bullet} + C_6H_5^{\bullet} + C_6H_6 \longrightarrow \text{Polymer} \quad (12)$$

Hydrogen and Acetylene Yield

In the photolysis of benzene low quantum yield are observed. It is due to collisional deactivation. Very low yield of gaseous products is explained by quenching of an appreciable fraction of the excited benzene molecules. Hydrogen is formed from the highly excited benzene molecules as in step (4) or by radical combination as in (6). There is also another probability that hydrogen might be formed by either of the reaction:

$$C_6H_6^{*} + C_6H_6^{*} \longrightarrow H_2 + C_6H_5.C_6H_5$$

$$\longrightarrow H_2 + \text{radicals}$$

The hydrogen atoms dissociated from the C-H bonds are scavenged rapidly by surrounding molecules. Hydrogen atoms react by addition rather than hydrogen abstraction and this accounts for lower yield of hydrogen. Patrick and Burton[19] using benzene-$d_6$ have shown that at least two mechanisms are necessary to account for the hydrogen atom and another involving a rearrangement process. This is also supported by the work of Gordon and Burton[20] who irradiated mixtures of benzene and $C_6D_6$ and found an appreciable proportion of HD in hydrogen. Burns[21] have postulated a similar reaction in explaining the variations in hydrogen yield with changing LET. The acetylene yield is explained in the same way as hydrogen yield. There is a competition between the reaction (3) and (4) and the former predominates the latter resulting in a low gaseous yield. Schuller[22] observed that iodine as a radical scavenger has little effect upon the overall yields of hydrogen. This suggests that hydrogen is almost formed by a molecular process rather than reaction involving hydrogen atoms.

## Diphenyl and Dihydrodiphenyl Yield

Reaction (8) explains the formation of diphenyl. The phenyl radical formed in the reaction (5) either goes to the formation of benzene or phenylcyclohexadienyl radical in step (7) leading ultimately to diphenyl and dihydrodiphenyl formation. De Tar and Long[23] have shown that phenylcyclohexadienyl radicals may disproportionate at least in dilute solutions into phenylbenzenes and phenyldihydrobenzenes. There are two phenylcyclohexadiene. The ratio of phenylcyclohexadiene (2,4) to (2,5) is 1:1.35 ± 0.15 and is probably independent of temperature and one of these dihydrodiphenyls is very unstable.

Tetrahydroquaterphenyl is formed in the reaction (9). Diphenyl can be excluded as a possible source of its formation because of its high radiation resistance compared with benzene. This statement is also supported by the fact that a small amount of phenylene and quarterphenylene are formed. In addition to the direct polymerization of recombining two dimer radicals, there is another possibility of polymerization by radical transfer. The phenylcyclohexadienyl radical can react with phenyl radicals to form trimers and it may couple in the cannonic forms to yield tetrahydroquaterphenyl.

## Polymer Yield

Analytical system is not so sensitive enough to detect all liquid products. However, Gordon[24] observed that the polymer contains a $C_{12}$-fraction (biphenyl, phenylcyclohexane and aromatic bicyclic compounds) and a $C_{18}$-fraction (hydrogenated triphenyls and high molecular weight materials). Tino Gaumann[25] found phenylhexatrien, 2,4 and 2,5 phenylcyclohexadiene, 1 and 3 phenylhexane, bicyclohexyl, phenylcyclohexane and diphenyl in the polymer. As discussed earlier the aromatic fragments after loss of hydrogen atom may also be scavenged by neighbouring aromatics giving rise to these products. The addition products are intermediates that form hydrogenated products by continued hydrogen atom scavenging and polymer is formed by the radical reactions or reactions involving excited molecules.

## Mechanism for cyclohexane radiolysis

All hydrogen atoms in cyclohexane are equivalent and it is structurally related to benzene. Therefore, the loss of any one of these gives the same product and this limits the number of radiolytic reactions. Despite a good deal of efforts the mechanism for radiolysis of cyclohexene cannot yet be considered established. However, the following mechanism is suggested:

$$C_6H_{12} \longrightarrow C_6H_{12}^{**},\ C_6H_{12}^{*} \qquad (1)$$

$$\longrightarrow C_6H_{11}^{\bullet},\ H^{\bullet}\ (85\%) \qquad (2)$$

$$\longrightarrow C_6H_{10} + H_2\ (15\%) \qquad (3)$$

$$H^{\bullet} + C_6H_{12} \longrightarrow C_6H_{11}^{\bullet} + H_2 \qquad (4)$$

$$2C_6H_{11}^{\bullet} \longrightarrow C_6H_{10} + C_6H_{12} \qquad (5)$$

$$\longrightarrow (C_6H_{11})_2 \qquad (6)$$

## Excited states of cyclohexane

LET independent of cyclohexane was demonstrated by Dyne[26] using γ-sources of different intensities. Energy transfer type protection is observed on the radiolysis of a mixture of benzene and cyclohexane. This process is called external conversion. In this process the excitation energy is transferred from at least one excited state of cyclohexane to benzene molecule. This may also take place by charge exchange[17]. Burton[6,10,19,20] has established that benzene dissipates the energy by internal conversion without decomposition. Freeman[17,27] is of the view that cyclohexane radiolysis involves at least two distinct species of excited cyclohexane molecule with G values 3.0 and 2.4 respectively. The former is deactivated by benzene and the latter is immune to benzene. According $C_6H_{12}^{**}$ is benzene deactivated species and $C_6H_{12}^{*}$ is benzene immune species. This result is similar to molecular and radical yields of hydrogen estimated by Hamill[28].

Hydrogen Yield

Mass-spectral evidence shows that parent cyclohexane ion $C_6H_{12}^{+}$ is highly stable[29]. Therefore C-C bond scission in cyclohexane ring contributes very little. The hydrogen yield is LET and temperature independent[30]. Majority of workers report that hydrogen yield is constant, while some others found that it decreases continuously as the radiolysis product build up in the system[31]. Hamill[28] have shown that hydrogen yield can be divided into three components. One due to the reactions of thermal hydrogen atoms, one to the reaction of hot high velocity hydrogen atoms and the other one corresponding to hydrogen formed by molecular processes.

The isotopic composition of hydrogen[32] formed in the radiolysis of a mixture of $C_6H_{12}$ and $C_6D_{12}$ showed that about 25% hydrogen was formed by direct detachment (unimolecular). It has also been concluded that about 40%

of hydrogen yield is due to the reaction of $H_2$ atoms and the remainder 35 to 60% might be formed in part by ion-molecule reaction such as:

$$C_6H^{+}_{12} + C_6H_{12} \longrightarrow C_6H^{+}_{13} + C_6H^{\cdot}_{11}$$

$$C_6H^{+}_{13} + e^{-} \longrightarrow C_6H^{\cdot}_{11} + H_2$$

But ion-molecule reaction is not observed in the mass spectrometer[33]. On irradiation of a mixture of $C_6H_{12}$ and $C_6D_{12}$, the reaction between the initially produced sibling free radicle:

$$H + C_6H^{\cdot}_{11} \longrightarrow H_2 + C_6H_{10}$$

$$D + C_6D^{\cdot}_{11} \longrightarrow D_2 + C_6D_{10}$$

is in competition with the back reactions

$$H^{\cdot} + C_6H_{11} \longrightarrow C_6H_{12}$$

$$D^{\cdot} + C_6D_{11} \longrightarrow C_6D_{12}$$

Thus it is estimated that hydrogen formed by unimolecular process is 10-20% of total yield of hydrogen and the remainder is formed by bimolecular processes.

Both iodine and benzene reduce the unimolecular and bimolecular yield of hydrogen in the same proportion as the total yield of hydrogen. Dyne[33] is of the opinion that both unimolecular and bimolecular reactions have the same precursors, an excited state of cyclohexane, and benzene and iodine acts as a quenching agent and not as a radical scavenger. The radical scavengers reduce the yield of hydrogen, but do not eliminate it completely showing that hydrogen is formed both by 'radical' and 'molecular' processes. Unsaturated radiolytic products act as scavengers and reduce hydrogen yield. It has been observed that added cyclohexane reduces $GH_2$. Other unsaturated radiolysis products act as scavengers and reduce the hydrogen yield.

## Cyclohexene Yield

Dyne and Fletcher[26], using gamma radiation of different intensities, found that the steady state concentration of cyclohexene increased slowly with dose rate, although at low intensities, the initial *G* cyclohexene is independent of dose rate. The product is temperature independent[29]. Cyclohexene, when added to cyclohexane, inhibits its own formation and also that of hydrogen but to a lesser extent. Other *G* values are also altered[17,27]. Radical scavengers reduce the yield of cyclohexene from cyclohexane, but do not eliminate them completely, showing that this product is formed both by radical and molecular processes.

## Bicyclohexyl Yield

The $(C_6H_{11})_2$ yield increases at high dose rates, while at lower dose rates unsaturated polymeric material may be formed[34]. No temperature effect has been observed for this product[30]. The added cyclohexene does not reduce bicyclohexyl and cyclohexyl radicals, which are precursors of bicyclohexyl and are produced by normal hydrogen atom reaction:

$$H^{\bullet} + C_6H_{12} \longrightarrow C_6H^{\bullet}_{11} + H_2$$

and by cyclohexene scavenging reaction:

$$H^{\bullet} + C_6H_{10} \longrightarrow C_6H_{11}$$

Cyclohexanol and Cyclohexanone Yield

In the presence of oxygen, cyclohexane, on radiolysis, gives cyclohexanol, $\underline{G} = 3.7$ and cyclohexanone, $G = 3.5$ and the yield of cyclohexene is reduced to $G = 0.7$ and negligible amount of the dimer is formed[29]. Two other products, cyclohexyl hydroperoxide, $C_6H_{11}OOH$, ($G = 1.0$) and a peroxide, $R_1OOR_2$ ($G = 0.2$) is also reported[35]. The suggested mechanism for cyclohexanol and cyclohexanone formation is:

$$H^{\bullet} + C_6H_{12} \longrightarrow C_6H^{\bullet}_{11} + H_2$$

$$C_6H^{\bullet}_{11} + O_2 \longrightarrow C_6H_{11}O^{\bullet}_2$$

$$2C_6H_{11}O^{\bullet}_2 \longrightarrow C_6H_{11}OH + C_6H_{10}O + O_2$$

Since $H_2O_2$ is not formed, it seems that hydrogen atoms react directly with cyclohexane, even when oxygen is present, rather than adding oxygen to form $HO_2$.

Radical scavengers reduce the yield of cyclohexanone from oxygenated cyclohexane, $G = 0.46$ and it is independent of the scavenger used. This limiting yield is due to molecular process, involving an excited cyclohexane molecule and oxygen

$$C_6H_{12}^{*} + O_2 \longrightarrow C_6H_{10}O + H_2O$$

Here the yield of cyclohexanol is always less than the yield of cyclohexane by an amount equal to the molecular yield of ketone. This is to be expected, if the radical forming processes and cyclohexanone are represented by disproportionation reaction:

$$2C_6H_{11}O_2^{\cdot} \longrightarrow C_6H_{11}OH + C_6H_{10}O + O_2$$

which gives equal amount of ketone and alcohol.

The mixture of benzene and cyclohexane exhibit behaviour more characteristics of benzene than is expected on the basis of their composition. The low yields of the chemical products cannot be explained satisfactorily either by scavenging reactions or either a composition by benzene for thermal electrons, that otherwise would neutralise $C_6H_{12}^{+}$ . Ionization transfer mechanism such as

$$C_6H_{12}^{+} + C_6H_6 \longrightarrow C_6H_{12} + C_6H_6^{+}$$

is most favoured[36].

# ORGANO-METALLIC COMPOUNDS OF LEAD AND TIN

The chemistry of organic compounds of germanium and tin has developed at rapid pace during the past 20 years. There has been little research on the organic compounds of the next higher element of Group IV, lead, until very recently[37]. The chemistry of organolead compounds dates back to 1853[38], when Lowig prepared the first alkyl lead compound, $Et_6Pb_2$. In 1921 Paneth et al.[39,40] proved the existence of the short lived free radicals with tetra alkyl lead. Later on compounds of the type $R_4Pb$, $R_2PbX_2$, $RPbX_3$, $R_3Pb$-$PbR_3$ were studied, where R is simple aromatic or alkyl substituents without functional group and X representing the negative group or metal. Gruttner, Krause et al. during 1915-1936[41] and Gilman et al.[42] have done remarkable work on the preparative aspect of these compounds.

During the past few years interests of research chemists have shifted towards theory of bonding and mechanism of known reactions and it has been shown that Pb-C bond is more reactive than was previously thought. The development in this branch until 1936, until 1952 and up to 1963 are remarkably treated in a number of reviews[41,42,43,44]. The account of chemistry of Pb-C, Pb-H bond for 1964[37] and for 1965, 1966 and 1967[45] is given in the other review[46]. All the organic compounds of lead atom possess $Sp^3$ hybridization. It forms four covalent bonds, for which the tetrahydral structure is valid. The orbitals of the lead atom up to and including 4f are fully occupied. Then follows the arrangement, $5S^2$, $5p^6$, $5d^{10}$, $6S^2$, $6p^2$. Empty orbitals can be used for the formation of stable complexes and for the formation of short lived transition state. Among the elements of Group IV, lead has the largest covalent radius. This leads to small amount of shielding of the lead atom by the substituents, large interatomic distances and correspondingly small bonding energies. In Group IV, Pb-C and Pb-H bond have greatest reactivity and the smallest thermal stability towards both polar and radical reagents.

The alkyl derivatives of lead are unstable and difficult to purify but the aryl derivatives are crystalline solids, considerably more stable and readily purified by crystallization. In the solid state, these aryl derivatives are stable for long periods, if they are protected from the strong light. It is common characteristic of all hexaalkyl dilead compounds to undergo the thermal disproportionation to tetra alkyl lead and metallic lead. The disporoportionation is also observed in highly boiling solvents, like toluene, xylene and pyridine[47]. This decomposition of hexa-alkyl di-lead to lead tetra alkyl has been observed using excited carbon black, silica gel type catalyst, aluminium chloride and u.v. light[48-51].

The yield of tetra-alkyl lead obtained by this disproportionation reaction is generally quite high (90%)[47]. Recently tetrakis (triphenyl plumbyl) $(C_6H_5)_3Pb_4Pb$ has been reported to disproportionation slowly to hexaphenyl dilead and lead oxide[52,53].

## THERMAL AND PHOTOCHEMICAL DECOMPOSITION

Thermal and photochemical decomposition of aliphatic and aromatic organometallic compounds take place at different temperatures. The decomposition follows the mechanism established by Paneth in the pyrolysis of tetramethyl and tetraethyl lead. In these cases the electron pair forming the covalent bonds split to form free radical with their odd electrons[54]. The reaction of tetramethyl lead with liquid hydrocarbons was studied at 200-270°C. It was shown that the ethyl radical formation takes place, which hydrogenated to ethane and disproportionated to ethylene and ethylene polymerised. Cycloparaffins dehydrogenated readily but aromatic hydrocarbons do not react with ethyl radical below 300°C.

During the study of thermal decomposition of aromatic organometallic compounds of mercury[55], it was observed that aryl radicals were formed in the solution which abstracted hydrogen and formed benzene. The phenyl radical is an intermediate formation, which is highly reactive and reacts immediately with the solvent that is why with a number of solvents the production of diphenyl was not reported. Penta phenyl phosphorous and penta phenyl antimony in solution gave aryl radical on thermal decomposition[56]. In a number of organometallic compounds homolytic rupture of C-metal bond occurs[57]. The free radical formation is definitely ruled out under mild conditions, which excluding the possibility of thermal decomposition of organometallic compounds to form free radical[58-62].

The homolysis of lead-C bond by u.v. light at 20°C[63] is also reported. Heating at 150°C results in homolytic cleavage of Pb-C bonds forming free radicals[64-67]. The ability of organometallic compounds to exchange organic groups and their catalytic polymerization activities, attracted attention and a large amount of work is reported on metal phenyl compounds and their applications in the polymerization of styrene, etc.

In the study of the photolysis of benzene, the main reaction product, hydrogen, could not be determined with certainty[68-70]. The lead tetra phenyl has not been investigated in the gas phase because it has a very low vapour pressure. In normal hexane it shows a decomposition quantum yield of 3.7 in the concentration range 0.000055 to 0.000109 molar at wavelength 2537 Å. This figure is lowered down to 0.23 in the presence of oxygen. The mechanism suggested by Leighton et al.[71], could not account with certainty the effect of oxygen and low quantum yield in the solution has been ascribed to the Franck-Rabinowitch principle.

The principle metallo-organic compounds of lead which has been subjected to photochemical studies are alkyl, aryl, and the carbonyls. Lead tetra ethyl gave methyl radical which was tested by the radioactivity of lead mirrors and it gave metallic lead and two molecules of ethane with 2537 Å. The quantum yield in the gaseous phase is 1.1 and in the hexane 0.4[71].

Photosensitized reaction of benzene induced by excited mercury atoms is thirty times faster than non-photosensitized rate of reaction[72-74]. The gaseous product is 60% hydrogen and 40% methane. Benzene at higher temperature produces biphenyl as major product with quantum yield 0.1 as suggested by Steacie et al[75]. The low quantum yield suggests that the primary act is excited molecule formation.

Photosensitization of cyclohexane with mercury over the range 60-400°C has been studied[76]. Below 0°C the major product are hydrogen, bicyclohexyl, and cyclohexene. These results are quite in conformity with other workers[77]. If the temperature is raised up to 200°C cyclohexyl radical is formed in the primary process and it decomposes to propylene, methane, ethylene ethane, butadiene, propane and butene.

Therefore the mechanism of these proportionation reactions tempted towards more complete understanding of this problem and the work was done to elucidate the thermal behaviour of some organo-lead compounds.

The photolysis of lead tetraphenyl in N-hexane was carried out by Leighton[71], which indicates biphenyl production. He concluded that biphenyl ought to be produced by recombination of phenyl radicals during photolysis. The validity of this production was of considerable importance in the investigation of organometallic compounds. Another possibility is that phenyl radical produced may not recombine but abstract from solvent molecules. The resulting free radicals then react by recombination and disproportionation. The study of the decomposition of tin tetraphenyl to tin diphenyl was done by Razuauev and Fetyufovav[77].

Therefore the mechanism of these disproportionation reaction tempted towards more complete understanding of this problem and the work was done to elucidate the thermal behaviour of some organolead compounds. Since different excited state of metal phenyls may be involved in the photolysis and gamma-radiolysis, therefore, photochemical studies of benzene and cyclohexane solutions of lead tetraphenyl, hexaphenyl dilead, lead triphenyl hydroxide and triphenyl lead chloride were undertaken.

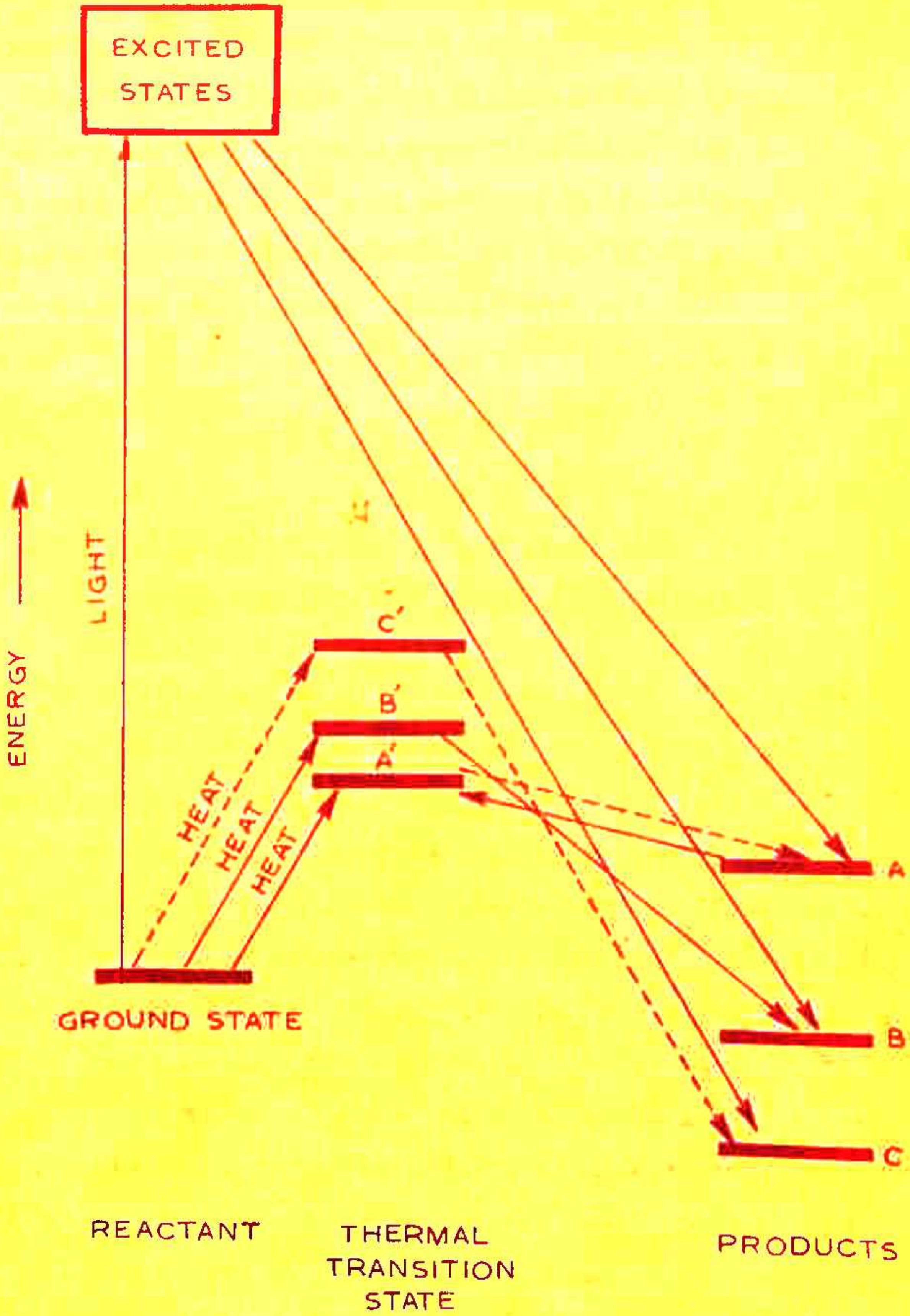
EXCITED STATES
LIGHT
ENERGY
HEAT
HEAT
HEAT
C'
B'
A'
GROUND STATE
A
B
C
REACTANT
THERMAL TRANSITION STATE
PRODUCTS

FIG 1·1

The important differences between thermal and photochemical activation as to the possibility to obtain various reaction products are schematized in Fig. 1.1. Schematic diagram shows that products which cannot be obtained with thermal excitation may be formed under photochemical excitation. The number of reaction paths are greater in photochemical reactions. It leads towards preferential formation of a certain product.

## RADIATION CHEMISTRY OF SOME LEAD PHENYL COMPOUNDS IN LIQUID HYDROCARBONS

The radiation chemistry of benzene and cyclohexane solutions of tetraphenyl Si, Ge, Sn and Pb were first investigated by Cramer[78]. He reported that lead tetraphenyl undergoes sensitized decomposition lead to the production of biphenyl as the major product. A conclusion from Cramer's studies was that the mechanism of sensitized decomposition of metal tetraphenyls in benzene solutions involves excitation transfer from benzene to metal phenyls. In an attempt further to elucidate the mechanism of sensitized decomposition, the work began by Cramer was extended to other organo-metallic compounds of metal phenyls. The study yielded data on the effect of gamma radiation as well as certain other informations.

Therefore the present study is based upon and extends recently reported work on lead tetraphenyl[79]. The investigation also includes a new attempt at direct study of the radiolysis of other metal phenyl compounds of lead, say, tetraphenyl lead, hexaphenyl dilead, triphenyl lead chloride and triphenyl lead hydroxide.

Thus the radiation chemistry of dilute benzene and cyclohexane solutions of a number of closely related organo-metallic compounds have been investigated, both to improve our knowledge of the radiation chemistry of the tetraphenyl lead, hexaphenyl dilead, triphenyl lead chloride and triphenyl lead hydroxide and also in an attempt to elucidate the mechanism by which solutes at low concentrations interact with excited species in the solvent by high energy radiation. In particular such study is aimed at to illustrate further the kinetic peculiarities of reactions of atoms and free radicals in the liquid state which depend largely on diffusion controlled process.

It has been suggested that a large fraction of energy absorbed in the solvent is available for decomposition of solute. Benzene behaves as a scintillator solvent when a benzene solution containing p-terphenyl as a solute is irradiated by $Co^{60}$ gamma-radiation. The luminiscence emitted is characteristic of p-terphenyl in spite of the fact that nearly all the absorption of energy occurs in the solvent. The properties of lead tetraphenyl as a quencher is very significant. Therefore it is contemplated to correlate the relative extent of sensitised decomposition of solute to the quenching efficiency. Quenching process of this kind involves interaction between solvent and quencher exclusively at these quencher concentration.

The chemistry of the organometallic compounds of tin has been reviewed upto 1959 by Ingham et al.[80] Other excellent reviews on various aspects of organic chemistry of tin are available[81-84]. A survey of the literature reveals that thermal stability of organotin compounds is greater than organolead compounds. Tetraphenyl tin has been selected from the very exhaustive list of organotin compounds. Selectivity is based upon its close resemblance to lead tetraphenyl. Like lead tetraphenyl tin tetraphenyl is also slightly soluble in organic solvents.

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* * *

# CHAPTER II

## THERMAL STUDY OF SOME ORGANO-LEAD COMPOUNDS

A survey of the literature[1-4] reveals that the organo-element compounds of the fourth main group are thermally more stable than organo-lead compounds. Most of the organo-lead derivatives decompose on heating to temperature between 100-200°C. These compounds are hydrolytically stable and are not affected by atmospheric oxygen. Phenyl lead derivatives have been reported to be more stable in comparison to alkyl lead derivatives. The decomposition studies have been made in solutions using a series of solvents, but no attempt has been made to study the effect of gradual heating on solid samples.

In view of the above facts, it was considered worthwhile to study the effect of heat on some phenyl lead derivatives. Four compounds, i.e., tetraphenyl lead, hexaphenyl dilead, triphenyl lead chloride and triphenyl lead hydroxide are chosen and are heated under reduced pressure as well as inside a specially designed furnace of an automatic recording thermobalance.

Low activation energy is available in thermal reactions. An activation energy of more than 40 Kcal/mole are quite rare in coordination chemistry[5]. The effect of thermal excitation is very selective and it will usually cause one reaction. On the other hand various processes are possible in a photochemical reaction. Several

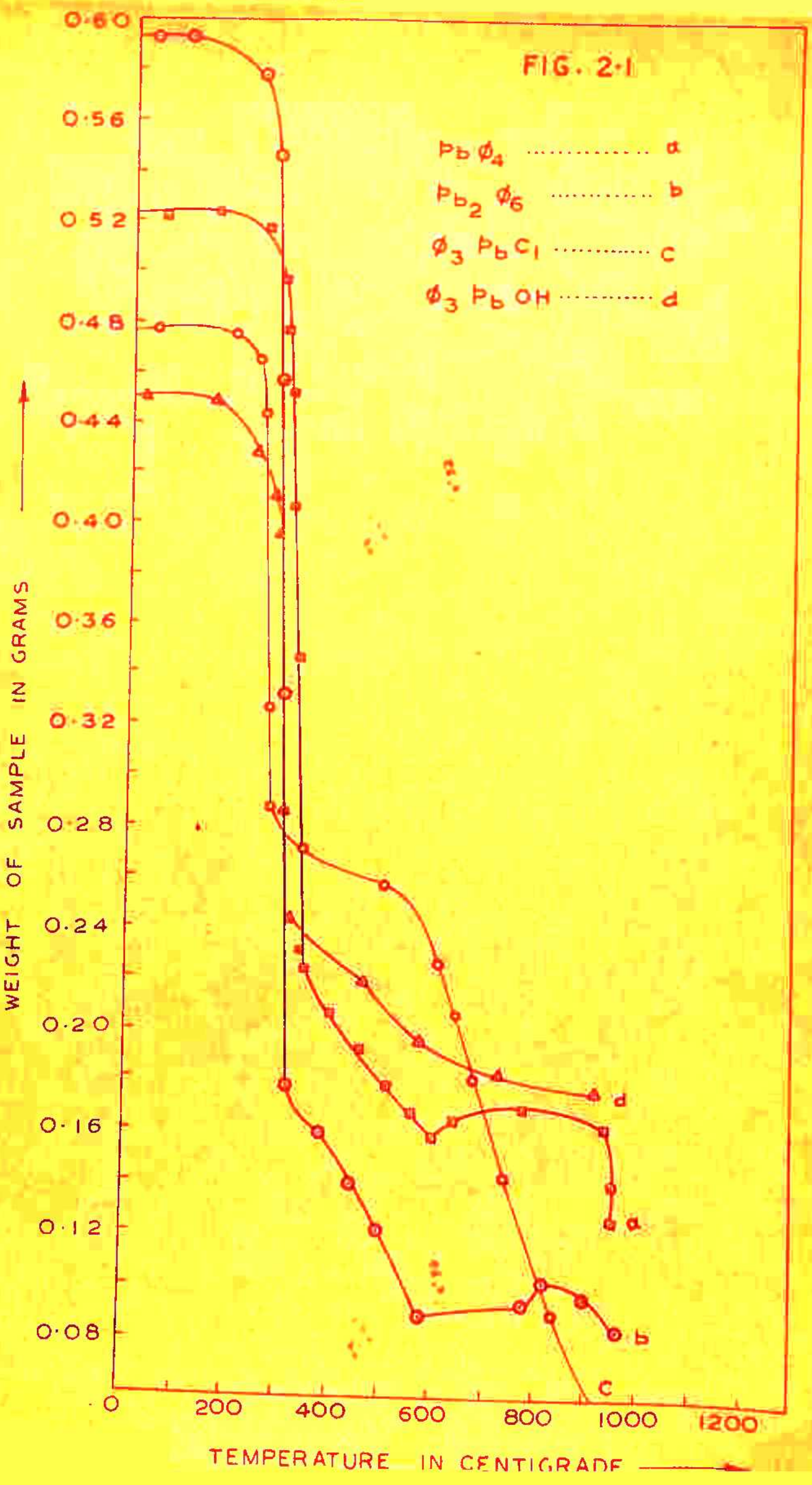
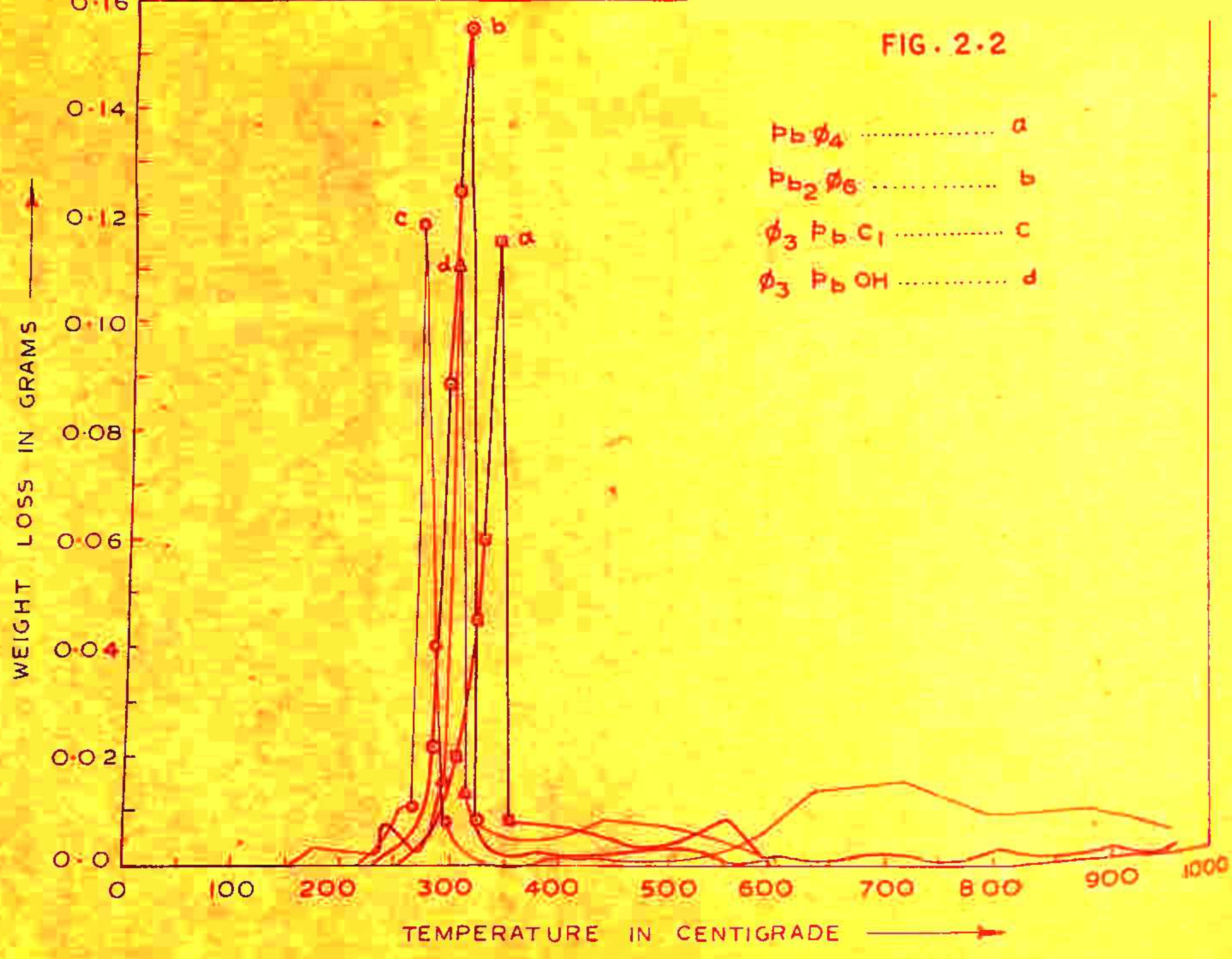


FIG. 2·1

Pb ϕ4 ................ a
Pb2 ϕ6 .............. b
ϕ3 Pb Cl .............. c
ϕ3 Pb OH ............. d
WEIGHT OF SAMPLE IN GRAMS
0·60
0·56
0·52
0·48
0·44
0·40
0·36
0·32
0·28
0·24
0·20
0·16
0·12
0·08
0
200
400
600
800
1000
1200
TEMPERATURE IN CENTIGRADE
a
b
c
d

FIG. 2.2


WEIGHT LOSS IN GRAMS
0·0
0·02
0·04
0·06
0·08
0·10
0·12
0·14
0·16
TEMPERATURE IN CENTIGRADE
0
100
200
300
400
500
600
700
800
900
1000
a
b
c
d
Pb $\phi_4$ .................. a
$Pb_2$ $\phi_6$ .................. b
$\phi_3$ Pb $C_1$ .................. c
$\phi_3$ Pb OH .................. d

additional products, which cannot be formed with thermal excitation because of either kinetic or thermodynamic reasons may be formed in photochemical reaction[16]. Therefore this study can also be used for a comparative study of thermal and photochemical reactions of lead aryls.

## EXPERIMENTAL

The samples were heated inside the furnace of a mass flow type thermobalance (Stanton) at a rate of 4 °C/minute. The loss in the weight and the rise in temperature was automatically recorded. Some of the volatile fragments were trapped and analysed.

The change in weight of the samples with the rise in temperature has been shown in figure 2.1. The loss per minute was calculated[7] from the original graph and plotted against temperature in Fig. 2.2. The differential thermal graphs (D.T.G.) obtained from the plot shows the rate of decomposition and formation of unstable intermediate compounds.

### Estimation of Carbon and Hydrogen

For estimation of carbon and hydrogen standard methods of analysis have been used[8-9]. The percentage error in C and H determination is 0.5% and 3% respectively. A weighed amount of sample (sublimate) is combusted in a measured volume of oxygen under controlled pressure to yield quantitatively carbon dioxide from the carbon and water from the hydrogen. The amount of these combustion products were determined gravimetrically. The combustion-tube filling was so arranged that the other elements presents in the sample will not interfere with the final quantitative absorption of carbon-dioxide and water by suitable absorption tube containing appropriate absorbing agents, for example, anhydrone for absorption of water and ascarite for absorption of carbondioxide.

$C + O_2 \longrightarrow CO_2$ (absorbed by Ascarite (sodium hydroxide on asbestos))

$H_2 + \frac{1}{2} O_2 \longrightarrow H_2O$ (absorbed by Anhydrone (magnesium perchlorate))

## Estimation of Lead

Lead analysis was carried out by dissolving a few mg. of the sample in nitric acid and analysed colorimetrically by dithizone method[10]. A few mg. of the sample is dissolved in nitric acid and the solution is made up to 1 litre containing 10% nitric acid. The solution is diluted to make it 1% nitric acid and lead must be less than 3 mg. per litre. Ten ml. of this solution is transferred to 150 ml separating funnel and 75 ml. of ammonia cyanide-sulfide mixture is added to this. The ammonia-cyanide-sulfide solution contains 400 ml. concentrated ammonia diluted to 750 ml. and 30 ml. of 10% potassium cyanide solution is added to 1.5 g. sodium sulfite and finally the volume is diluted to 1 litre with water. The

## TABLE 1

Thermolysis of lead tetraphenyl (0.5238 g)

| Temperature (°C) | Wt. of $PbPh_4$ (g) |
|---|---|
| 0 | 0.5238 |
| 80 | 0.5228 |
| 160 | 0.5238 |
| 220 | 0.5228 |
| 260 | 0.5178 |
| 270 | 0.5138 |
| 280 | 0.5068 |
| 290 | 0.4978 |
| 300 | 0.4778 |
| 310 | 0.4328 |
| 320 | 0.4078 |
| 330 | 0.3478 |
| 340 | 0.2328 |
| 350 | 0.2248 |
| 360 | 0.2198 |
| 400 | 0.2078 |
| 460 | 0.1928 |
| 520 | 0.1798 |
| 560 | 0.1678 |
| 640 | 0.1668 |
| 700 | 0.1688 |
| 780 | 0.1708 |
| 880 | 0.1688 |
| 940 | 0.1648 |
| 950 | 0.1548 |
| 950 | 0.1428 |
| 950 | 0.1288 |

## TABLE 2

Thermolysis of lead tetraphenyl (0.5238 g)

| Temperature (°C) | Weight loss (g) |
|---|---|
| 20 | 0.0000 |
| 140 | 0.0000 |
| 220 | 0.0000 |
| 280 | 0.0070 |
| 290 | 0.0090 |
| 300 | 0.0200 |
| 310 | 0.0250 |
| 320 | 0.0450 |
| 330 | 0.0600 |
| 340 | 0.1150 |
| 350 | 0.0080 |
| 360 | 0.0050 |
| 420 | 0.0050 |
| 460 | 0.0050 |
| 500 | 0.0040 |
| 580 | 0.0090 |
| 600 | 0.0000 |
| 700 | 0.0000 |
| 760 | -0.0010 |
| 880 | 0.0000 |
| 950 | 0.0050 |
| 950 | 0.0020 |
| 950 | 0.0030 |

## TABLE 3

### Thermolysis of Hexaphenyldilead (0.8764 g)

| Temperature (°C) | Weight (g) |
|---|---|
| 120 | 0.8934 |
| 160 | 0.8874 |
| 230 | 0.8824 |
| 250 | 0.8764 |
| 260 | 0.8744 |
| 270 | 0.8674 |
| 280 | 0.8464 |
| 290 | 0.7574 |
| 300 | 0.6324 |
| 310 | 0.4774 |
| 320 | 0.4694 |
| 340 | 0.4684 |
| 380 | 0.4604 |
| 400 | 0.4544 |
| 420 | 0.4484 |
| 460 | 0.4354 |
| 500 | 0.4224 |
| 540 | 0.3934 |
| 580 | 0.3914 |
| 800 | 0.4024 |
| 820 | 0.4044 |
| 860 | 0.4034 |
| 900 | 0.3994 |
| 920 | 0.3944 |
| 960 | 0.3864 |

# TABLE 4

Thermolysis of Hexaphenyl dilead (0.8764 g)

| Temperature (°C) | Weight loss (g) |
|---|---|
| 20 | 0.0000 |
| 120 | 0.0000 |
| 160 | 0.0070 |
| 230 | 0.0010 |
| 260 | 0.0040 |
| 270 | 0.0070 |
| 280 | 0.0210 |
| 290 | 0.0890 |
| 300 | 0.1250 |
| 310 | 0.1550 |
| 320 | 0.0080 |
| 360 | 0.0050 |
| 400 | 0.0060 |
| 440 | 0.0080 |
| 500 | 0.0070 |
| 540 | 0.0060 |
| 600 | 0.0010 |
| 680 | 0.0000 |
| 800 | -0.0070 |
| 840 | 0.0000 |
| 900 | 0.0020 |
| 940 | 0.0060 |

# TABLE 5

Thermolysis of Triphenyl lead chloride
(0.4503 g)

| Temperature (°C) | Weight (g) |
|---|---|
| 0 | 0.4503 |
| 120 | 0.4503 |
| 140 | 0.4493 |
| 160 | 0.4483 |
| 170 | 0.4453 |
| 180 | 0.4433 |
| 200 | 0.4403 |
| 210 | 0.4393 |
| 220 | 0.4383 |
| 230 | 0.4363 |
| 240 | 0.4283 |
| 250 | 0.4243 |
| 270 | 0.4193 |
| 280 | 0.4123 |
| 290 | 0.3973 |
| 300 | 0.2873 |
| 310 | 0.2543 |
| 330 | 0.2443 |
| 360 | 0.2403 |
| 390 | 0.2323 |
| 430 | 0.2263 |
| 460 | 0.2203 |
| 480 | 0.2153 |
| 510 | 0.2043 |
| 540 | 0.1993 |

## TABLE 6

Thermolysis of Triphenyl lead hydroxide
(0.4589 g)

| Temperature (°C) | Weight loss (g) |
|---|---|
| 20 | 0.0000 |
| 70 | 0.0000 |
| 130 | 0.0000 |
| 160 | 0.0010 |
| 170 | 0.0030 |
| 210 | 0.0010 |
| 230 | 0.0020 |
| 240 | 0.0080 |
| 260 | 0.0030 |
| 290 | 0.0150 |
| 300 | 0.1100 |
| 310 | 0.0130 |
| 320 | 0.0090 |
| 340 | 0.0020 |
| 370 | 0.0030 |
| 390 | 0.0030 |
| 420 | 0.0000 |
| 440 | 0.0020 |
| 470 | 0.0030 |
| 490 | 0.0040 |
| 520 | 0.0030 |
| 540 | 0.0000 |

# TABLE 7

Thermolysis of Triphenyl lead chloride
(0.4772 g)

| Temperature (°C) | Weight of $Ph_3PbCl$ (g.) |
|---|---|
| 0 | 0.4772 |
| 140 | 0.4782 |
| 200 | 0.4772 |
| 230 | 0.4722 |
| 240 | 0.4662 |
| 250 | 0.4552 |
| 260 | 0.4452 |
| 270 | 0.3272 |
| 280 | 0.2872 |
| 290 | 0.2792 |
| 310 | 0.2752 |
| 340 | 0.2712 |
| 360 | 0.2092 |
| 400 | 0.2652 |
| 440 | 0.2622 |
| 500 | 0.2572 |
| 560 | 0.2502 |
| 580 | 0.2542 |
| 610 | 0.2282 |
| 640 | 0.2072 |
| 680 | 0.1822 |
| 740 | 0.1442 |
| 780 | 0.1292 |
| 800 | 0.1202 |
| 840 | 0.0922 |
| 900 | 0.0642 |
| 960 | 0.0462 |
| 960 | 0.0302 |
| 960 | 0.0222 |

## TABLE 8

Thermolysis of Triphenyl lead chloride
(0.4772 g)

| Temperature (°C) | Weight loss (g) |
|---|---|
| 20 | 0.0000 |
| 120 | 0.0000 |
| 180 | 0.0000 |
| 220 | 0.0020 |
| 240 | 0.0060 |
| 250 | 0.0110 |
| 260 | 0.0100 |
| 270 | 0.1180 |
| 280 | 0.0400 |
| 290 | 0.0080 |
| 310 | 0.0020 |
| 350 | 0.0010 |
| 400 | 0.0020 |
| 440 | 0.0010 |
| 560 | 0.0030 |
| 600 | 0.0090 |
| 620 | 0.0110 |
| 640 | 0.0100 |
| 660 | 0.0130 |
| 720 | 0.0150 |
| 840 | 0.0160 |
| 880 | 0.0090 |
| 920 | 0.0060 |
| 960 | 0.0040 |

pH is maintained at 9.5 by addition of hydrochloric acid. This is treated with 7.5 ml. of 0.005% dithizone in carbon tetrachloride followed by 17.5 ml. of carbon tetrachloride. The solution is vigorously shaken and layer is allowed to separate. Lead thizone is red. The upper layer is yellowish. If carbon tetrachloride is bright deep red and the upper layer is colorless, there is a probability of too much lead in the sample. Enough of carbon tetrachloride layer is carefully transferred to fill one cm experimental cell and the optical density is determined at 520 mμ by a Beckmann spectrophotometer. Optical density is also determined by 1% $HNO_3$ standard lead solution.

The results of these analysis are given in Table I.9

## RESULTS AND DISCUSSION

The above mentioned derivatives on heating under reduced pressure give tetraphenyl lead in quantitative yield, which sublimed out at the temperature above 240°C.

When tetraphenyl lead (0.524 g) was heated inside the furnace of the thermobalance, it sublimed out between the temperature range of 250-350°C, yield being about 57%. The remaining tetraphenyl lead may probably decompose with the formation of free radicals and metallic lead as reported earlier[2]. But the decomposition mechanism is not yet clear[3]. The rate of sublimation was very fast at about 300°C and become slow after 350°C. The loss in weight continued up to 580°C, but no loss was observed between 580 and 620°C. The product shows a gain in weight from 620 to 800°C. It is due to the oxidation of metallic lead to lead oxide or due to partial conversion of lower oxide to higher oxide. Lead silicate glasses are formed above 690°C. In this case the color was dark yellow due to the formation of ortho silicate glass ($Pb_2SiO_4$). Its formation takes place above 717°C. However, when silicate glasses are heated above 876°C, they dissociate into the following manner[4]:

$$PbO.nSiO_2 \longrightarrow PbO + nSiO_2$$

On heating above 800°C, the residue shows a continuous slow loss in weight, probably due to the formation of some mixed oxides of lead. The definite composition of the residue could not be ascertained at any stage above 350°C. The slow loss in weight continued even on heating the sample at 950°C for an hour. The probable decomposition fragments except tetraphenyl lead could not be ascertained due to unsuitable trapping device. A perusal of the Fig. 2.1A and 2.2B clearly shows the nature of decomposition of tetraphenyl lead as discussed above.

Similarly hexaphenyl dilead (0.876 g) was heated in the range of 25°-950°C. From 240°C the compound showed similar decomposition pattern as observed in the case of tetraphenyl lead (Fig. 2.1B and 2.2B). The probable decomposition may take place according to the following manner:

### TABLE IX

1 g. of each compound was taken in each case

| Compound | Temp. °C and 2 mm | Wt. of sublimed product | Analysis of sublimed product | | | | | |
|---|---|---|---|---|---|---|---|---|
| | | | % Found | | | % Calculated | | |
| | | | C | H | Pb | C | H | Pb |
| $PbPh_4$ | 285 | 0.9187 | 59.0 | 2.36 | 38.63 | 55.9 | 3.88 | 40.22 |
| $Ph_6Pb_2$ | 250-280 | 0.7984 | 58.0 | 2.62 | 39.2 | 55.9 | 3.88 | 40.22 |
| $Ph_3PbCl$ | 220-270 | 0.6234 | 57.1 | 3.6 | 38.9 | 55.9 | 3.88 | 40.22 |
| $Ph_3PbOH$ | 200-265 | 0.6936 | 60.7 | 3.2 | 35.1 | 55.9 | 3.88 | 40.22 |

$$2(C_6H_5)_6Pb_2 \longrightarrow 3(C_6H_5)_4Pb + Pb \qquad (1)$$

or

$$(C_6H_5)_6Pb_2 \longrightarrow (C_6H_5)_4Pb + (C_6H_5)_2Pb \qquad (2)$$

Both the decomposition processes have been reported earlier[1]. If diphenyl dilead is formed as shown in step 2, it is unstable and further decomposes as:

$$3(C_6H_5)_2Pb \longrightarrow (C_6H_5)_6Pb_2 + Pb \qquad (3)$$

$$(C_6H_5)_2Pb + H_2O \longrightarrow PbO + 2C_6H_6 \qquad (4)$$

The decomposition process mentioned in step (4) is not observed by us because no loss in weight was observed below 240°C. If this process is at all possible, then simultaneous hydrolysis[11] and evolution of two moles of benzene (loss 0.156 g approximately) must be observed below 250°C. Benzene was not detected here. It is possible that oxidation of benzene might have taken place. The products during the oxidation of benzene at 380 to 565°C are CO, $CO_2$ and small amount of phenol and benzoquinone[12]. None of these products have been detected.

Triphenyl lead chloride (0.477 g) does not show any loss on heating up to 230°C and after that a rapid loss between 240-300°C (Fig. 2.1C and 2.2C) has been observed. The probable decomposition mechanism may take place according to the following scheme[13,14]:

$$2(C_6H_5)_3PbCl \longrightarrow (C_6H_5)_2PbCl_2 + (C_6H_5)_4Pb \qquad (5)$$

$$2(C_6H_5)_2PbCl_2 \longrightarrow (C_6H_5)_3PbCl + C_6H_5PbCl_3 \qquad (6)$$

$$C_6H_5PbCl_3 \longrightarrow C_6H_5Cl + PbCl_2 \qquad (7)$$

During decomposition of part of tetraphenyl lead sublimed out and the remaining part decomposes as described earlier. The other decomposition fragments like $(C_6H_5)_3PbCl$ or $C_6H_5PbCl_3$ could not be detected. The yield of $PbCl_2$ was quantitative. The $PbCl_2$ was found stable up to 570°C and after that a slow loss in weight was observed due to slow evaporation of $PbCl_2$, which is not completed even up to 950°C. The second part of the experiment was verified by taking same weight of $PbCl_2$ and repeating the experiment under similar conditions.

Lastly triphenyl lead hydroxide was heated (0.450 g) This shows a loss in weight between 150-190°C corresponding to one molecule of water.

$$2(C_6H_5)_3PbOH \longrightarrow (C_6H_5)_2PbO + (C_6H_5)_4Pb + H_2O \qquad (8)$$

This particular compound starts decomposing near about 230°C and become rapid from 250°C, very fast from 280°C and become slow after 320°C (Fig. 2.1D and 2.2D). The slow loss continued up to 550°C and no appreciable change was observed beyond 550°C. The different nature of the decomposition curve clearly indicates that the major part of the compound decomposes to metal oxide. The mechanism of decomposition of $(C_6H_5)_2PbO$ could not be ascertained.

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# CHAPTER III

# PHOTOCHEMISTRY AND RADIATION CHEMISTRY OF TIN TETRAPHENYL IN BENZENE AND CYCLOHEXANE

## INTRODUCTION

The effects of high energy radiations on a number of organic substances have been studied during the past three decades. One of the main objective in such studies was to find out some new products. Other aim was to find out the stability of these compounds near a nuclear reactor. Still other interest was to find the basic entities that are formed by the interaction of radiation with these substances. The products thus formed may react with the original compound, with themselves and with the solute.

When a small quantity of a solute is added to a pure solvent and it is subjected to photolysis or radiolysis, the products and its quantities are changed considerably. The decomposition products of the solvent can react with the solute in several ways such as ion-molecule reactions, excitation, charge transfer, radical scavenging, negative ion formation and several other processes[1-2]. It has been found out that benzene when mixed with cyclohexane reduces the yield of $H_2$.[3] This is explained by a charge transfer mechanism and benzene is protected.

If scintillator solutes such as p-terphenyl or anthracene is added to benzene and subjected to high energy gamma radiation, luminescence is emitted. It is concluded that benzene molecules transfer energy to the scintillator solutes. However, the entire energy is not transferred to the receptor molecule. This leads to the decomposition of benzene. Another possibility is that the energy transfer takes place through a different excited benzene molecule which does not decompose by itself.

Therefore tin tetraphenyl was selected for this study to find out its stability towards radiation, as well as its effect on different photolytic and radiolytic product of benzene and cyclohexane. Such study might help in assessing the extent of radiological protection of the solvent by addition of a small amount of solute which may act either as a scintillator or quencher.

## EXPERIMENTAL

### PURIFICATION OF MATERIALS

**Benzene:** Analar grade benzene is purified by three successive crystallizations with rejection of about 20% of benzene at each freezing. It is distilled after the addition of sodium metal.

Cyclohexane: The impurities are extracted by concentrated sulphuric acid and the organic layer is separated from the acid, washed with a solution of sodium hydroxide and then several times with distilled water, dried with $CaCl_2$ and refluxed and distilled over sodium in a column. The middle fraction, of the constant boiling point, is collected and stored over sodium.

## Sample Preparation

Calibrated cells of approximately 20 ml. volume, constructed from about 12 mm O.D. pyrex tubing is used. It is attached to a high vacuum manifold. Depending on personal preference, there are two methods to prepare samples. Appropriate volume of the liquid is pipetted into a number of sample cells which are attached to a vacuum line through greased ground glass joints. Conventional freeze and thaw technique is used to degas the sample. In an adjacent section of the vacuum line pure benzene or cyclohexane is rigorously degasses by a reflux method. In this method liquid in a 500 ml round bottom flask, is agitated by a magnetic stirrer. Purified nitrogen is passed through a glass spiral immersed in liquid nitrogen before entering the cyclohexane. After approximately 15 minutes, the container is closed with a ground glass joint, the liquid is frozen at liquid air temperature and the system is evacuated. The liquid is melted and nitrogen is passed through a second time. The freezing and evacuation

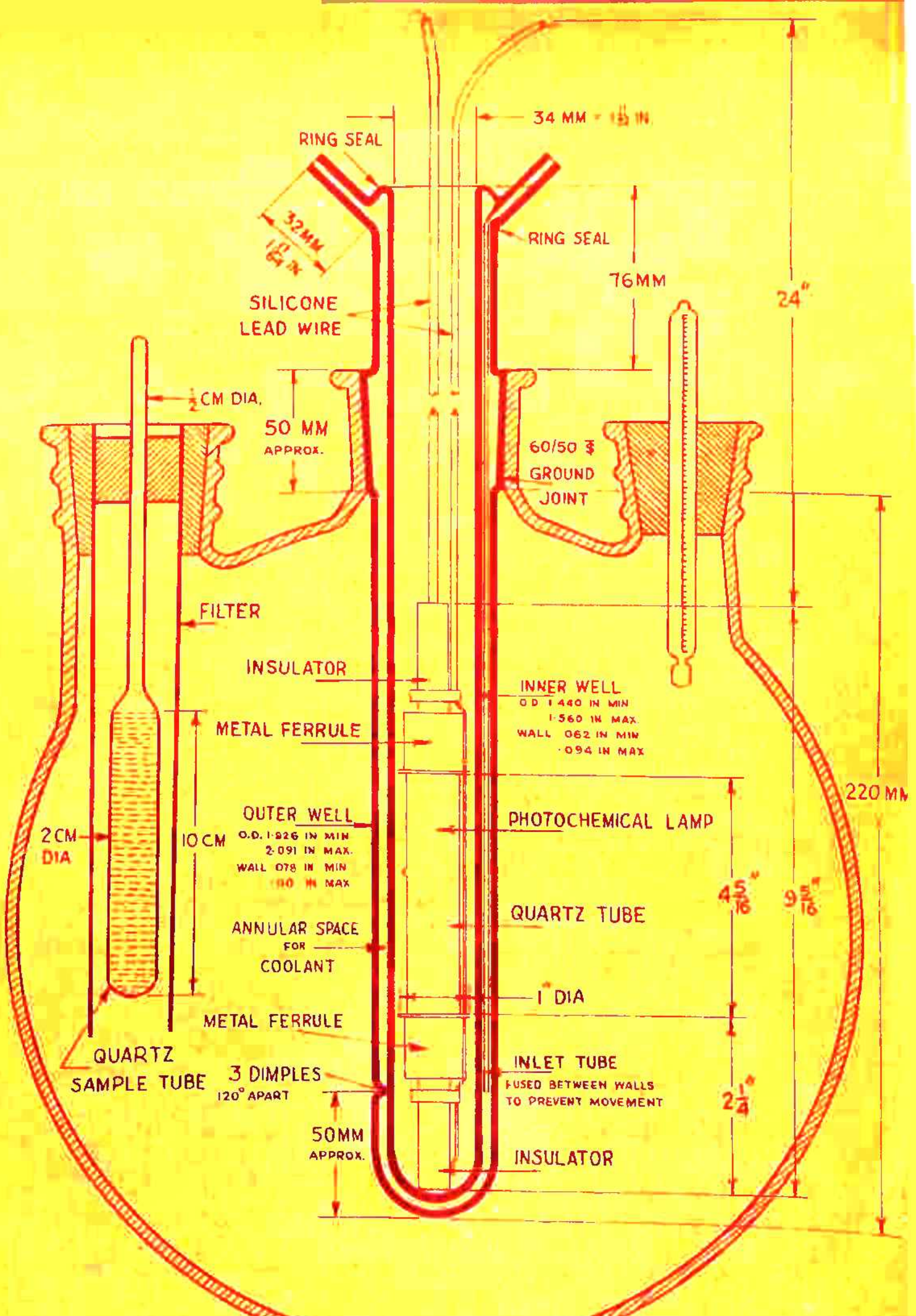


FIG 3·1 HANOVIA PHOTOCHEMICAL EQUIPMENT

process is repeated. A glass cold finger cooled by copper rod itself immersed in a Dewar containing liquid nitrogen is introduced into a glass distillation column above the flask containing the liquid, the latter still agitated by a magnetic stirrer, is refluxed continuously in the column. The organic vapour is condensed around the cold finger, while nitrogen is collected in an external trap. The gas is removed regularly at frequency intervals by opening the stopcock to the vacuum line for a short time. This procedure is continued for four hours until all gas is removed. Then approximately 20 ml degassed liquid is distilled under vacuum into each of the reaction vessels in turn. The exact amount of liquid added is determined later by weighing. After filling a cell, it was isolated from the liquid reservoir and sealed off under vacuum before filling the next cell. Due to limitations, the former method was used for sample preparations.

A brief description of the U.V. and gamma irradiation sources and measurements of radiation dose are described below.

## Hanovia Laboratory Scale Photochemical Apparatus

Each component of the light source and relative accessories are shown in Fig. 3.1. An Immersion Well assembalies No. 19434 in clear fused quartz was fitted in a five litres flask. The assembalies are available in

Quartz or heat-resistant vycer glass No. 7910. Quartz has been preferred because it transmits the complete ultraviolet spectrum 1849 Å to 4000 Å, visible light and infra-red. In addition quartz is more resistant to polarization than Vycer.

Double-walled well assembalies are fabricated from two concentric tubes circumferentially sealed at bottom and telescoped one within the other. A ring seal at top joins both tubes. An inlet and outlet at top provides entrance and exit of coolant, water. A small diameter tube attached to inlet extends down annual space to ensure flow of water from bottom of well upwards to the outlet.

The outer well contains a 60/50 standard tapered ground joint to fit the 60/50 center neck available on standard 5 liter flask. The 60/50 dimension is required to accommodate, outer well, inner well, coolant space, absorption sleeve and laboratory type lamp.

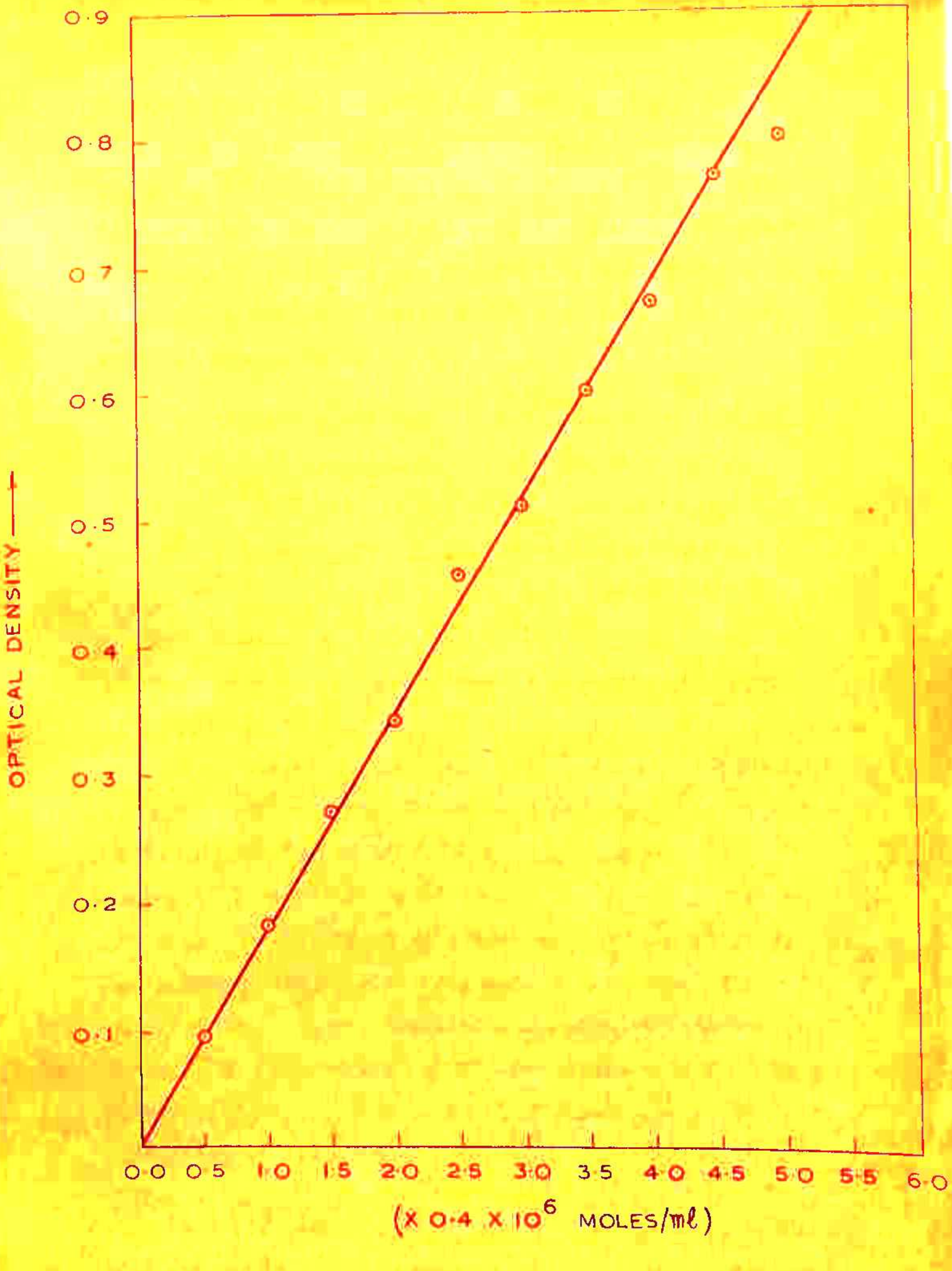
The source of radiant energy in the laboratory reactor is a Hanovia high-pressure quartz mercury-vapour lamp No.679A-36 of 450 watts. Of the total energy radiated, approximately 30% is in the ultraviolet portion of the spectrum, 18% in the visible and the balance in infra-red. The lamp is operated by Hanovia made reactive type transformers, which supply the extra voltage and current required to initiate the arc and reduced power for operation.

Absorption sleeve made of 7910 Vycor glass are used. The sleeve telescopes into well assembly to surround the light source. The absorption quality of Vycor 7910 restricts the radiant energy near the region 2537 Å.

The Determination of Quantum Yield

The potassium ferrioxalate system developed by Parker[5] and Hatchard[6] is the best solution-phase chemical actinometer. It is very sensitive over a wide range of wavelengths and it is simple to use. If $K_3Fe(C_2O_4)_3$ is dissolved in sulfuric acid and irradiated in the range 2500-5770 Å, Fe(III) is reduced to Fe(II) and oxalate ions are oxidized. The product ferrous ion and its oxalate complex in these solutions do not absorb the incident radiation measurably during the photolysis. After exposure Fe(II) is made to form a complex with 1,10-phenonthroline. The complex absorbs very highly and can be used in spectrophotometric analysis. The other advantage of this actinometer is that the time of irradiation is cut off considerably. The greater utility of this actinometer over the classical uranyl oxalate actinometer is that the quantum yield is almost independent of reactant and product concentrations, intensity of incident light and temperature. The experimental details are described below.

The volumes of 1.5 M $K_2C_2O_4$ solution and one volume of 1.5 M $FeCl_3$ solution (A.R. grade) are mixed with



CONCENTRATION IN MOLES/ml

FIG 3·2 DETERMINATION OF ABSORBANCE OF POTASSIUM FERRIOXLATE AT DIFFERENT CONCENTRATIONS.

vogorous stirring. A precipitate of $K_3Fe(C_2O_4)_3.3H_2O$ is obtained. It is crystallized thrice from warm water and dried in a current of warm air at 45°C. The solid is stored in dark for a long period of time. A 0.006 M solution of $K_3Fe(C_2O_4)_3$ is prepared by dissolving 2.947 g. of solid in 800 ml of water and 100 ml 1.0 N sulfuric acid and making up to 1 litre.

A standard 0.1 M $FeSO_4$ solution in 0.1 M sulfuric acid is freshly prepared and diluted so that $Fe^{++}$/ml is about $0.4 \times 10^{-6}$ mole in 0.1 N $H_2SO_4$ called a. A buffer solution containing 600 ml of 1 N sodium acetate and 360 ml 1N sulfuric acid is made to 1 litre, called b. Another solution containing 0.1% (by weight) 1,10-phenonthroline in water is also prepared, called c. Eleven 25 ml volumetric flasks are taken and with a graduated pipette 0, 0.5, 1.0, 1.5, ....., 4.5, 5.0 ml of solution a is dropped into it. The volume in each flask is made to 10 ml by addition of 0.1 N $H_2SO_4$. Add about 2 ml solution b and 5 ml solution c, make upto the mark and allow the solutions to stand for one hour in dark. The transmission of each solution is determined at 5100 A in 1.1 CM cell, using the blank iron-free solution. The plot of log $I/I_0$ versus molar concentration of $Fe^{++}$ is linear (Fig. 3.2). Its slope will give slope of the molar extinction coefficient.

The ferrioxalate solution is added to the reaction cell and irradiated for a known time t. Let the volume of the solution taken be $V_1$. The irradiated solution is mixed well and an aliquot volume $V_2$ is pipetted out and added to a volumetric flask $V_3$. It is made upto the mark by distilled water and allowed to stand for one hour. An identical but unirradiated solution is used as a blank. The transmission of the solution in the spectrophotometer at 5100 Å in 1.1 cm cell is measured using the blank solution in the reference beam. The number of ions of $Fe^{2+}$ formed during the photolysis ($n_{Fe^{2+}}$) may be calculated by using the expression

$$n_{Fe^{2+}} = \frac{6.023 \times 10^{20}\, V_1 V_3 \log_{10}(I_o/I)}{V_2\, l\, \epsilon}$$

where $V_1$ = the volume of actinometer solution irradiated (ml)

$V_2$ = the volume of aliquot taken for analysis (ml)

$V_3$ = the final volume to which aliquot $V_2$ is diluted (ml)

$\log_{10} I_o/I$ = the measured O.D. of the solution at 5100 Å

$l$ = the path length of the spectrophotometer cell used (cm)

$\epsilon$ = the experimental value of the molar extinction coefficient of the $Fe^{2+}$ complex ($1.11 \times 10^4$ litres/mole-cm is the standard value).

The quantum yield of $Fe^{+2}$ in the potassium ferrioxalate chemical actinometer at room temperature for wavelength 2537 Å is 1.25.[7]

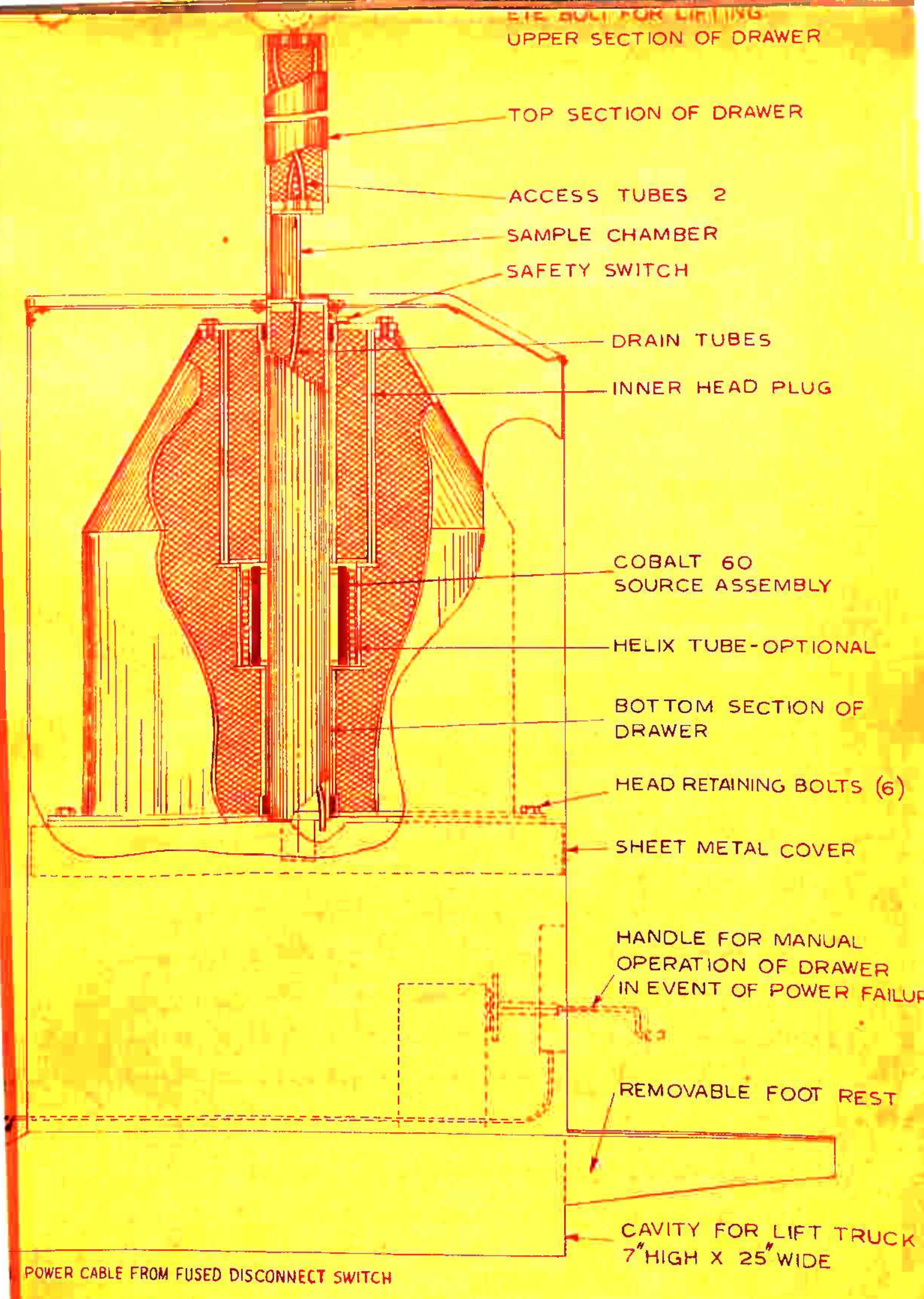


FIG. 3.3 SIDE ELEVATION SHOWING SECTION OF HEAD AND DRAWER GAMMACELL 200

The experimental data determined for this purpose is as follows:

$V_1 = 10$ ml $\qquad \log_{10} I_o/I = 0.305$

$V_2 = 5$ ml $\qquad l = 1.1$ cm

$V_3 = 25$ ml $\qquad \epsilon = 1.11 \times 10^4$

$$n_{Fe^{2+}} = \frac{6.023 \times 10^{20} \times 10 \times 25 \times 0.305}{5 \times 1.1 \times 1.11 \times 10^4}$$

$$= 7.5 \times 10^{16}$$

Therefore intensity of light $= \frac{7.5 \times 10^{16}}{1.25 \times 60} = 10^{16}$ quanta/sec

$$= 10^{16} \times \frac{1000}{10} \times 60$$

$$= 6 \times 10^{19} \text{ quanta } l^{-1} \text{ minute}^{-1}$$

## Irradiation Research Equipment-Gammacell 200

The Gammacell 200 Irradiator for high intensity gamma irradiation research is given in Fig. 3.3. It is capable of housing an annular cobalt 60 source having a total activity of two kilocuries corresponding to an output of approximately $6 \times 10^5$ roentgen per hour at the midpoint of the irradiation chamber without exceeding tolerance levels of radiation about the unit as established by the United States National Committee on Radiation Protection[6].

The cobalt 60 source consists of 24 linear source elements arranged in a stainless steel rack to form the equivalent of a radioactive cylinder or annulus. Each source element consists of a welded stainless steel pencil filled with Cobalt 60 in the form of metallic cobalt. The inner dimensions of each pencil are 0.395" diameter and 5.671" length. The diameter of the cylindrical source measured from centre to centre of the pencil is 5.5". The position of the source remains fixed relative to the source housing at all times. The source housing consists of a steel-encased lead shield. Provision is made in the shield for location of the cylindrical source and an optional helix together with a head plug which rests above the source.

A power driven drawer, containing the sample chamber, moves vertically inside both the source and the shielding. When the drawer is raised to its maximum position, the sample chamber is outside the shielding, where it can be safely loaded. For irradiation the drawer is lowered until the sample chamber locates automatically within the cobalt source. The drawer is made up of three parts: (a) the top section, (b) the sample chamber, and (c) the lower section. The top section of the drawer consists of a steel encased lead cylinder. Two stainless steel tubes 5/16" internal diameter pass down the full length of the cylinder. The tubes are in the form of a spiral to prevent gamma radiation leakage. The sample chamber is located above the lower section of the drawer and is constructed of chromium-plated mild steel. A removable cover plate provides easy access to the chamber. The cover is locked by means of a simple spring retainer at the top of the cover. The lower section of the drawer is made up of lead encased in a cylindrical steel shell. A stainless steel drainage tube 5/16" inside diameter passes through the full length of this section. The drawer is moved upto two feet by an electric motor operating through a suitable screw driver.

## Measurement of the Radiation Dose

The measurement of energy absorbed in a medium exposed to ionizing radiation is called radiation dosimetry. Radiations are classified into two groups: electromagnetic radiations and corpuscular radiations. When X-rays and gamma rays pass through the matter and are absorbed, ionization takes place by virtue of secondary electrons released Since alpha and beta particles, eléctrons, and protons are charged particles, they produce primary ionisation on collision with substrate.

A dosimeter solution should not be affected by concentration of reactants and products, pH changes, quality and dose rate of radiation over a wide range. The analytical procedure should be as simple as possible and all solutions should be usable in equilibrium with natural surroundings.

The ferrous-ferric system is the most widely used and universally accepted system of dose measurement at the present time. It was first suggested by Fricke and Morse[9]. They suggested the use of $Fe\,SO_4$ in air-saturated, 0.4 molar sulfuric acid as a method for measuring X-ray dose. This concentration of sulfuric acid was selected because it raises the gram absorption coefficient of the medium to that of air for X-rays of 0.9 to 0.2 Å in wavelengh[10]. Krenz and Dewhurst[11] have proposed the following mechanism.

1. $H_2O \rightleftharpoons H^{\cdot} + {}^{\cdot}OH$
2. $Fe^{2+} + {}^{\cdot}OH \longrightarrow Fe^{3+} + OH^-$
3. $H^{\cdot} + O_2 \longrightarrow HO_2^{\cdot}$
4. $Fe^{2+} + HO_2^{\cdot} \longrightarrow Fe^{3+} + HO_2^-$
5. $HO_2^- + H^+ \rightleftharpoons H_2O_2$
6. $Fe^{2+} + H_2O_2 \longrightarrow Fe^{3+} + OH^- + {}^{\cdot}OH$
7. $H^+ + OH^- \longrightarrow H_2O$

It has been shown that the primary radiation process in water involves the formation of molecular hydrogen and hydrogen peroxide formation. The mechanism involves the following steps each of which may interact with the ferrous ion.

1. $H_2O \longrightarrow H^{\cdot} + OH^{\cdot} + H_2 + H_2O_2$
2. $OH^{\cdot} + H_2 \longrightarrow H_2O + H^{\cdot}$

3. $H^{\cdot} + H_2O_2 \longrightarrow H_2O + {}^{\cdot}OH$

4. ${}^{\cdot}OH + H_2O_2 \longrightarrow H_2O + HO_2^{\cdot}$

5. $HO_2^{\cdot} + HO_2^{\cdot} \longrightarrow H_2O_2 + O_2$

6. $H^{\cdot} + O_2 \longrightarrow HO_2^{\cdot}$

The number of atoms reacted per 100 ev is known as G value. The most accepted G value for the $Fe^{+++}$ formation is 15.6[12-14]. The concentration of $Fe^{++}$ ions in the dosimeter solution should be kept between $10^{-3}$-$10^{-4}$ molar. When the concentration drops to a value lower than $2 \times 10^{-5}$ molar lower yields of $Fe^{3+}$ ions are obtained. The sulfuric acid concentration in the solution may vary from 0.1 to 0.75 molar. The yield of $Fe^{3+}$ ions is diminished, when the acidity is below 0.1 molar. The temperature coefficient of $Fe^{3+}$ yield is very small between $0^{\circ}$ and $50^{\circ}C$. Since the oxidation of $Fe^{2+}$ ion requires oxygen, the yield of $Fe^{3+}$ ion is reduced when solutions are depleted in oxygen. However, it is not necessary to consider the availability of oxygen at moderate dose rate.

### The Dosimetry Solution and Sample

Ordinary distilled water is purified by redistillation from an alkaline permanganate solution and then from an acid dichromate solution to reduce the amount of organic impurities present. Better purification is achieved by refluxing the alkaline and acid solutions for a long time before distillation. The glassware is treated with concentrated sulfuric acid containing few crystals of potassium dichromate. This solution should be handled very carefully. The glassware is washed with tap, distilled and triply distilled water.

The undue wall effects are eliminated by using a pyrex glass container having an inner diameter of at least 8 mm for gamma radiation[15-16]. Thus practically all the secondary electrons contributing to the energy absorption originate in the solution.

Analytical reagent grade 0.4 g. of $Fe\ SO_4 . 7H_2O$ 0.06 g of sodium chloride and 22 ml of 95-98 per cent sulfuric acid is dissolved in sufficient triply distilled water to make one litre of solution. Chloride is added to the dosimeter solution to inhibit the oxidation of ferrous ions by organic impurities[17].

The sample containers are filled with this solution and the dose rate at the midpoint of the sample chamber is measured. This is done to get an uniform isodose gamma flux. The time of irradiation is carefully noted. The mean absorbed dose for the volume occupied by the dosimeter solution is derived in the following manner.

By definition

$$G_{(\text{Product})} = \frac{\text{Molecules product formed}}{\text{100 ev energy absorbed}}$$

$$1 \text{ rad} = \frac{\text{energy absorption of 100 ergs}}{\text{g}}$$

Therefore energy absorbed $= \frac{100 \times \text{molecules product formed/g}}{G_{(\text{Product})}}$

$$\times \frac{\text{ev}}{\text{g}} \times 1.602 \times 10^{-12} \ \frac{\text{erg}}{\text{ev}} \times \frac{1}{100} \ \frac{\text{g.rad}}{\text{ergs}}$$

$$= 1.602 \times 10^{-12} \times \frac{\text{molecules product formed/gram}}{G_{(\text{Product})}} \ \text{rads}$$

For the ferrous sulfate dosimeter, when the yield of ferric ions is measured spectrophotometrically,

$$\text{Fe}^{+++} \text{ ions formed (moles/l)} = \frac{\text{O.D}_i - \text{O.D}_b}{\varepsilon \ d},$$

where $\text{O.D}_i$ and $\text{O.D}_b$ are the optical density of the irradiated and non-irradiated dosimeter solution respectively, $\varepsilon$ is the molar extinction coefficient for ferric ions at the wavelengths of maximum absorption (litres/mole cm) and $d$ is the thickness of the sample (cm) used during the measurement of the optical density.

Therefore $\text{Fe}^{+++}$ ions formed (molecules/g) =

$$\frac{(\text{O.D}_i - \text{O.D}_b)}{\varepsilon \ d} \ \frac{\text{moles}}{\text{litre}} \times \frac{1}{1000\rho} \ \frac{\text{litre}}{\text{g}} \times 6.023 \times 10^{20} \ \frac{\text{molecules}}{\text{mole}}$$

Hence energy absorbed

$$= \frac{\text{O.D}_i - \text{O.D}_b}{\varepsilon \ d \ G(\text{Fe}^{+++})} \times \frac{6.023 \times 10^{20}}{\rho} \times 1.602 \times 10^{-12}$$

$$= \frac{0.965 \times 10^{9} \ (\text{O.D}_i - \text{O.D}_b)}{\varepsilon \ d \ \rho \ G(\text{Fe}^{+++})} \ \text{rads}$$

The density of the dosimeter solution is that of 0.8 N sulfuric acid i.e. 1.024 ± 0.001 between 15° and 25°C.[18]

The value of the molar extinction coefficient[19-21] at 305 mμ is 2176 ± 6 litres/mole cm at 23.7°C. The value of $G(Fe^{+++})$ is taken as 15.6 (for $Co^{60}$-gamma rays).

$$\text{Hence the dose absorbed} = \frac{0.965 \times 10^{9}\,(O.D_{i} - O.D_{b})}{2174 \times 1.024 \times 15.6\,d}\ \text{rads}$$

$$= \frac{1.75 \times 10^{18}\,(O.D_{i} - O.D_{b})}{d}\ \frac{ev}{g}$$

Since the density of the dosimeter solution is 1.024

$$\text{Dose absorbed} = \frac{1.79 \times 10^{18}\,(O.D_{i} - O.D_{b})}{d}\ \frac{ev}{cm^{3}}$$

The $Fe^{++}/Fe^{+++}$ system can be analysed by estimation of either $Fe^{++}$ or $Fe^{+++}$ ions. The ferrous ion may be determined and the amount of ferric ion is obtained by difference or the ferric ion may be determined directly. The system is most accurately determined after the solution is irradiated to the point of about 50% oxidation provided that the measurement of the desired ion is made under optimum conditions. The most accurate result is obtained by the solution whose transmittance is 36.8%. However the transmittance can vary between 13-70%. There are two most commonly used analytical procedures for ferrous-ferric system. The dosimeter solution is diluted and the phenonthroline complex is formed with ferrous ion at pH 4-5 in a buffered solution at 510 mμ. Ferric ion is directly determined by its ultraviolet absorption at 305 mμ. The procedure involves only transfer of the irradiated solution to the quartz cell and the measurement of absorbance at 305 mμ. Since the molar absorption coefficient has a temperature coefficient of +0.7 per cent per degree centigrade, temperature control must be maintained.

Other alternative method for the determination of $Fe^{+++}$ ion is by O-phenonthroline complex. The dosimetry solution must be diluted to a point where $Fe^{++}$ ion concentration is about $4 \times 10^{5}$ molar. The solution is then buffered to a pH 4-5 with 2 M sodium acetate. 1 ml of 1% aqueous O-phenonthroline solution is then added and the solution diluted to a fixed volume with triply distilled water. The color development takes place rapidly and the solutions measured in 10-15 minutes. The absorbance is measured at 510 mμ. An overall dilution of 1 to 20 should suffice for a solution that has been irradiated to 50% conversion. Thus 5 ml of dosimeter solution would have its color developed in 100 ml of analysis solution.

For the dose determination, dosimetry solutions were irradiated for 5 and 10 minutes respectively. The optical density at 305 mμ was measured using unirradiated solution as a reference.

$O.D_i - O.D_b$ was found to be 0.266 and 0.534 for 5 minutes and 10 minutes respectively.

Hence the dose rates are:

$$\frac{1.79 \times 10^{18} \, (O.D_i - O.D_b)}{d} \text{ ev/ml}$$

$$= \frac{1.79 \times 10^{18} \times 0.266}{d} \times \frac{60}{5} \text{ ev hr}^{-1}$$

$$= 5.1942 \times 10^{18} \text{ ev hr}^{-1}$$

and $$\frac{1.79 \times 10^{18} \times 0.534}{1.1} \times \frac{60}{10} \text{ ev hr}^{-1}$$

$$= 5.2137 \times 10^{18} \text{ ev hr}^{-1}$$

The average dose is taken as $5.204 \times 10^{18}$ ev hr$^{-1}$.

Approximate corrections were made for the difference of electron density of the dosimeter solution and organic liquids. For this purpose Fricke Dosimeter is multiplied by the ratio of the electron density of organic liquid to that of the electron density of dosimeter solution. The value of this ratio for benzene is taken as 0.845 and for cyclohexane as 0.785. Since the intensity of gamma radiation varies with distance, the geometry of the system is properly maintained by keeping pyrex glass cells of the same diameter and shape and always kept inthe same position.

## Samples and Irradiation

Tetraphenyl tin (m.p. 228°C) was dissolved in benzene and cyclohexane respectively at room temperature. Almost saturated solutions were prepared by dissolving maximum soluble metal phenyl at room temperature. Ten ml of tin tetraphenyl solution were taken in pyrex glass cells and were degassed by freeze and thaw technique at $10^{-2}$ mm of mercury using liquid air. Samples frozen under liquid air were sealed in vacuum. They were irradiated by 2 kilocuries $Co^{60}$-gamma radiation source at ambient temperature for half an hour or one hour. The time of irradiation by ultra violet lamp was 1 minute.

## Analysis

Due to the lack of facilities gaseous products could not be analysed. Analysers was made of the condensable products. Vapour phase chromatography was used for the analysis. It was apprehended that tin tetraphenyl could pyrolyse to some of these condensable products, giving erroneous results. Therefore, unirradiated samples of tin tetraphenyl in benzene or cyclohexane were analysed and it was found to be stable under experimental conditions.

A vapour phase chromatograph, containing a flame ionisation detector was used. For the analysis of

## TABLE 1

Photolysis of tin tetraphenyl by 2537 A° in Benzene

| Conc. of tin tetraphenyl × $10^{-3}$ M | Photoly-tic Products | | | |
|---|---|---|---|---|
| | Diphenyl × $10^{-4}$M | Q.Y. × $10^{-4}$ | Dihydrodiphenyl × $10^{-4}$M | Q.Y. $10^{-4}$ |
| 1 | 0.75 | 50.65 | 0.14 | 9.33 |
| 2 | 1.34 | 90.48 | 0.21 | 14.01 |
| 3 | 1.66 | 112.10 | 0.25 | 16.47 |
| 4 | 1.86 | 125.60 | 0.30 | 20.00 |
| 5 | 2.00 | 135.10 | 0.30 | 20.00 |
| 6 | 2.01 | 135.70 | 0.30 | 20.00 |
| 7 | 2.01 | 135.70 | 0.30 | 20.00 |
| 8 | 2.10 | 141.10 | 0.30 | 20.00 |
| 9 | 2.30 | 155.30 | 0.31 | 20.67 |
| 10 | 2.46 | 166.20 | 0.31 | 20.67 |

## TABLE 2

Radiolysis of tin tetraphenyl by $Co^{60}$-γ radiation in Benzene

| Conc. of tin tetraphenyl $\times 10^{-3}$ M | G (Diphenyl) |
|---|---|
| 0 | 0.09 |
| 1 | 0.25 |
| 2 | 0.35 |
| 3 | 0.48 |
| 4 | 0.60 |
| 5 | 0.74 |
| 6 | 0.86 |
| 7 | 0.90 |
| 8 | 0.94 |
| 9 | 0.96 |
| 10 | 1.00 |

## TABLE 3

Radiolysis of tin tetraphenyl by $Co^{60}$ - $\gamma$ radiation in Benzene

| Conc. of tin tetraphenyl × $10^{-3}$ M | G (Dihydrodiphenyl) |
|---|---|
| 0.0 | 0.045 |
| 1.0 | 0.060 |
| 1.5 | 0.065 |
| 3.5 | 0.073 |
| 4.5 | 0.071 |
| 6.0 | 0.080 |
| 7.0 | 0.085 |
| 8.0 | 0.096 |
| 9.0 | 0.096 |
| 10.0 | 0.097 |

## TABLE 4

Photolysis of tin tetraphenyl in cyclohexane

| Conc. of tin tetraphenyl × $10^{-3}$ M | Photolytic products | | | |
|---|---|---|---|---|
| | Benzene × $10^{-3}$M | Q.Y. × $10^{-3}$ | Cyclohexene × $10^{-3}$M | Q.Y. × $10^{-3}$ |
| 0.5 | 0.60 | 77 | 0.14 | 17 |
| 1.0 | 0.82 | 106 | 0.21 | 26 |
| 1.5 | 0.89 | 115 | 0.34 | 42 |
| 2.0 | 0.99 | 128 | 0.33 | 41 |

## TABLE 5

Photolysis of tin tetraphenyl in cyclohexane

| Conc. of tin tetraphenyl × $10^{-3}$ M | Photolytic products | | | |
|---|---|---|---|---|
| | Dicyclohexyl × $10^{-5}$ M | Q.Y. × $10^{-4}$ | Cyclohexanol+ cyclohexanone × $10^{-5}$ M | Q.Y. × $10^{-4}$ |
| 0.5 | 0.26 | 1.58 | 0.16 | 0.815 |
| 1.0 | 0.28 | 1.69 | 0.175 | 0.891 |
| 1.5 | 0.29 | 1.75 | 0.17 | 0.866 |
| 2.0 | 0.28 | 1.69 | 0.17 | 0.866 |

## TABLE 6

Effect of radiation dose on photolytic products of 1 × $10^{-3}$M tin tetraphenyl in cyclohexene

| Time in minutes | Photolytic products | | | |
|---|---|---|---|---|
| | Conc. of benzene × $10^{-3}$M | Q.Y. × $10^{-3}$ | Cyclohexene × $10^{-3}$ M | Q.Y. × $10^{-3}$ |
| 0.5 | 0.50 | 128 | 0.087 | 21 |
| 1.0 | 0.95 | 122 | 0.175 | 21 |
| 1.5 | 1.50 | 229 | 0.262 | 21 |
| 2.0 | - | - | 0.325 | 20 |

## TABLE 7

Effect of radiation dose on photolytic products of 1 × $10^{-3}$M tin tetraphenyl in cyclohexene

| Time in minutes | Photolytic products | | | |
|---|---|---|---|---|
| | Conc. of Dicyclohexyl $10^{-3}$ M | Q.Y. × $10^{-4}$ | Conc. of Cyclohexenol+ Cyclohexanone × $10^{-5}$M | Q.Y. × $10^{-4}$ |
| 0.5 | 0.25 | 3.02 | 0.037 | 0.38 |
| 1.0 | 0.39 | 2.36 | 0.075 | 0.38 |
| 1.5 | 0.52 | 2.10 | 0.075 | 0.29 |
| 2.0 | 0.66 | 2.00 | 0.075 | 0.19 |

## TABLE 8

Radiolysis of tin tetraphenyl by $Co^{60}$-γ radiation in cyclohexane

| Conc. of tin tetraphenyl × $10^{-3}$ M | G (Benzene) | G (Dicyclohexyl) |
|---|---|---|
| 0.00 | 0.62 | 1.5 |
| 0.25 | 1.25 | 1.5 |
| 0.50 | 2.25 | 1.5 |
| 1.00 | 4.62 | 1.5 |
| 1.50 | 5.40 | 1.75 |
| 2.00 | 5.50 | 1.5 |

## TABLE 9

Radiolysis of tin tetraphenyl by $Co^{60}$ - γ radiation in cyclohexane

| Conc. of tin tetraphenyl × $10^{-3}$ M | G (Cyclohexene) |
|---|---|
| 0.00 | 3.00 |
| 0.25 | 3.10 |
| 0.50 | 3.25 |
| 1.00 | 3.00 |
| 1.50 | 3.50 |
| 2.00 | 3.25 |

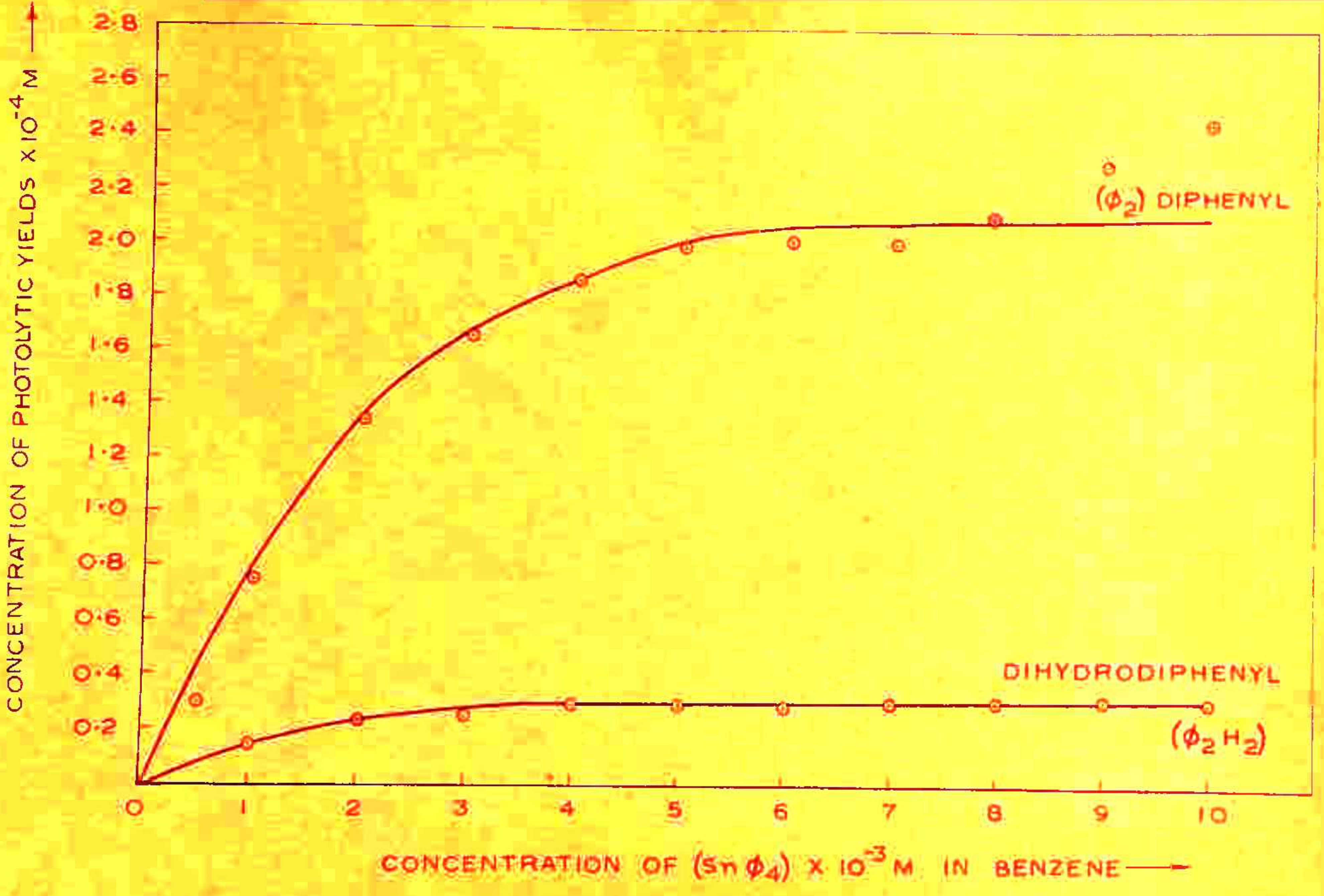


FIG. 3·4 PHOTOLYSIS OF TIN TETRAPHENYL BY 2537 Å

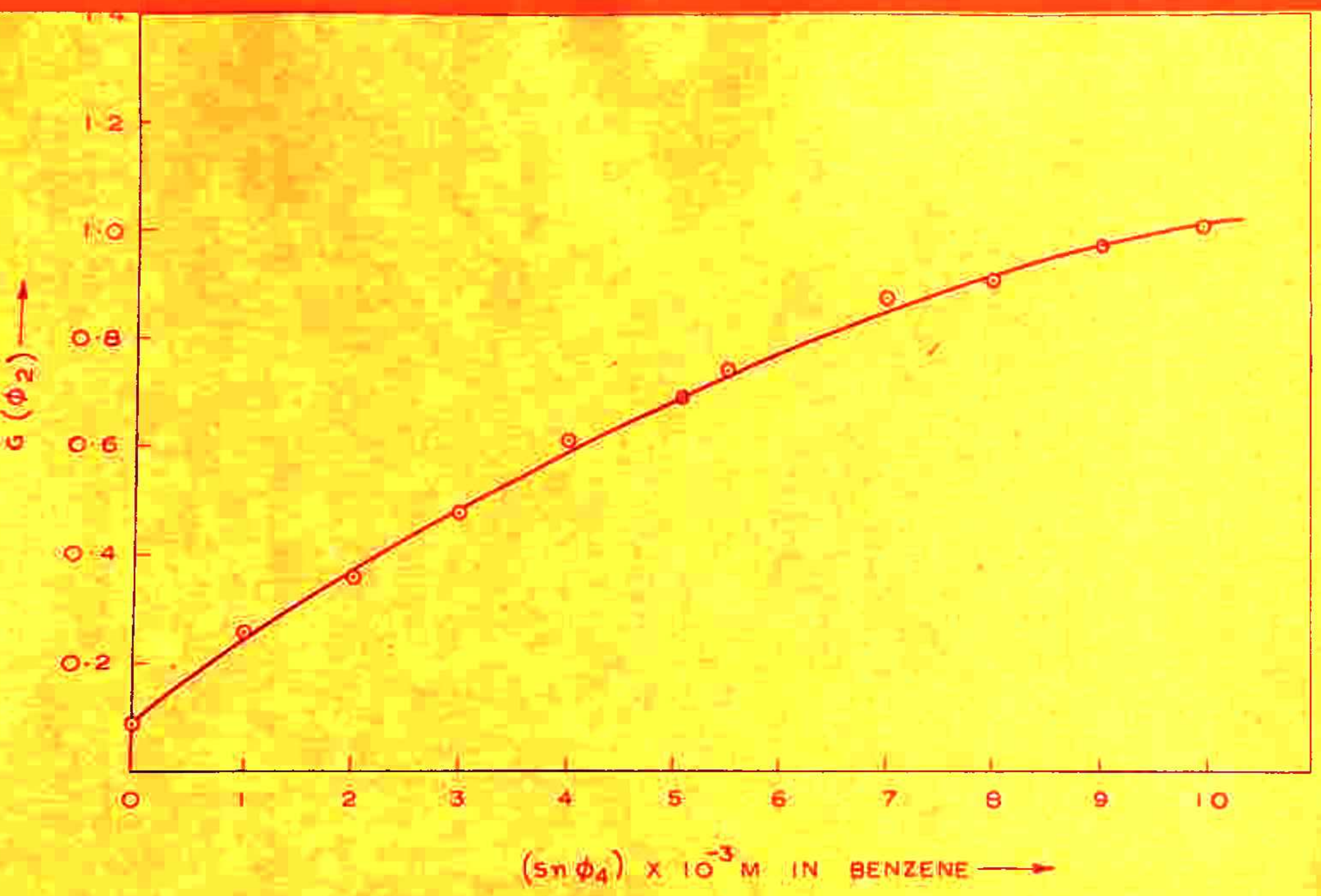


FIG. 3-5 RADIOLYSIS OF TIN TETRAPHENYL.

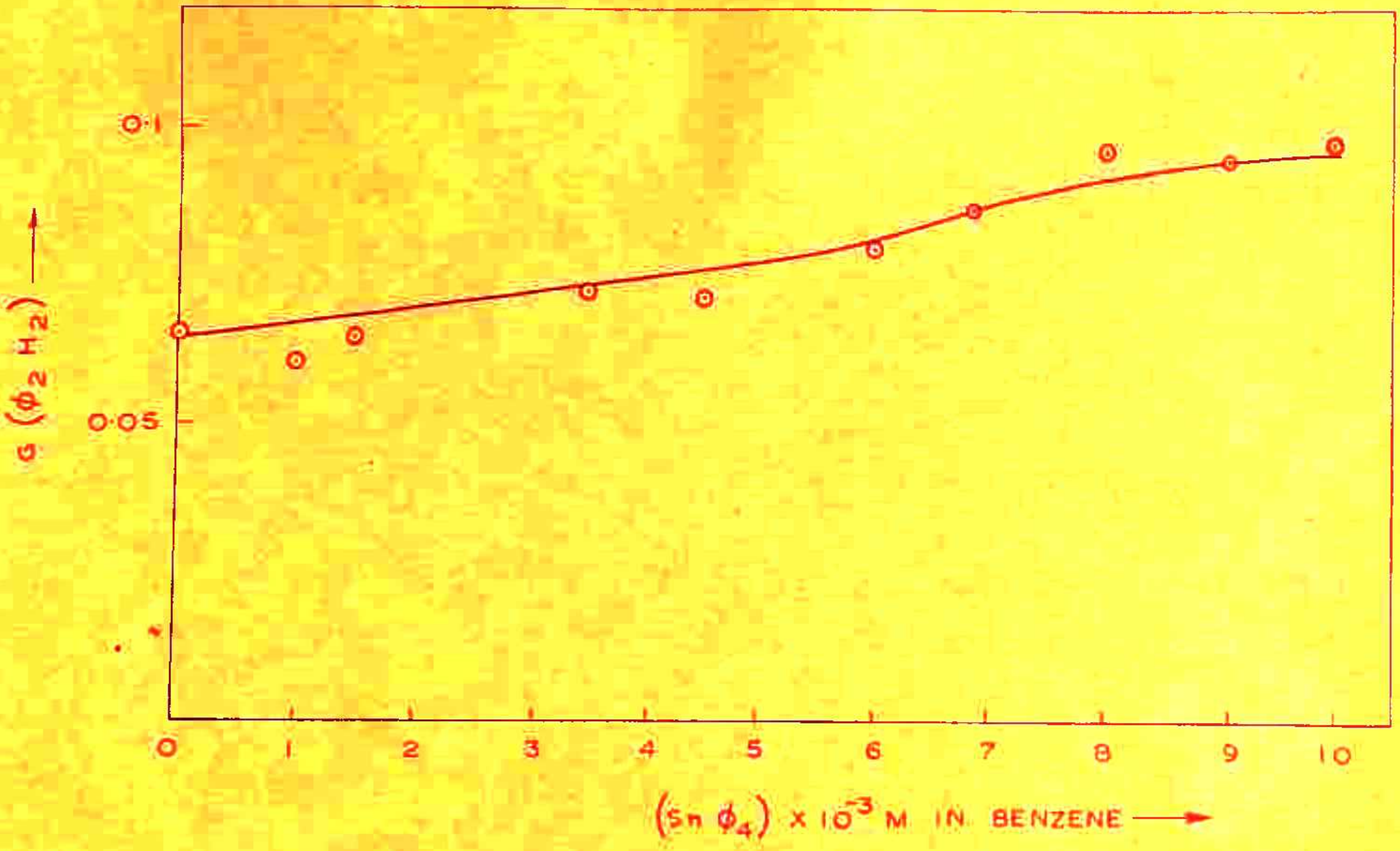


FIG. 3·6 RADIOLYSIS OF TIN TETRAPHENYL.

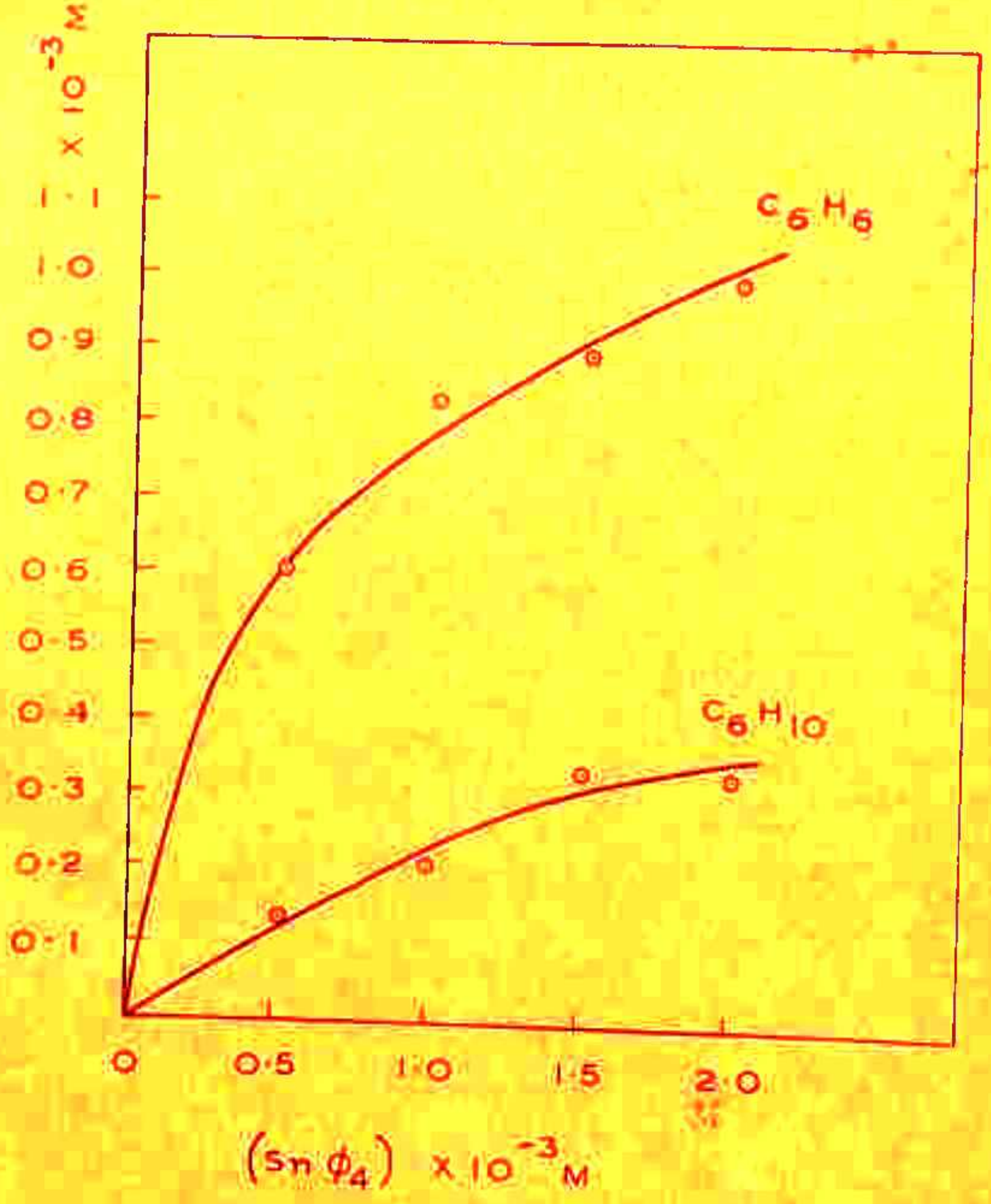


FIG. 3·7 PHOTOLYSIS OF $Sn\phi_4$ IN CYCLOHEXANE.

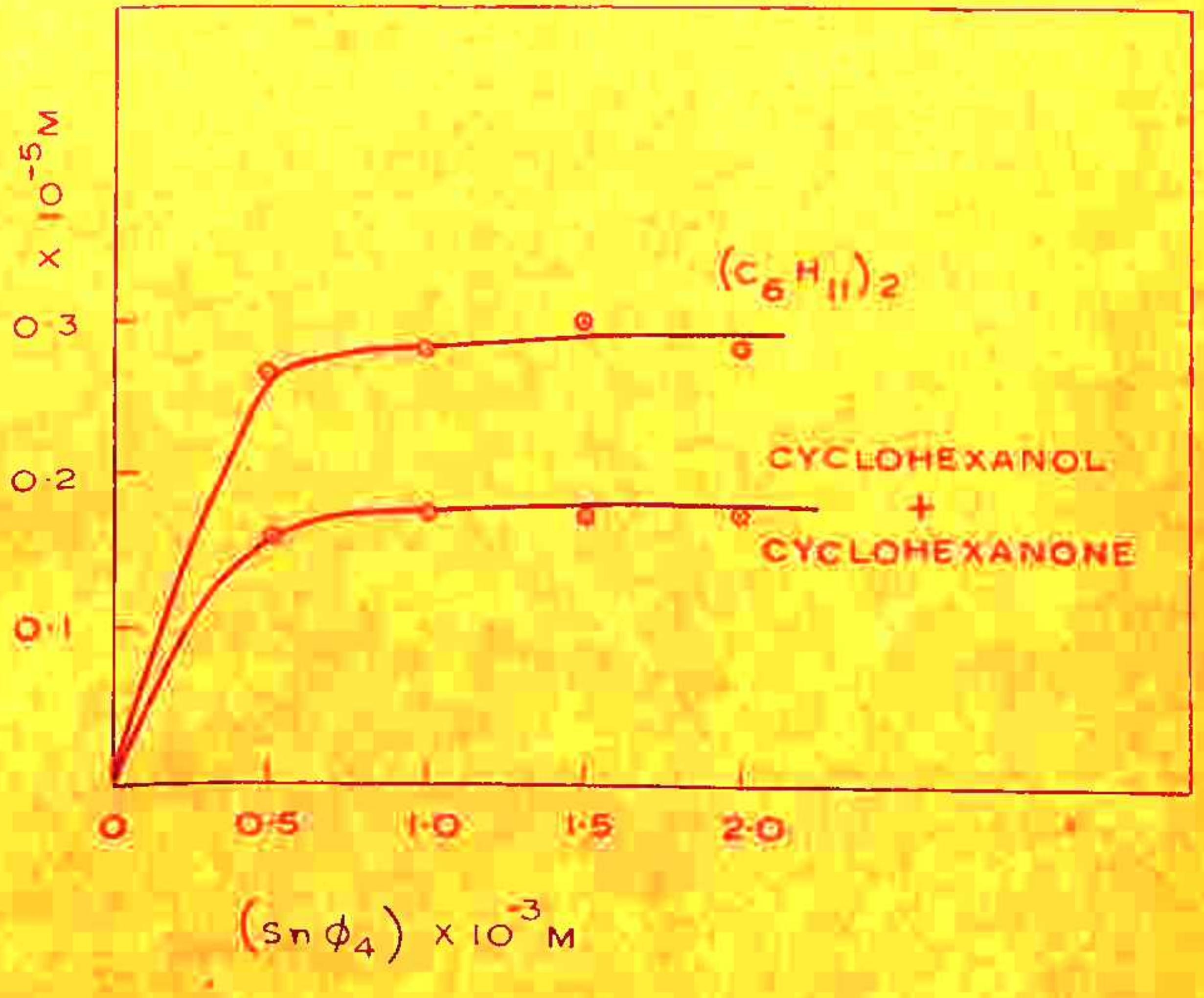


FIG. 3·8 PHOTOLYSIS OF Sn $\phi_4$ IN CYCLOHEXANE

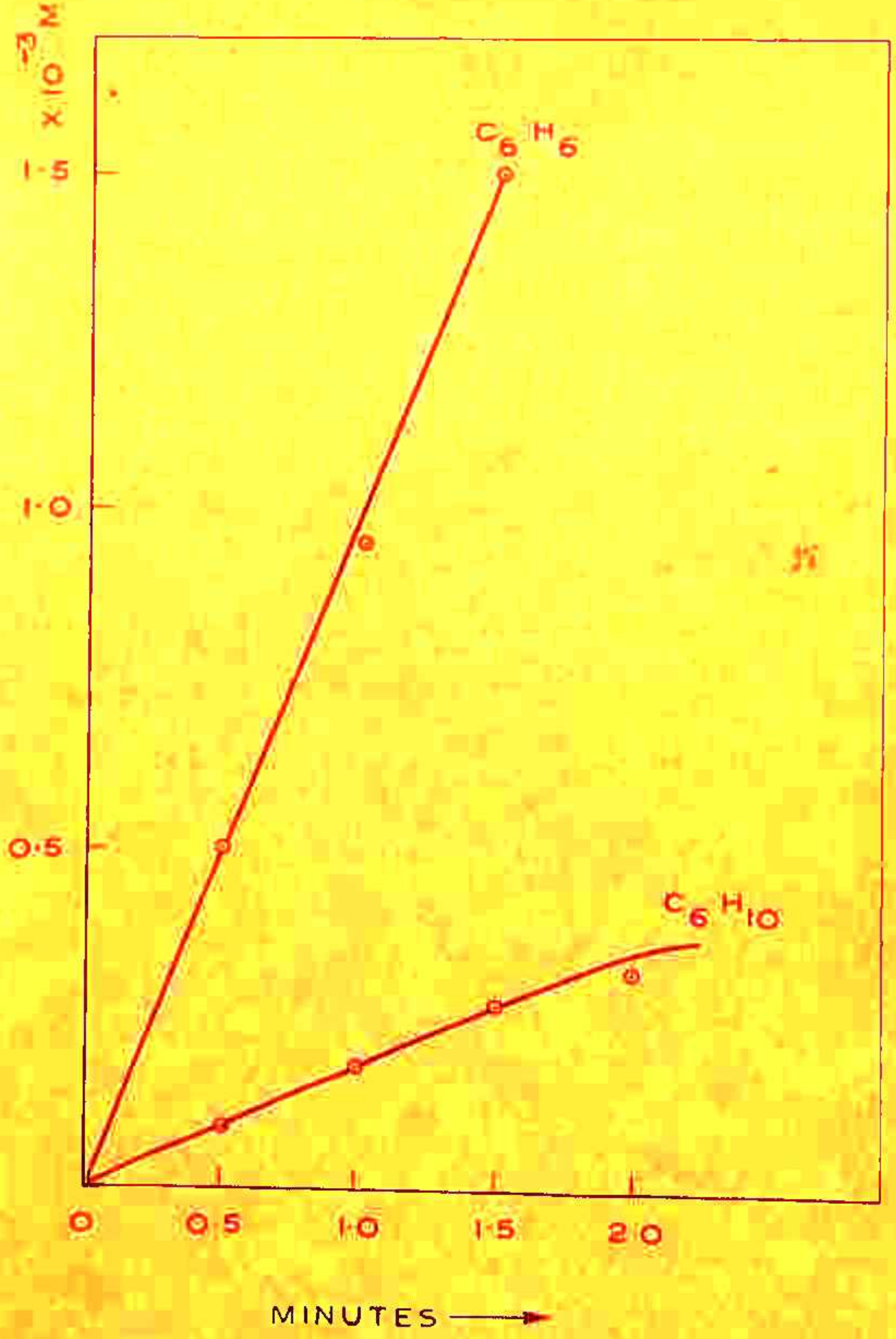


FIG. 3·9 EFFECT OF DOSE ON PHOTOLYTIC PRODUCTS OF 1 X 10$^{-3}$M Sn$\phi_4$ IN CYCLOHEXANE.

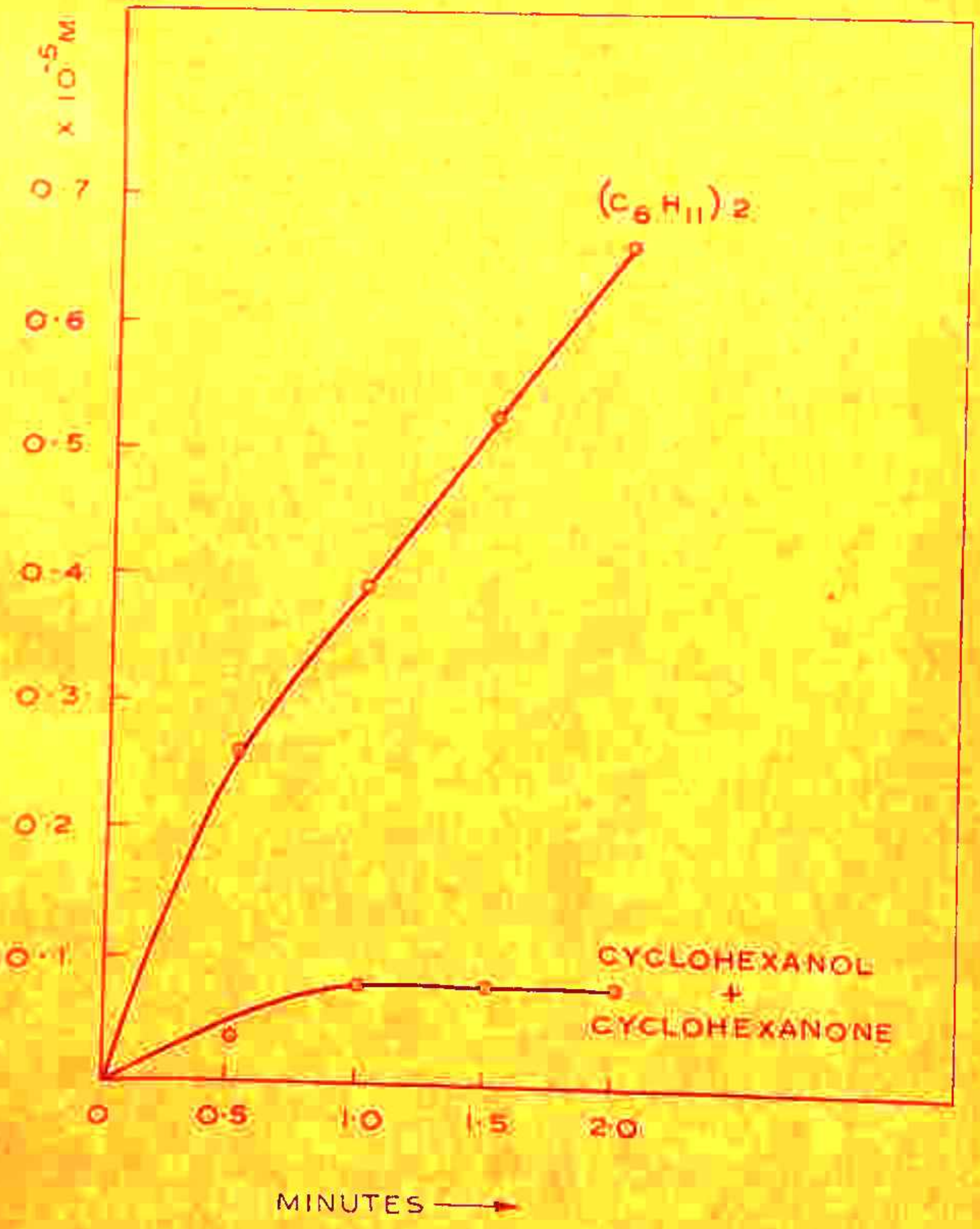


FIG. 3·10 EFFECT OF DOSE ON PHOTOLYTIC PRODUCTS OF $1 \times 10^{-3}$M $Sn\phi_4$ IN CYCLOHEXANE.

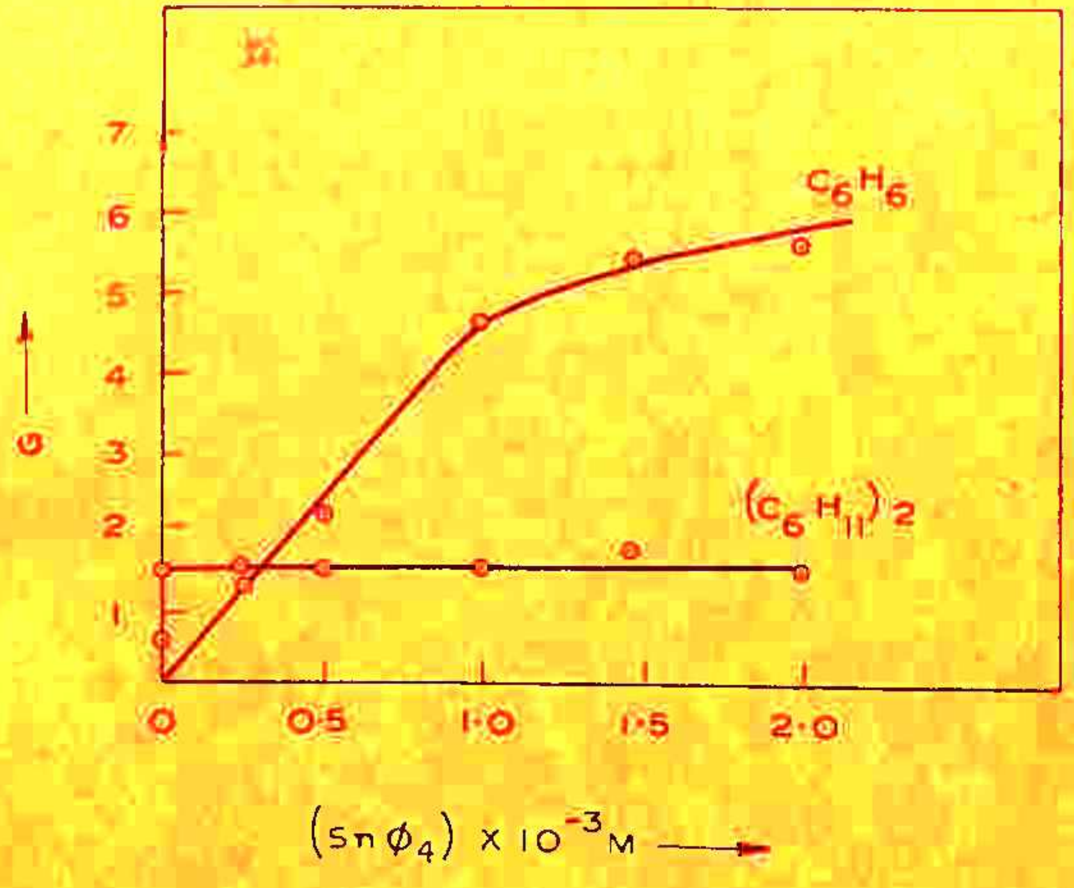


FIG. 3·11 GAMMA RADIOLYSIS OF $Sn\phi_4$ IN CYCLOHEXANE.

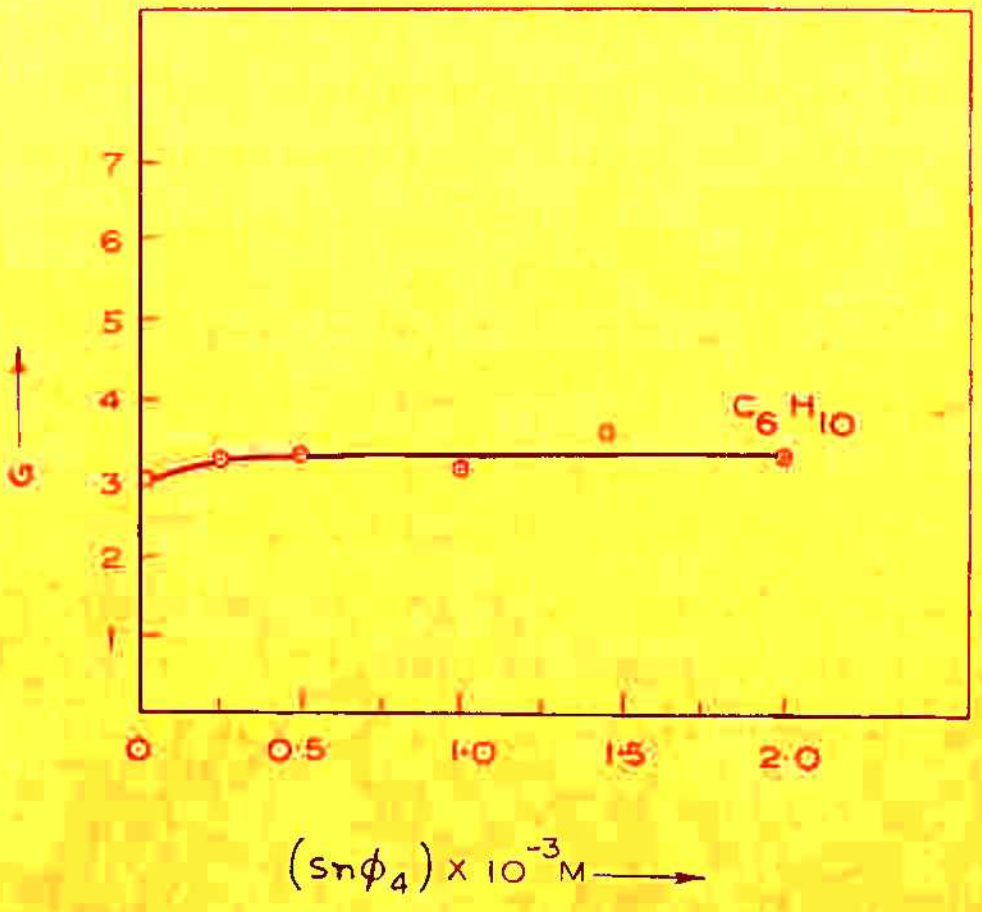


FIG. 3.12 GAMMA RADIOLYSIS OF $Sn\phi_4$ IN CYCLOHEXANE.

products in benzene, column was made up of high vacuum silicon grease over firebricks and the working temperature was 160°C. The products were confirmed by the time of evolution with standard substance. Samples were analysed directly for phenylcyclohexadiene and diphenyl. The evolution of phenylcyclohexadiene takes place first and diphenyl comes next to it.

The products in the irradiated tin tetraphenyl in cyclohexane were analysed. Dinonyl and carbowax column was used. Cyclohexanol and cyclohexanone were evolved before cyclohexane. Benzene comes out next to it. A column containing high-vac silicon grease was used for bicyclohexyl. Cyclohexene and benzene are obtained on a column of dibenzyl ether on diatomaceous earth at 78°C.

## RESULTS

Results are presented in Tables1-9 and are plotted in Figs. 3.4 to 3.12.

### Photolysis of tin tetraphenyl in benzene

Results of Table 1 are plotted in Fig. 3.4. Concentrations of photolytic products, diphenyl and phenyl cyclohexadiene, increase with increasing concentration of tin tetraphenyl and a plateau is obtained. The quantum yield also increases in the same way and it is higher for diphenyl.

## Radiolysis of tin tetraphenyl in benzene

Results of Tables 2 and 3 are plotted in Figs. 3.5 and 3.6 respectively. The yield per 100 ev (G value) for diphenyl and phenylcyclohexadiene increases with increasing concentrations of metal phenyl. The G values of diphenyl are greaer than phenylcyclohexadiene (dihydrodiphenyl).

## Photolysis of tin tetraphenyl in cyclohexane

The results presented in table 4 and 5 are plotted in Fig. 3.7 and 3.8 respectively. The concentrations and the quantum yields of benzene and cyclohexene ($C_6H_{10}$) increase regularly with increasing concentration of tin tetraphenyl. The concentration and the quantum yield of bicyclohexyl $(C_6H_{11})_2$ and cyclohexanol and cyclohexanone increase and attain a plateau. The effect of intensity of U.V. radiation (dose) on photolytic products of tin tetraphenyl in cyclohexane are given in Table 6 and 7 and are plotted in Fig. 3.9 and 3.10 respectively. It is observed that the concentration of benzene, cyclohexene and bicyclohexyl increase linearly with time of irradiation. The quantum yield of cyclohexene does not change with the increase of time of irradiation.

## Radiolysis of tin tetraphenyl in cyclohexane

Results in table 8 and 9 are plotted in Fig. 3.11 and 3.12. The G value of benzene increases with increasing concentration of tin tetraphenyl. However, G value of cyclohexene and bicyclohexyl are nearly constant.

## DISCUSSION

### Photolysis and Radiolysis of tin tetraphenyl in benzene

The work done by other workers did not furnish any data on dihydrodiphenyl[22] yield. Further the diphenyl yields in photolysis were very ambiguous[23]. Hence the present work improves upon the work of previous work. The photolysis of benzene in vapour phase was studied by Braun, Kato and Lipsky[24]. They reported that they did not observe any emission or internal conversion of benzene molecules to emitting state. The internal conversion of benzene molecule takes place to the ground state and photochemical reaction was not observed. It has been reported that in the liquid phase photolysis of benzene at 50°C, fulvene is formed. This finding was not confirmed[25]. Therefore the formation of diphenyl and phenyl cyclohexadiene must take place through some mechanism involving tin tetraphenyl and benzene. Since ultraviolet irradiation of dilute solutions of tin tetraphenyl in cyclohexane did not give diphenyl and phenylcyclohexadiene (loc. cit.), it is obvious that benzene is reacting in some way with metal phenyl to form diphenyl.

Benzene and tin tetraphenyl absorb in the same region at 2537 A° and tin tetraphenyl absorb greater than benzene. However, in all experiments concentrations of solute is very low in comparison to the solvent. Therefore it is safe to assume that all ultraviolet radiation is observed by benzene.

Absorption of energy by benzene molecules lead to the formation of several undefined excited states of benzene. It has been shown that the first excited singlet state of benzene $^1B_{2u}$, is responsible for transferring its energy to some quencher[26]. Therefore the following mechanism is suggested.

$$C_6H_6 \longrightarrow C_6H_6^* \text{ and other states} \quad (0)$$

$$C_6H_6^* \longrightarrow C_6H_6 \quad (1)$$

$$C_6H_6^* + Sn(C_6H_5)_4 \longrightarrow Sn(C_6H_5)_4 + C_6H_6 \quad (2)$$

$$C_6H_6^* + Sn(C_6H_5)_4 \longrightarrow Sn(C_6H_5)_4^* + C_6H_6 \quad (3)$$

$$Sn(C_6H_5)_4^* \longrightarrow Sn(C_6H_5)_{4-n} + n(C_6H_5) \quad (4)$$

$$Sn(C_6H_5)_4^* \longrightarrow Sn(C_6H_5)_4 \quad (5)$$

Here the first excited singlet state of benzene transfers its energy to the tin tetraphenyl in step (3). The excited tin tetraphenyl forms either the $C_6H_5$ radical as in step (4) or is self-quenched.

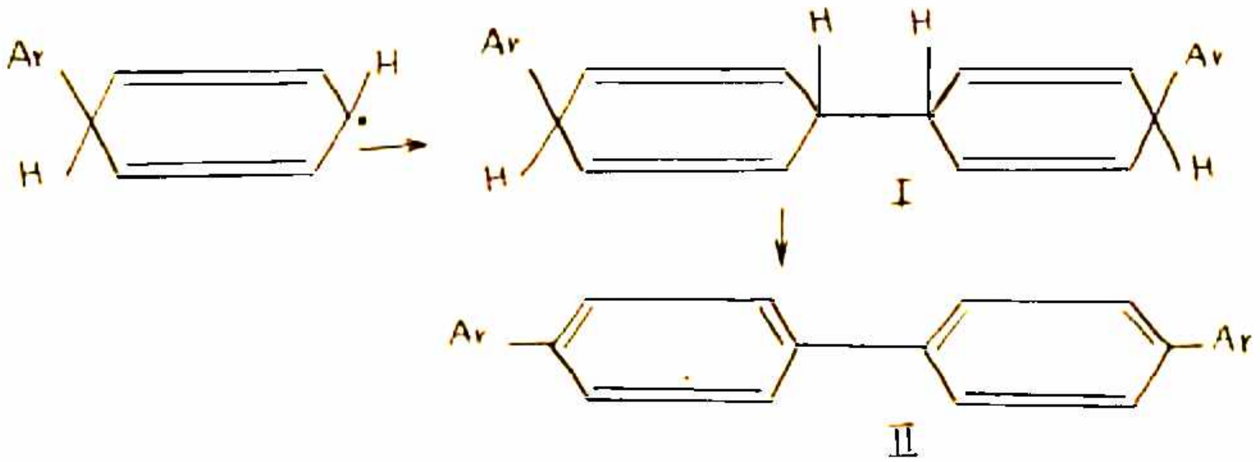
The initial phenyl radicals are relatively short lived and it is possible that first it may abstract a hydrogen atom from the aromatic substrate to produce an aryl radical which then couples with another phenyl radical to give a biaryl. This mechanism will need high activation energy because aromatic C-H bond has large bond dissociation energy. For the same reason it should give rise to a high isotope effect, when deutrated substrates are used, whereas in fact isotope effect is low or nil[27-28]. Therefore the aryl radical is added to benzene and the addition is very fast[29] and forms aryl cyclohexadienyl radical, which disproportionates to aryl benzene and aryl cyclohexadiene[30]. Thus

$$C_6H_5^{\cdot} + C_6H_6 \longrightarrow C_{12}H_{11}^{\cdot}$$

$$2\ C_{12}H_{11}^{\cdot} \begin{cases} \longrightarrow (C_6H_5)_2 + C_{12}H_{12} \\ \\ \longrightarrow C_{24}\cdot H_{22} \end{cases}$$

Diphenyl $(C_6H_5)_2$ and phenylcyclohexadiene $(C_{12}H_{12})$ is formed.

The formation of $C_{24}\cdot H_{22}$ can be explained by synchronous mechanism, assuming that the phenylcyclohexadienyl radicals couple in the canonic forms to give tetrahydro p-quaterphenyl (I), which may be dehydrogenated to p-quaterphenyl (II).



This compound was not detected by the gas-liquid chromatography, since the quantum yield of diphenyl is greater than dihydrodiphenyl, it is due to the following reaction.

$$C_6H_5^{\bullet} + C_{12}H_{11}^{\bullet} \longrightarrow C_6H_6 + (C_6H_5)_2.$$

Since the conversion of tin tetraphenyl to diphenyl and dihydrodiphenyl is only a few per cent, its concentration is low and it is highly reactive, a stationary state approximation[31] of the mechanism gives the following expression.

$$\begin{array}{l} Q.Y.\ (C_6H_5)_2 \\ \quad \text{or} \\ Q.Y.(C_6H_{12}) \end{array} = \frac{AK_2\ [Sn(C_6H_5)_4]}{K_1 + K_3\ [Sn(C_6H_5)_4]}$$

where $A = \dfrac{K_4(Q.Y.)(C_6H_6^*)}{K_4 + K_5}\ B$

and B = a factor which relates the depletion of tin tetraphenyl and simultaneous formation of diphenyl

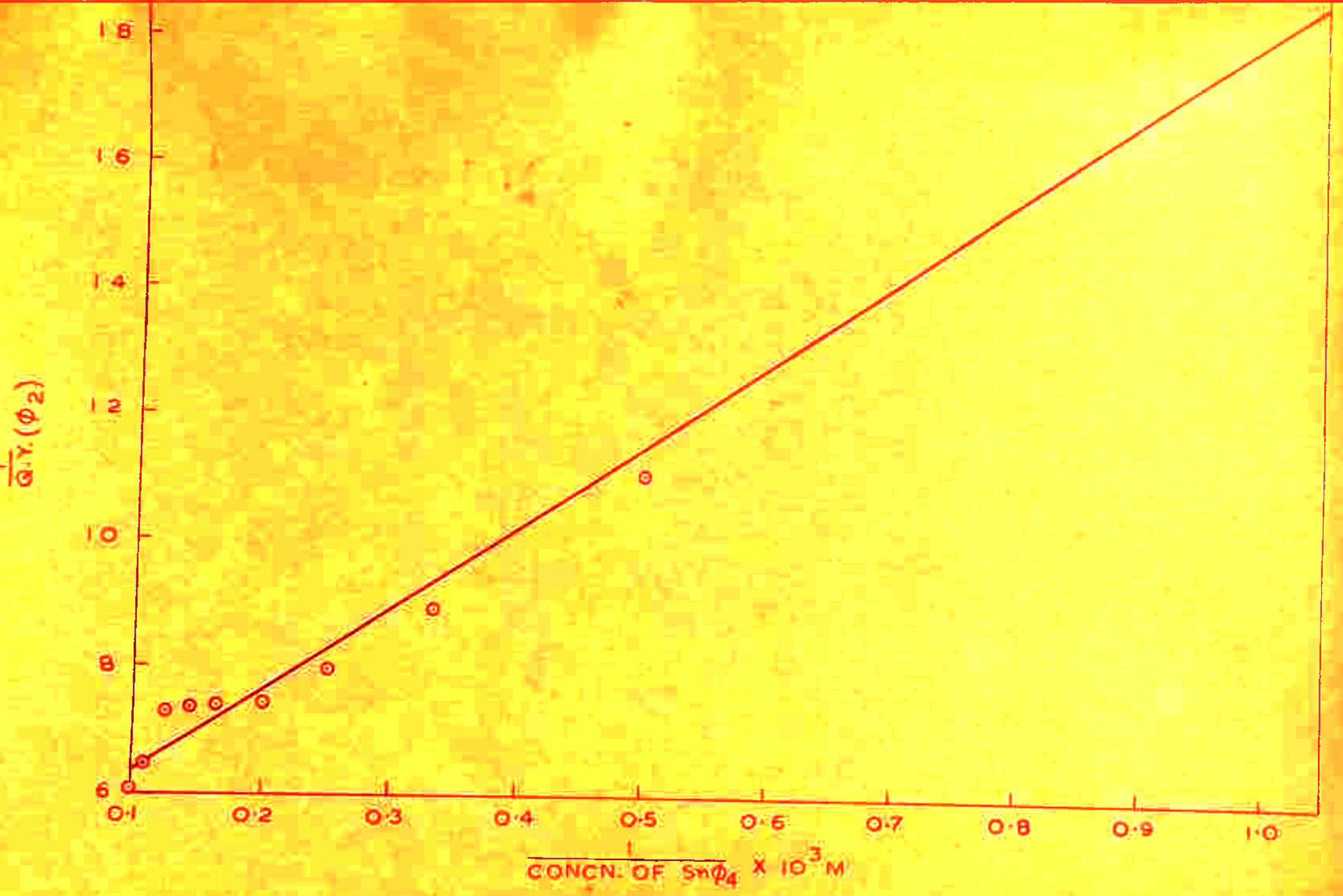


FIG. 3·13 PHOTOLYSIS OF $Sn\phi_4$ IN BENZENE.

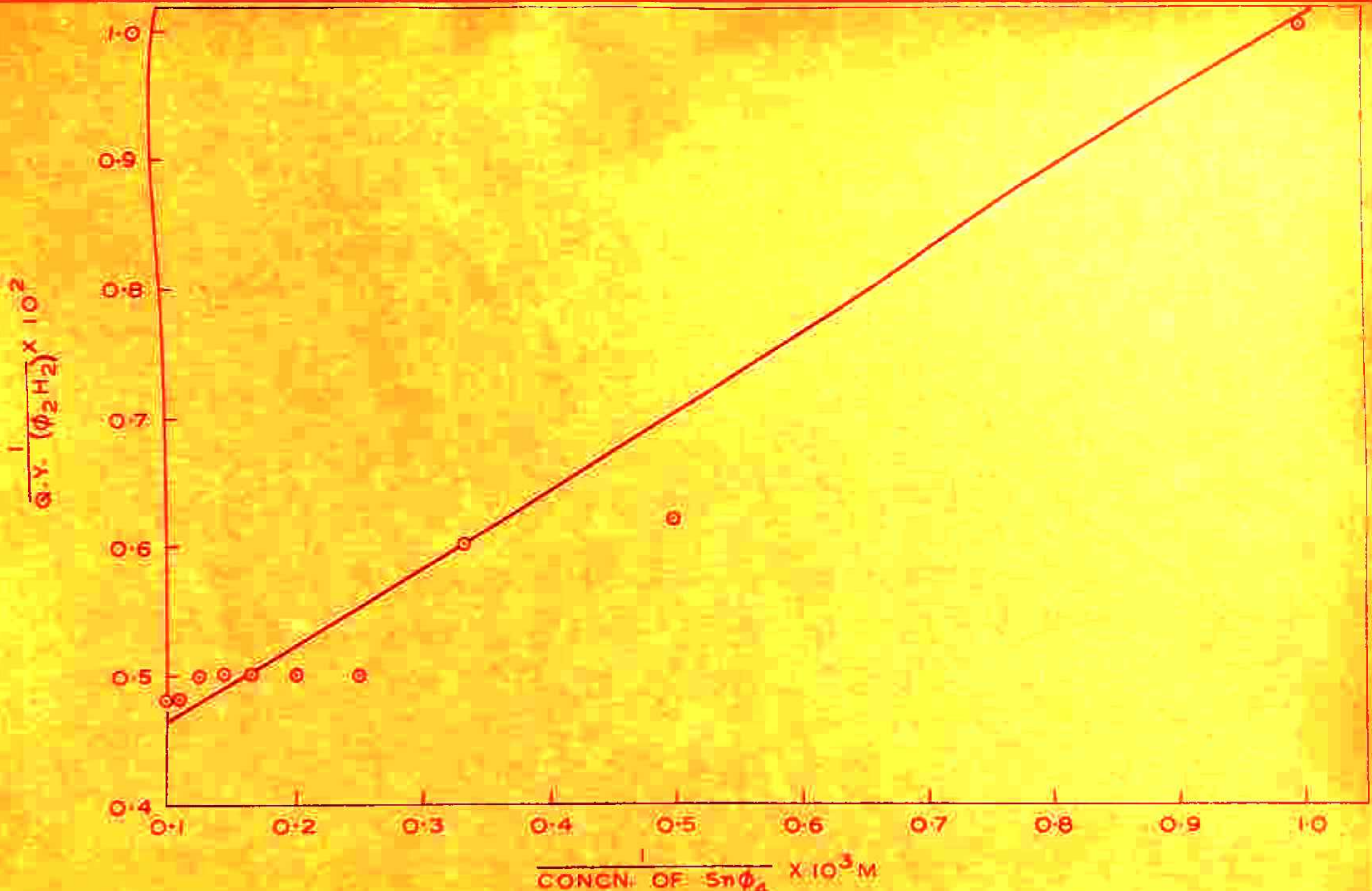


FIG.3.14 PHOTOLYSIS OF $Sn\phi_4$ IN BENEZENE.

A plot of $\frac{1}{Q.Y.(C_6H_5)_2}$ or $\frac{1}{Q.Y.(C_{12}H_{12})}$ versus $\frac{1}{[\text{Tin tetraphenyl}]}$ is linear (Fig. 3.13 and 3.14).

The radiolysis of tin tetraphenyl has been studied with an objective to find out the process by which the energy is transferred to the solute at low concentration from the solvent. The formation of diphenyl and dihydrodiphenyl is not reported in the radiolysis of benzene. Luminescence study has shown that fluorescence of p-terphenyl and 9,10 diphenyl anthracene in benzene is quenched by some metal phenyls[32]. The energy transfer process from excited benzene molecule to tin tetraphenyl during its photolysis by ultraviolet radiation has been discussed and a suitable mechanism is suggested The products and the nature of variations in the quantum yield and yield per 100 ev (G value) is identical for U.V. and gamma radiation. Therefore the same mechanism is operative in both cases and the stationary state approximation gives the expression:

$$G(Sn(C_6H_5)_4) = \frac{A\ K_3\ \left[Sn(C_6H_5)_4\right]}{1 + \frac{K_3}{K_1}\left[Sn(C_6H_5)_4\right]}$$

where $A = \frac{K_4.G(\text{Benzene})^*}{K_4 + K_5}$

G(Benzene*) is the 100 ev yield of excited benzene molecules, which transfer energy to the tin tetraphenyl. The K's refer to the specific rates indicated by subscripts. Experimental difficulties did not permit the determination of $G(Sn(C_6H_5)_4)$. Therefore it was replaced by its products $G(C_6H_5)_2$ and $G(C_6H_{12})$ respectively. Hence the expression can be written as

$$G(C_6H_5)_2 = G_B(C_6H_5)_2 + \frac{A' \left[Sn(C_6H_5)_4\right]}{1 + \frac{K_3}{K_1}\left[Sn(C_6H_5)_4\right]}$$

and

$$G(C_6H_{12}) = G_B(C_6H_{12}) + \frac{A'' \left[Sn(C_6H_5)_4\right]}{1 + \frac{K_3}{K_1}\left[Sn(C_6H_5)_4\right]}$$

Here $G_B(C_6H_5)_2$ and $G_B(C_6H_{12})$ is the 100 ev yield of diphenyl and dihydrodiphenyl from pure benzene.

It is evident from the expression that if the concentration of tin tetraphenyl is very low, the product $\frac{K_3}{K_1}\left[Sn(C_6H_5)_4\right]$ is less than unity and $G(C_6H_5)_2$ and $G(C_6H_{12})$ increase linearly with concentration. If the concentration is high, this value is greater than unity and $G(C_6H_5)_2$ or $G(C_6H_{12})$ is independent of the solute concentration.

Above expressions can be written as

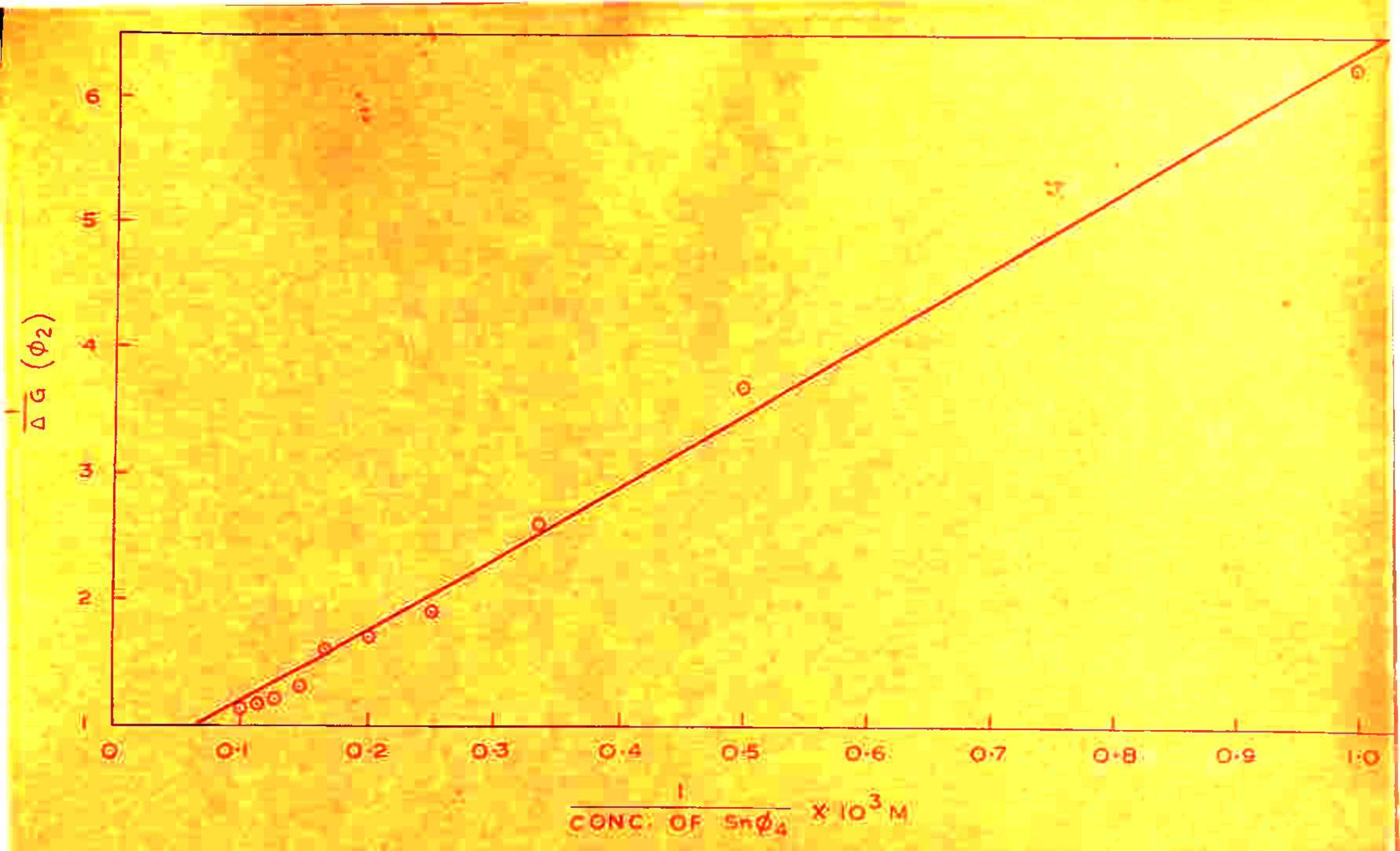


FIG.3.15 RADIOLYSIS OF $Sn\phi_4$ IN BENZENE.

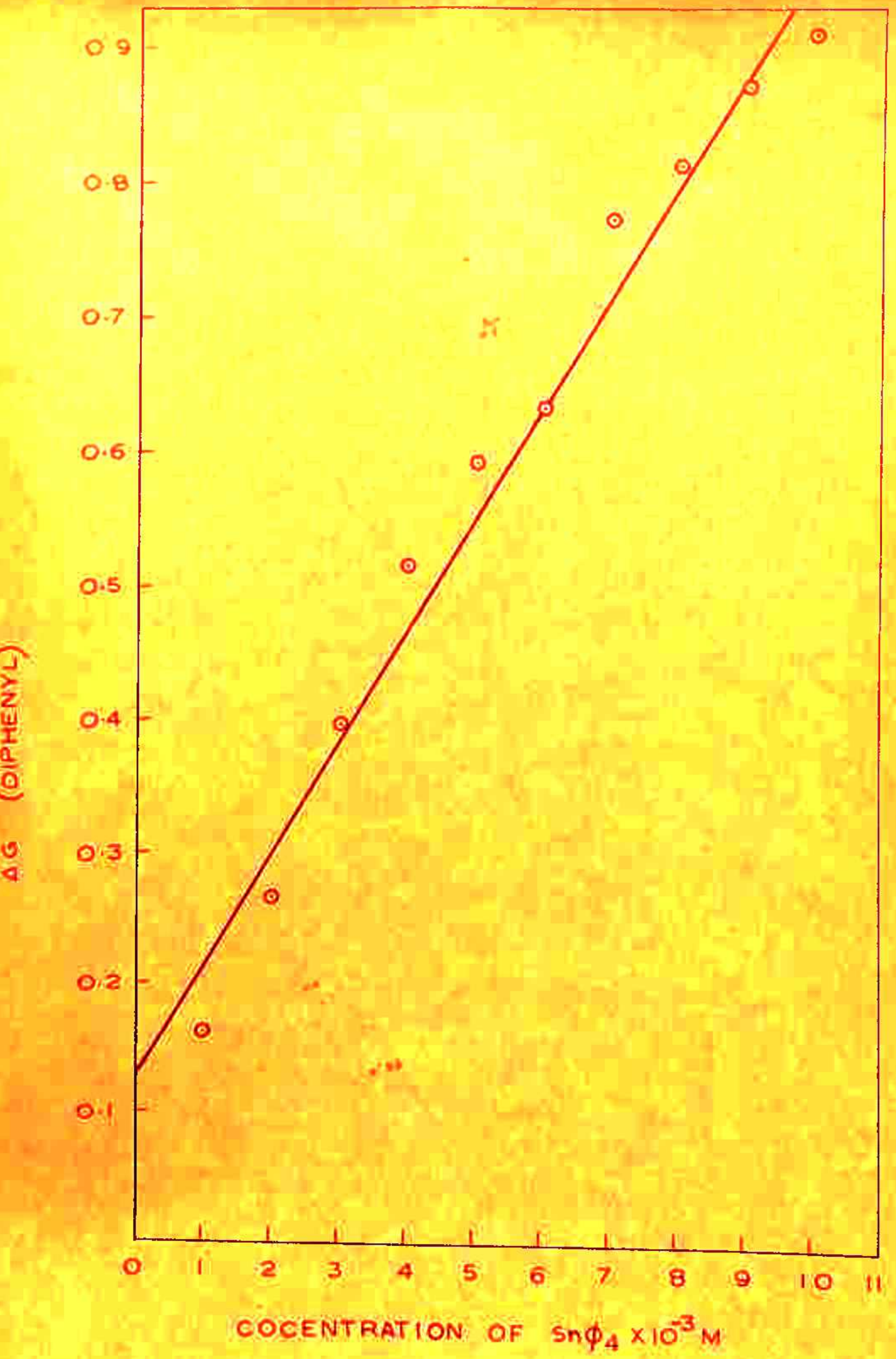


FIG.3·16 RADIOLYSIS OF $Sn\phi_4$ IN BENZENE.

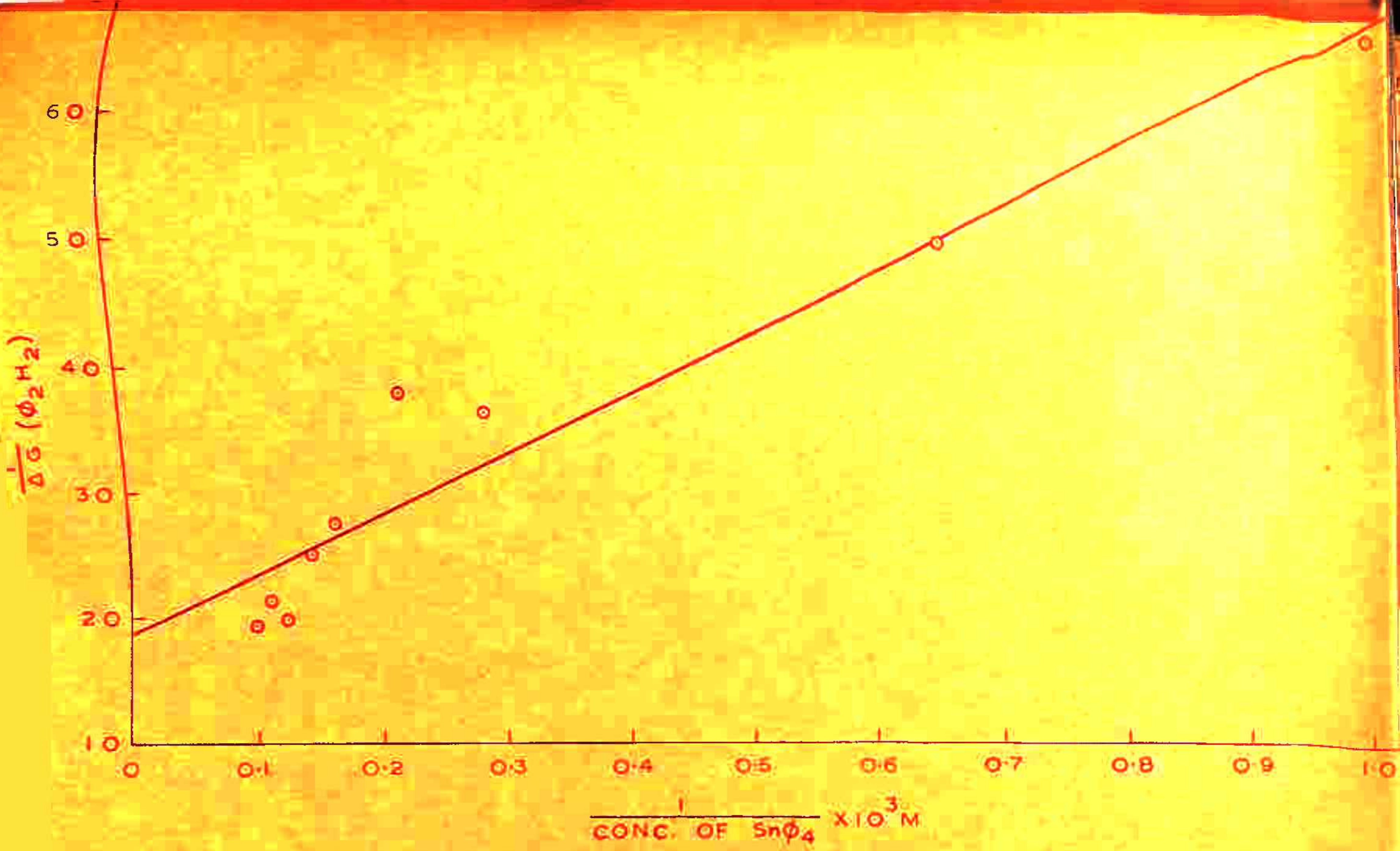


FIG.3.17 RADIOLYSIS OF $Sn\phi_4$ IN BENZENE.

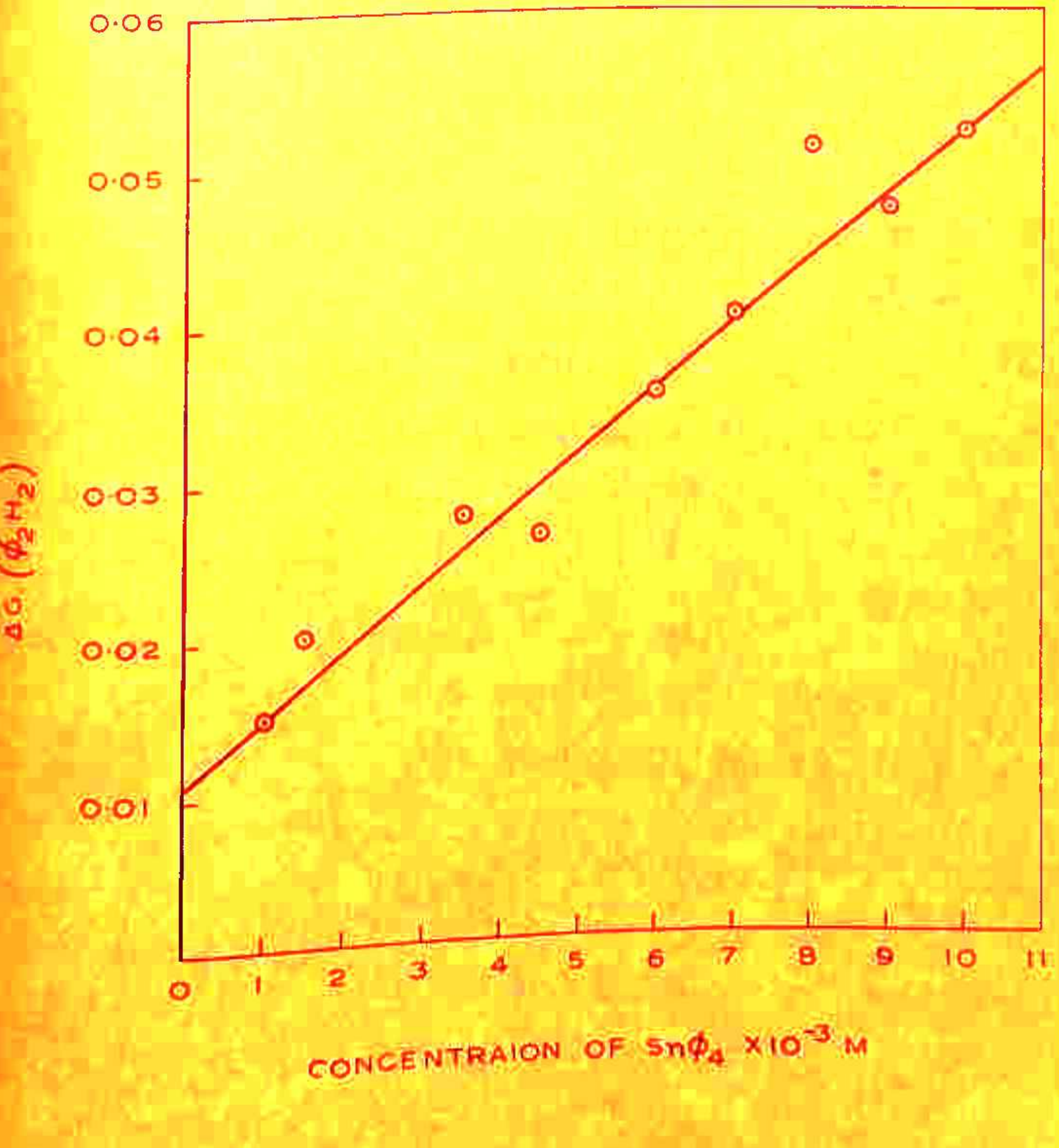


FIG.3·18 RADIOLSIS OF Sn$\phi_4$ IN BENZENE.

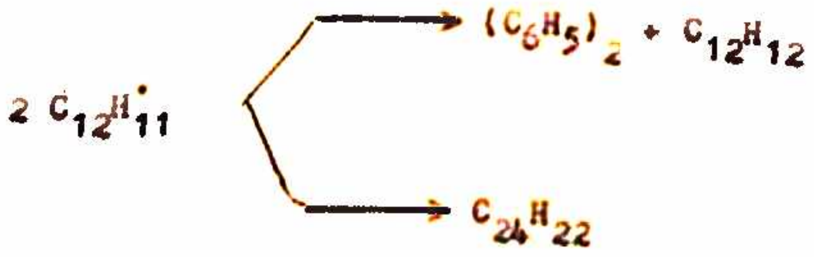
$$\Delta G(C_6H_5)_2 = G(C_6H_5)_2 - G_B(C_6H_5)_2 = \frac{A'\left[Sn(C_6H_5)_4\right]}{1 + \frac{K_3}{K_1}\left[Sn(C_6H_5)_4\right]}$$

and

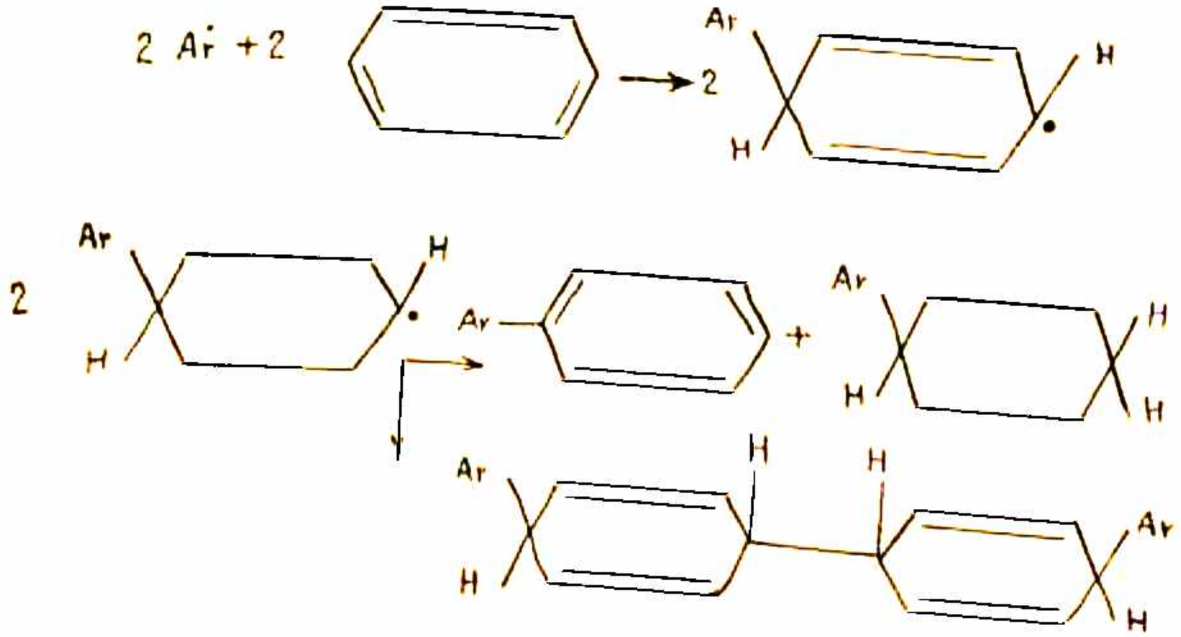
$$\Delta G(C_6H_{12}) = G(C_6H_{12}) - G_B(C_6H_{12}) = \frac{A'\left[Sn(C_6H_5)_4\right]}{1 + \frac{K_3}{K_1}\left[Sn(C_6H_5)_4\right]}$$

The plots of $\Delta G(C_6H_5)_2$, $\frac{1}{\Delta G(C_6H_5)_2}$, $\Delta G(C_{12}H_{12})$ and $\frac{1}{\Delta G(C_{12}H_{12})}$ versus the $\left[Sn(C_6H_5)_4\right]^{-1}$ given in Fig. 3.15-3.18 give straight lines.

Since the yield of diphenyl is considerably greater than dihydrodiphenyl, it does not look plausible to assume that



is only operative in diphenyl production. The production of diphenyl and dihydrodiphenyl from cyclohexadienyl radical is favoured than tetrahydroquaterphenyl. The reaction is given below.



It has been reported that tin tetraphenyl is capable to dissociate as tin diphenyl and diphenyl[33]. Since tin tetraphenyl in cyclohexane by ultraviolet radiation do not give diphenyl, this contention is ruled out. Therefore the other possibility is that tin tetraphenyl dissociates as:

$$Sn(C_6H_5)_4 \longrightarrow Sn(C_6H_5)_2 + 2\ C_6H_5\cdot$$

The phenyl radical subsequently reacts with cyclohexadienyl radical to give benzene and diphenyl, as already discussed in photochemical reaction. The fate of tin diphenyl could not be investigated. However, it is possible that it might react with hydrogen or acetylene (gaseous products of radiolysis).

## Photolysis and Radiolysis of tin tetraphenyl in cyclohexane

Since cyclohexane is related structurally to benzene and all hydrogen atoms are equivalent, the loss of any of them gives the same product. Gunning[34] found that photochemical reaction with cyclohexane is solely free radical in nature and direct C-H bond split takes place. Arai, Sato and Shida[35] found that hydrogen, cyclohexene and bicyclohexyl is formed in the reaction. The primary photochemical act is the formation of cyclohexyl radical ($C_6H_{11}^{\bullet}$). Thus when cyclohexene is irradiated by ultraviolet light, cyclohexyl radical is formed along with hydrogen. Subsequently cyclohexyl radical disproportionates into cyclohexene and bicyclohexyl $(C_6H_{11})_2$. Thus cyclohexyl radicals are precursors of bicyclohexyl. Scavenger reduces the yield of cyclohexene. Unsaturated products formed during irradiation can act as scavenger. Another possible step for reducing cyclohexene yield is the combination of hydrogen atom with cyclohexene forming cyclohexyl radical. In the presence of hydrogen cyclohexanol and cyclohexanone are formed. Following mechanism explains clearly the formation of different products from U.V. irradiation of cyclohexane.

$$C_6H_{12} \longrightarrow C_6H_{11}^{\bullet} + H^{\bullet} \qquad (1)$$

$$2\,C_6H_{11}^{\bullet} \begin{cases} \longrightarrow C_6H_{10} + C_6H_{12} & (2a) \\ \longrightarrow (C_6H_{11})_2 & (2b) \end{cases}$$

$$H^{\bullet} + C_6H_{10} \longrightarrow C_6H_{11}^{\bullet} \qquad (3)$$

$$C_6H_{11}^{\bullet} + O_2 \longrightarrow C_6H_{11}O_2^{\bullet} \qquad (4)$$

$$2\,C_6H_{11}O_2^{\bullet} \longrightarrow C_6H_{11}OH + C_6H_{10}O \qquad (5)$$

In addition to the common products listed above, benzene is formed in sufficient amount during the photolysis of tin tetraphenyl in cyclohexane. Since benzene is not present in the normal photolytic products of cyclohexane, it can be assumed that tin tetraphenyl is directly involved in its formation through energy transfer process from cyclohexane. In the radiolysis of lead tetraphenyl is deuterated cyclohexane, benzene and deuterated benzene are formed in the following manner.

$$(C_6H_5)_4\,Pb + C_6D_{12} \longrightarrow C_6H_6 + C_6H_5D$$

This goes to establish that some excited state of tin tetraphenyl is involved in the production of benzene. Following mechanism is suggested for benzene formation.

$$C_6H_{12} \longrightarrow C_6H_{11}^{\bullet} + H^{\bullet} \qquad (1)$$

$$C_6H_{12} \longrightarrow C_6H_{12}^{*} \qquad (2)$$

$$2\,C_6H_{11}^{\bullet}\begin{cases}\longrightarrow C_6H_{10} + C_6H_{12} & (3a)\\ \longrightarrow (C_6H_{11})_2 & (3b)\end{cases}$$

$$C_6H_{12}^{*} + S_n(C_6H_5)_4 \longrightarrow C_6H_{12} + Sn(C_6H_5)_4^{*} \qquad (4)$$

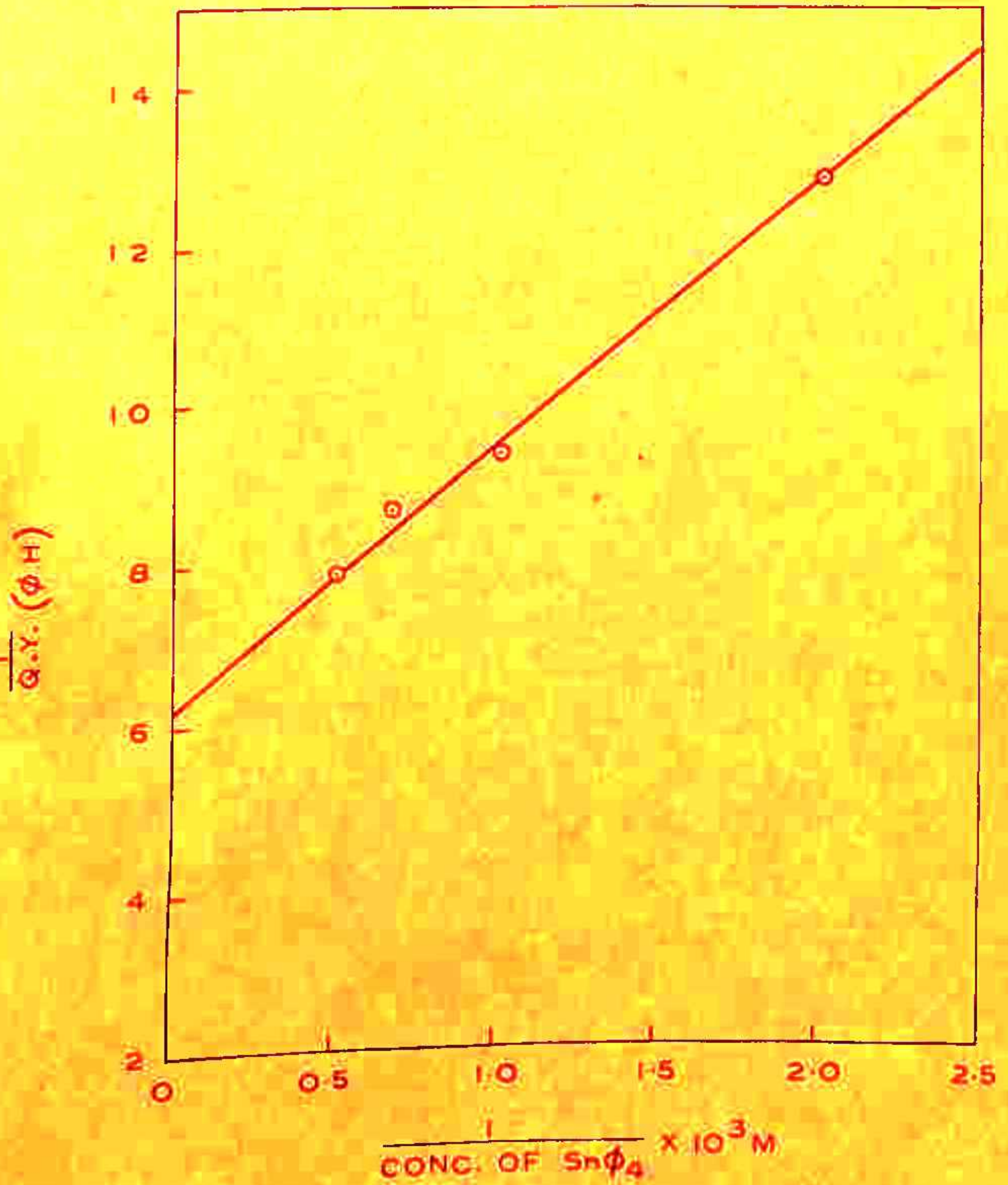


FIG. 3·19 PHOTOLYSIS OF $Sn\phi_4$ IN CYCLOHEXANE.

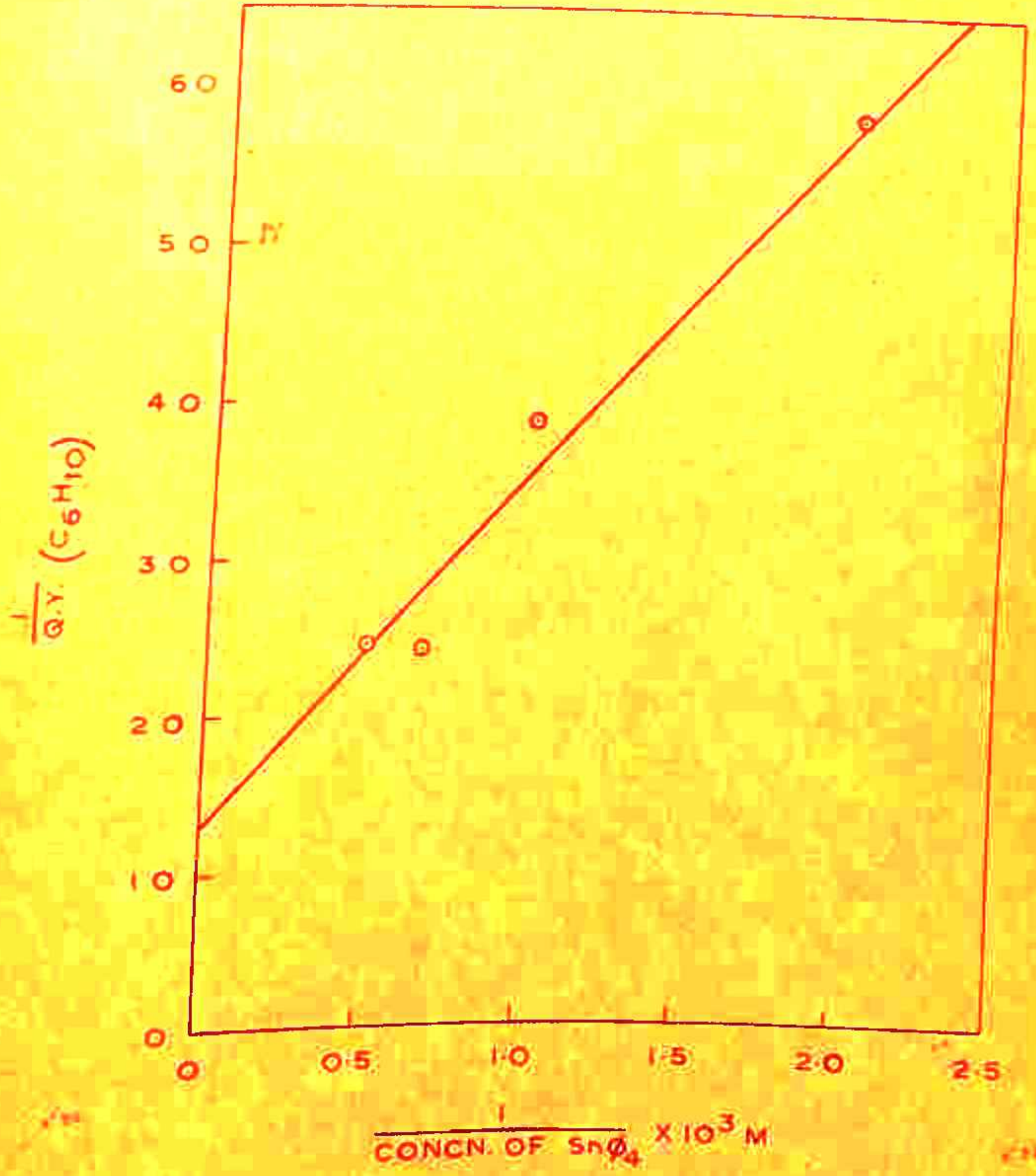


FIG.3·20 PHOTOLYSIS OF Sn$\phi_4$ IN CYCLOHEXANE.

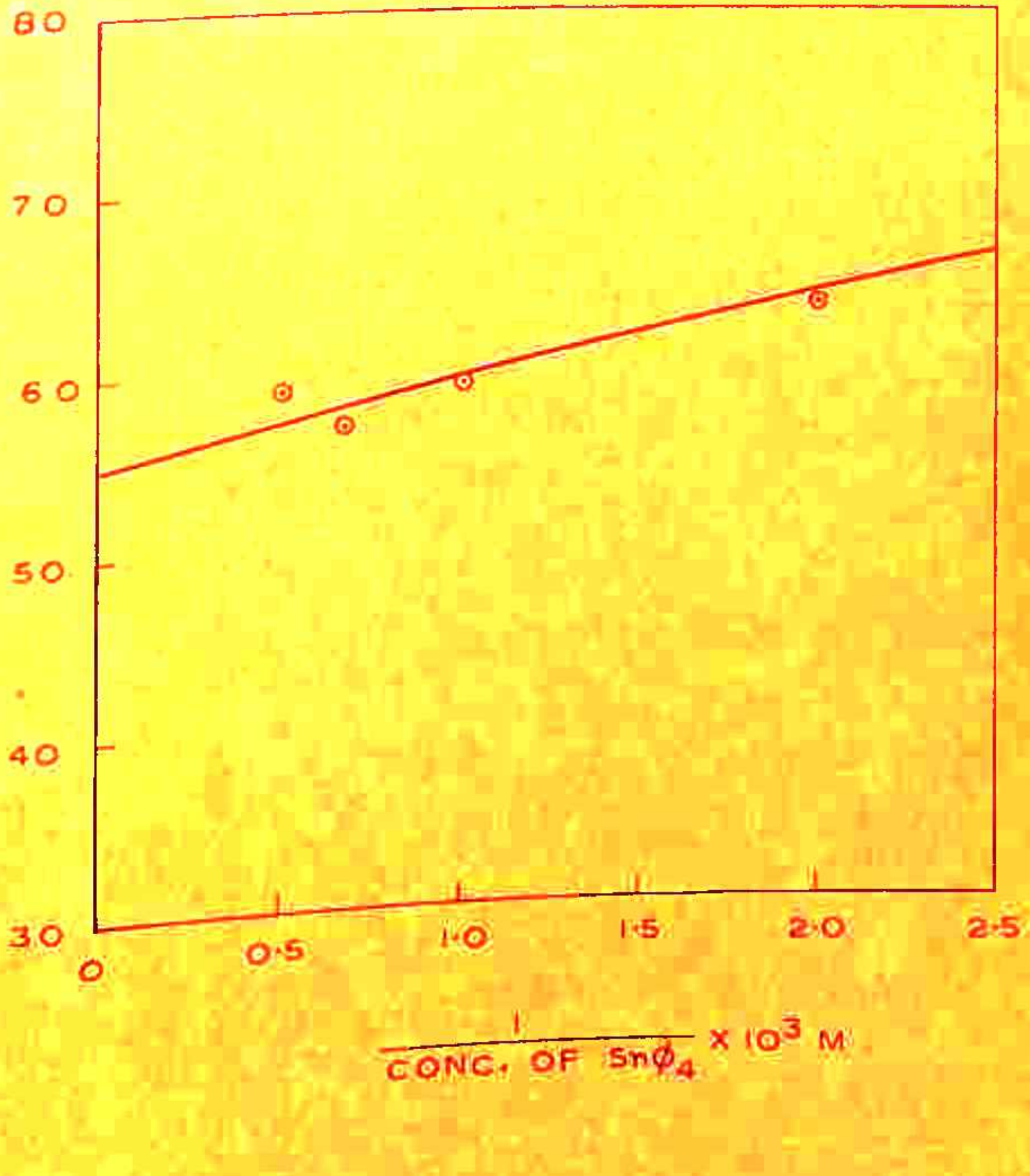


FIG.3·21 PHOTOLYSIS OF $Sn\phi_4$ IN CYCLOHEXANE.

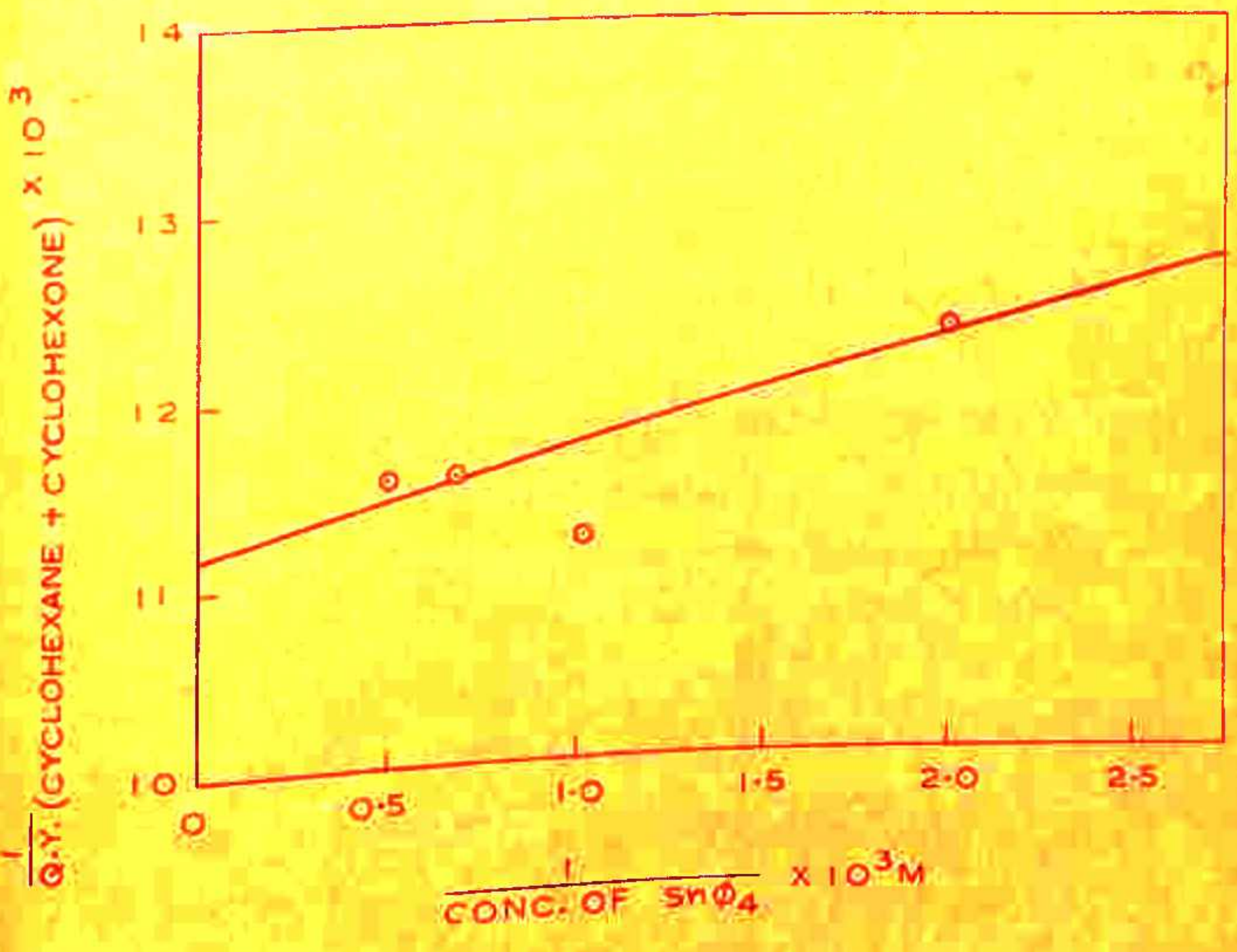


FIG.3·22 PHOTOLYSIS OF $Sn\phi_4$ IN CYCLOHEXANE.

$$Sn(C_6H_5)_4^* \longrightarrow Sn(C_6H_5)_{4-n} + n\,C_6H_5^{\cdot} \qquad (5)$$

$$C_6H_5^{\cdot} + C_6H_{12} \longrightarrow C_6H_6 + C_6H_{11}^{\cdot} \qquad (6)$$

It is shown in the Figs.3-19-3.22 that 1/quantum yield versus 1/concentration of tin tetraphenyl practically gives straight line, which can be expressed in the form

$$\frac{1}{\text{Quantum yield}} = K\,\frac{1}{[Sn(C_6H_5)_4]} + \text{constant}$$

Since the quantum yield is proportional to the concentration of tin tetraphenyl and also the concentration of products versus concentration of tin tetraphenyl is non-linear, it seems plausible to assume that two independent processes are involved in the formation of photolytic products. One of these is concentration dependent and the other is not dependent upon concentration.

It has been already pointed out that different excited states of tin tetraphenyl are involved in the photochemistry and radiation chemistry. Dyne and Jenkinson[36] found out that an excited molecule of cyclohexane is quenched by benzene and iodine. Forrestal and Hamill[37] postulated two kinds of excited cyclohexane molecules . One of it is formed by ion recombination and can dissociate to give molecular products such as hydrogen and unsaturated products. Its G value is 3.0. The other one is not formed by ionic precursors and dissociates into cyclohexyl radical and thermal or a hot hydrogen atom. Its G value is 7.65. The dissociation of excited molecules into molecular products is less common than dissociation into free radicals. Further the unsaturated products are not found and the yield of cyclohexene is practically constant, it is safe to reject the formation of excited tin tetraphenyl through excitation transfer from excited cyclohexane.

The other alternative is the charge transfer mechanism, because parent $C_6H_{12}^{+}$ ion is highly stable. Cyclohexane is ionized by γ radiation and the electron ejected during ionization has considerable energy. The fate of cyclohexane ion is either to react with an ion of opposite sign to form a neutral entity such as,

$$C_6H_{12}^{+} + e^{-} \longrightarrow C_6H_{12}^{\pm} \longrightarrow C_6H_{12}^{*} \quad \text{or}$$

$$C_6H_{12}^{+} + C_6H_{12}^{-} \longrightarrow C_6H_{12} + C_6H_{12}$$

As the excitation transfer from cyclohexane to tin tetraphenyl is ruled out, the other path seems to be the charge transfer. Hence the mechanism can be as follows:

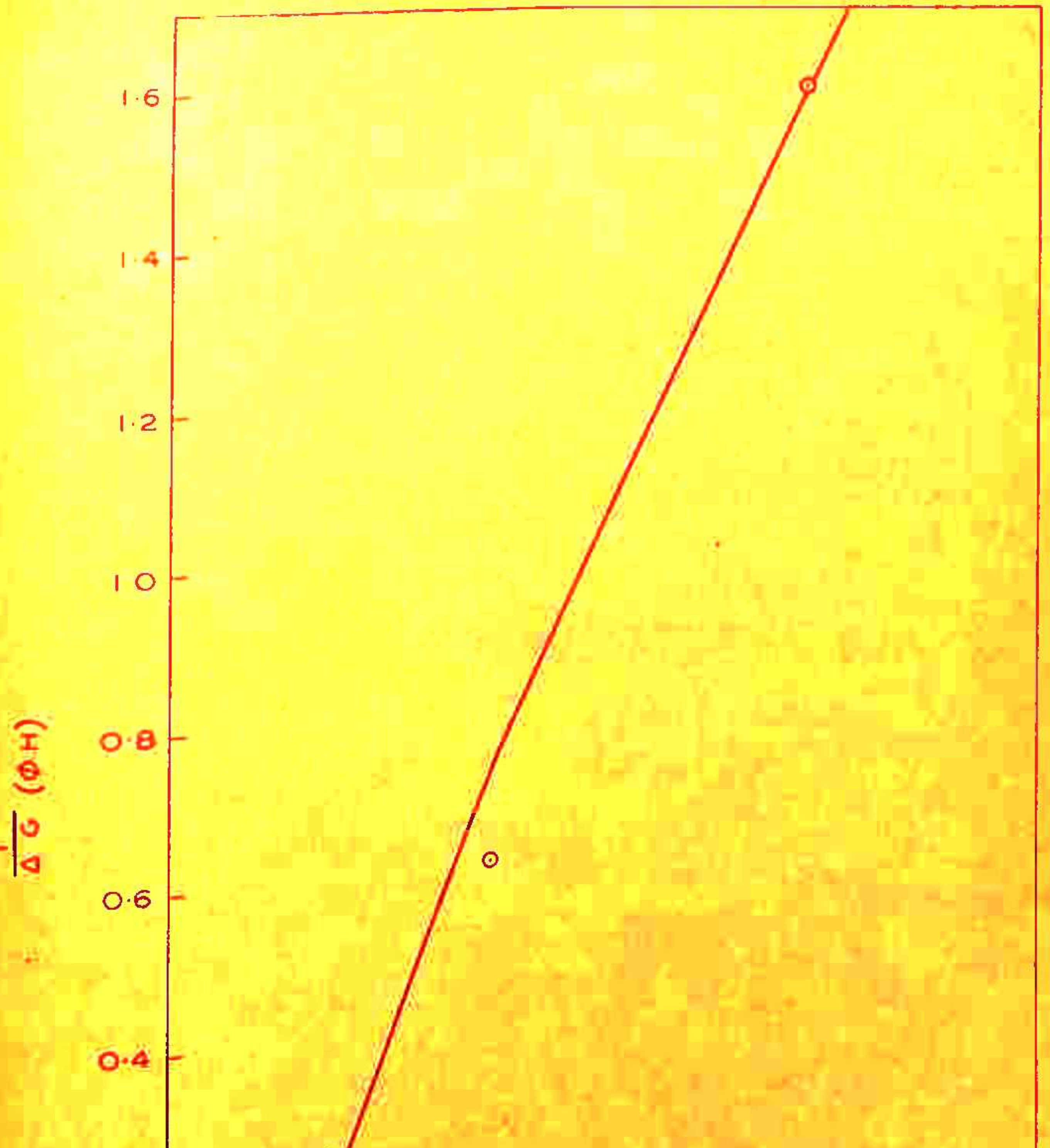


FIG. 3·23 RADIOLYSIS OF $Sn\phi_4$ IN CYCLOHEXANE.

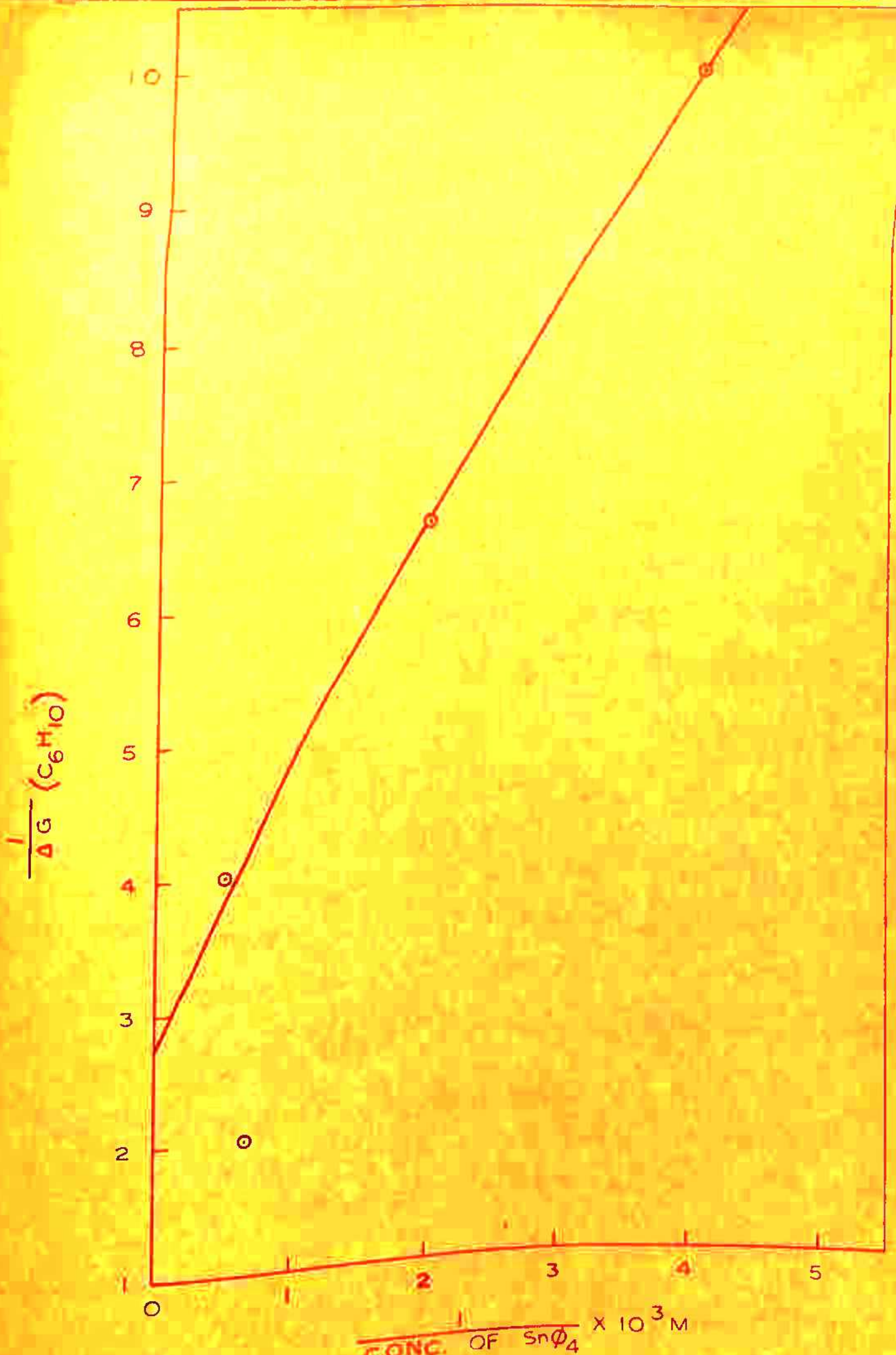


FIG. 3 24 RADIOLYSIS OF $Sn\phi_4$ IN CYCLOHEXANE.

$$C_6H_{12} \longrightarrow C_6H_{12}^{+} + e^{-} \qquad (1)$$

$$C_6H_{12}^{+} + Sn(C_6H_5)_4 \rightarrow C_6H_{12} + Sn(C_6H_5)_4^{+} \qquad (2)$$

$$Sn(C_6H_5)_4^{+} + e^{-} \longrightarrow (C_6H_5)_4\ Sn^{*} \qquad (3)$$

$$Sn(C_6H_5)_4^{*} \longrightarrow (C_6H_5)_{4-n}\ Sn + n\ C_6H_5^{\cdot} \qquad (4)$$

$$C_6H_5^{\cdot} + C_6H_{12} \longrightarrow C_6H_6 + C_6H_{11}^{\cdot} \qquad (5)$$

Thus the reaction (2) protects cyclohexane and the concentration of $C_6H_{11}$, which is the precursors of cyclohexene and bicyclohexyl, is decreased. This suggestion is contrary to the observations of Leighton and Mortenson[38], who irradiated lead tetraphenyl in n-hexane and reported the formation of diphenyl. Based on experimental findings, they concluded that phenyl radical does not react much with each other or the compound. Benzene is formed in reaction (5), but its value attains a plateau. This will take place, by self-quenching,

$$Sn(C_6H_5)_4^{*} + Sn(C_6H_5)_4 \longrightarrow 2\ Sn(C_6H_5)_4 \qquad (6)$$

while step (3) is linear in benzene production, but the rate is affected by self-quenching. A simplified kinetic expression can be given in the form

$\frac{1}{\Delta G(C_6H_6)} = K \frac{1}{[(C_6H_5)_4\ Sn]} + K'$ and the plot of $\frac{1}{\Delta G(C_6H_6)}$ versus $\frac{1}{[Sn(C_6H_5)_4]}$ is linear (Fig. 3.23).

The yield of cyclohexene ($C_6H_{10}$) is practically the same as with pure cyclohexane. It is not affected by benzene. Similarly the yield of bicyclohexyl is also almost equal to the yield from pure solvent. None of these products are equal to each other or benzene. Since the formation of these products more or less the same, as from pure solvent, cyclohexyl radical formed in step (5) reacts with hydrogen to form cyclohexane. Consequently it does not contribute towards the formation of products like cyclohexene and bicyclohexyl.

The ratio of intercept/slope for different products is given in Table 10.

TABLE 10

| Product | Intercept/slope |
|---|---|
| Photolytic ($C_6H_6$) from $C_6H_{12}$ | 183.0 |
| Photolytic ($C_6H_{10}$) from $C_6H_{12}$ | 590.0 |
| Photolytic $(C_6H_{11})_2$ from $C_6H_{12}$ | 117.0 |
| Photolytic cyclohexanol + cyclohexanone from $C_6H_{12}$ | 48.0 |
| Photolytic $(C_6H_5)_2$ from $C_6H_6$ | 69.0 |
| Photolytic ($C_{12}H_{12}$) from $C_6H_6$ | 670.0 |
| Radiolytic product $C_6H_6$ from $C_6H_{12}$ | 590.0 |
| Radiolytic product $C_6H_{10}$ from $C_6H_{12}$ | 1500.0 |
| Radiolytic product $(C_6H_5)_2$ from $C_6H_6$ | 115.0 |
| Radiolytic product $(C_{12}H_{12})_2$ from $C_6H_6$ | 400.0 |

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* * *

# CHAPTER IV

# PHOTOCHEMISTRY AND RADIATION CHEMISTRY OF SOME LEAD ARYLS IN BENZENE AND CYCLOHEXANE

## INTRODUCTION

The photochemistry and radiation chemistry of tin tetraphenyl in benzene or cyclohexane have been presented in Chapter 3. It has been established by luminescence study that energy is transferred from solvent to the solute at low concentrations. The energy transfer takes place from an excited state of the solvent to the solute, which subsequently undergoes sensitized decomposition. According to the current theoretical views an excited state of cyclohexane in vapour phase is highly unstable and it decomposes into a single vibration period. If such excited state is present in the liquid state, cyclohexane will transfer the energy to the solute resulting in the protection of the hydrocarbon.

The work in this chapter deals with the effect of some closely related organometallic compounds of lead on the photolysis and radiolysis of benzene and cyclohexane. It is aimed at to get some further understanding of the mechanism by which a low concentration solute interacts with an excited species formed in benzene and cyclohexane by ultraviolet and gamma radiation. The organometallic compounds investigated are lead tetraphenyl, hexaphenyl di lead, triphenyl lead chloride and triphenyl lead hydroxide and the solvents chosen are benzene and cyclohexane. Protection and sensitization of these organometallic compounds in benzene and cyclohexane was studied in an attempt to improve our understanding of the decomposition in these closely related compounds of lead.

## EXPERIMENTAL

Purification of solvents, sample preparation, irradiation and the analysis of condensable products were done exactly in the same manner as described in Chapter 3. The gaseous products were analysed due to experimental limitations. Lead was found in metallic state after irradiation so samples were analysed in the following manner.

### Lead Analysis

Colorimetric method of analysis has been used for lead. Lead in the irradiated sample is recovered by filtration of solution using a fine sintered glass disc. Following precautions are taken prior to the filtration of the sample. The filtrate disc is washed several times with warm 10% nitric acid to remove any trace of lead. The disc is washed several times with pure distilled water until washings are acid free. It is tested by a litmus paper. The disc is washed with alcohol to remove water from the filter pores. The contents of the irradiation cell are filtered through the disc and the cell is rinsed several times with warm 5 ml benzene or cyclohexane, as the case may be, and rinsings are all filtered. The filtered disc is finally washed with benzene or cyclohexane to remove last trace of compound. Now the disc should hold only lead or its oxide and the cell may retain some lead on the wall. The lead on the cell wall is removed by 10% nitric acid and the disc is also washed several times with 10% nitric acid solution and all the washings are transferred to a volumetric flask and the solution is diluted to the mark by 10% nitric acid. Ten per cent nitric acid solution is diluted to 1% nitric acid and lead must be less than 3 mg 1 litre. Ten ml of this solution is transferred to 50 ml erlenmeyer flask. To this is added 10 ml A.C.S. solution. An A.C.S. solution contains 400 ml conc. ammonia diluted to 750 ml and 30 ml 10% potassium cyanide added to 1.5 g sodium, thiosulfate solution and finally the volume is diluted to 1 litre with water. This is treated with 10 ml 0.001% (weight/volume) diethiazone in carbon tetrachloride. The solution is vigorously shaken and the layer is allowed to separate. Lead thiazone is red. The upper layer should be yellowish. If the carbon tetrachloride

## TABLE 1

Photolysis of Lead Tetraphenyl in Benzene

| $(Pb\phi_4) \times 10^{-3}$ M | Quantum yield | | |
|---|---|---|---|
| | $\phi_2$ | $\phi_2H_2$ | Pb |
| 0.25 | 0.05 | 0.01 | 0.026 |
| 1.00 | 0.09 | 0.02 | 0.047 |
| 2.00 | 0.12 | 0.02 | 0.055 |
| 3.00 | 0.15 | 0.03 | 0.068 |
| 4.00 | 0.17 | 0.03 | 0.089 |
| 5.00 | 0.18 | 0.04 | 0.090 |
| 6.00 | 0.19 | 0.04 | 0.096 |
| 7.00 | 0.19 | 0.04 | 0.098 |
| 8.00 | 0.20 | 0.04 | 0.099 |
| 9.00 | 0.20 | 0.04 | 0.099 |
| 10.00 | 0.20 | 0.04 | 0.099 |

## TABLE 2

Photolysis of Hexaphenyl dilead in Benzene

| $(\O_3Pb_2) \times 10^{-3}$ M | Quantum Yield | | |
|---|---|---|---|
| | $\O_2$ | $\O_2H_2$ | Pb |
| 0.25 | 0.025 | 0.007 | 0.024 |
| 1.00 | 0.045 | 0.014 | 0.044 |
| 2.00 | 0.056 | 0.015 | 0.052 |
| 3.00 | 0.075 | 0.016 | 0.066 |
| 4.00 | 0.085 | 0.017 | 0.087 |
| 5.00 | 0.090 | 0.017 | 0.089 |
| 6.00 | 0.095 | 0.017 | 0.093 |
| 7.00 | 0.095 | 0.017 | 0.095 |
| 8.00 | 0.096 | 0.017 | 0.096 |
| 9.00 | 0.097 | 0.017 | 0.097 |
| 10.00 | 0.100 | 0.017 | 0.098 |

## TABLE 3

### Photolysis of Tetraphenyl lead chloride in Benzene

| $(\text{Ø}_2\text{Pb}_2) \times 10^{-3}$ M | Quantum yield | | |
|---|---|---|---|
| | $\text{Ø}_2$ | $\text{Ø}_2\text{H}_2$ | Pb |
| 0.25 | 0.023 | 0.007 | 0.022 |
| 1.00 | 0.043 | 0.013 | 0.043 |
| 2.00 | 0.052 | 0.014 | 0.050 |
| 3.00 | 0.067 | 0.015 | 0.064 |
| 4.00 | 0.083 | 0.016 | 0.085 |
| 5.00 | 0.087 | 0.017 | 0.089 |
| 6.00 | 0.092 | 0.017 | 0.091 |
| 7.00 | 0.097 | 0.017 | 0.096 |
| 8.00 | 0.099 | 0.017 | 0.097 |
| 9.00 | 0.099 | 0.017 | 0.098 |
| 1.00 | 0.099 | 0.017 | 0.099 |

## TABLE 4

Photolysis of Triphenyl Lead Hydroxide in Benzene

| $(\phi_3PbOH) \times 10^{-3}M$ | Quantum Yield | | |
|---|---|---|---|
| | $\phi_2$ | $\phi_2H_2$ | Pb |
| 0.25 | 0.027 | 0.008 | 0.028 |
| 1.00 | 0.047 | 0.015 | 0.049 |
| 2.00 | 0.054 | 0.016 | 0.056 |
| 3.00 | 0.068 | 0.017 | 0.070 |
| 4.00 | 0.090 | 0.018 | 0.091 |
| 5.00 | 0.094 | 0.018 | 0.095 |
| 6.00 | 0.096 | 0.018 | 0.097 |
| 7.00 | 0.098 | 0.018 | 0.099 |
| 8.00 | 0.099 | 0.018 | 0.100 |
| 9.00 | 0.099 | 0.018 | 0.101 |
| 10.00 | 0.099 | 0.018 | 0.102 |

## TABLE 5

### $Co^{60}$ - γ Radiolysis of Lead Tetraphenyl in Benzene

| $(Pb\phi_4) \times 10^{-3}$ M | G value (100 e.v. yield) | | |
|---|---|---|---|
| | Pb | $\phi_2$ | $\phi_2H_2$ |
| 0 | 0 | 0.095 | 0.07 |
| 1 | 0.3 | 0.70 | 0.11 |
| 2 | 0.45 | 0.92 | 0.14 |
| 3 | 0.52 | 1.10 | 0.16 |
| 4 | 0.58 | 1.26 | 0.16 |
| 5 | 0.62 | 1.40 | 0.16 |
| 6 | 0.70 | 1.42 | 0.16 |
| 7 | 0.68 | 1.50 | 0.16 |
| 8 | 0.72 | 1.54 | 0.16 |
| 9 | 0.74 | 1.55 | 0.16 |
| 10 | 0.74 | 1.60 | 0.16 |

## TABLE 6

$Co^{60}$ - γ Radiolysis of Hexaphenyl dilead in Benzene

| $(Pb_2\phi_6) \times 10^{-3}$ M | G Value | | |
|---|---|---|---|
| | Pb | $\phi_2$ | $\phi_2H_2$ |
| 0 | 0 | 0.095 | 0.07 |
| 1 | 0.28 | 0.48 | 0.10 |
| 2 | 0.44 | 0.70 | 0.121 |
| 3 | 0.52 | 0.78 | 0.14 |
| 4 | 0.56 | 0.92 | 0.14 |
| 5 | 0.60 | 0.96 | 0.14 |
| 6 | 0.69 | 1.02 | 0.14 |
| 7 | 0.68 | 1.08 | 0.14 |
| 8 | 0.70 | 1.10 | 0.14 |
| 9 | 0.72 | 1.12 | 0.14 |
| 10 | 0.72 | 1.16 | 0.14 |

## TABLE 7

Co$^{60}$ - $\gamma$ Radiolysis of Triphenyl lead chloride in Benzene

| $(\phi_3PbCl) \times 10^{-3}$ M | G Value | | |
|---|---|---|---|
| | Pb | $\phi_2$ | $\phi_2H_2$ |
| 0 | 0.0 | 0.095 | 0.07 |
| 1 | 0.25 | 0.45 | 0.10 |
| 2 | 0.42 | 0.66 | 0.11 |
| 3 | 0.50 | 0.73 | 0.13 |
| 4 | 0.54 | 0.89 | 0.13 |
| 5 | 0.59 | 0.97 | 0.13 |
| 6 | 0.66 | 0.99 | 0.13 |
| 7 | 0.67 | 1.03 | 0.13 |
| 8 | 0.68 | 1.04 | 0.13 |
| 9 | 0.68 | 1.05 | 0.14 |
| 10 | 0.68 | 1.07 | 0.14 |

## TABLE 8

$Co^{60}$ - γ Radiolysis of Triphenyl Lead Hydroxide in Benzene

| $(\phi_3PbOH) \times 10^{-3}M$ | G Value | | |
|---|---|---|---|
| | Pb | $\phi_2$ | $\phi_2H_2$ |
| 0 | 0.0 | 0.075 | 0.07 |
| 1 | 0.30 | 0.47 | 0.11 |
| 2 | 0.46 | 0.68 | 0.12 |
| 3 | 0.53 | 0.74 | 0.13 |
| 4 | 0.57 | 0.91 | 0.14 |
| 5 | 0.63 | 0.94 | 0.15 |
| 6 | 0.69 | 1.00 | 0.15 |
| 7 | 0.69 | 1.05 | 0.15 |
| 8 | 0.70 | 1.07 | 0.15 |
| 9 | 0.73 | 1.09 | 0.15 |
| 10 | 0.73 | 1.10 | 0.15 |

## TABLE 9

Effect of dose on photolysis of $PbØ_4$, $Pb_2Ø_6$, $Ø_3PbCl$ and $Ø_3PbOH$ in Benzene

Concentration = $5 \times 10^{-3}$M

| Irradiation time in minutes | Quantum yield of Pb from | | | |
|---|---|---|---|---|
| | $PbØ_4$ | $Pb_2Ø_6$ | $Ø_3PbCl$ | $Ø_3PbOH$ |
| 60 | 0.0629 | 0.0780 | 0.0734 | 0.0830 |
| 90 | 0.2415 | 0.2338 | 0.2204 | 0.2490 |
| 120 | 0.4831 | 0.4671 | 0.4409 | 0.4979 |
| 150 | 0.8050 | 0.7793 | 0.7347 | 0.8254 |
| 180 | 0.8810 | 0.9353 | 0.8816 | 0.9906 |
| 210 | 1.1260 | 1.1160 | 1.0280 | 1.1550 |

## TABLE 10

Effect of dose on $Co^{60}$ - γ radiolysis of $PbØ_4$, $Pb_2Ø_6$, $Ø_3PbCl$ and $Ø_3PbOH$ in Benzene

Concentration = $5 \times 10^{-3}$M

| Irradiation time in minutes | $G_{Pb}$ from | | | |
|---|---|---|---|---|
| | $PbØ_4$ | $Pb_2Ø_6$ | $Ø_3PbCl$ | $Ø_3PbOH$ |
| 30 | 0.473 | 0.542 | 0.375 | 0.375 |
| 45 | 0.726 | 0.850 | 0.593 | 0.602 |
| 60 | 1.039 | 1.119 | 0.761 | 0.840 |
| 75 | 1.385 | 1.442 | 0.981 | 1.126 |
| 90 | 1.731 | 1.731 | 1.142 | 1.436 |
| 105 | 2.081 | 2.039 | 1.332 | 1.797 |

## TABLE 11

### Photolysis of Tin Tetraphenyl in Cyclohexane

| $(Pb\emptyset_4)$ $\times 10^{-3}$ M | Quantum yield of | | | |
|---|---|---|---|---|
| | $C_6H_6$ | $C_6H_{10}$ | $(C_6H_{11})_2$ | Pb |
| 0.25 | 0.080 | 0.019 | 0.159 | 0.045 |
| 0.5 | 0.141 | 0.029 | 0.168 | 0.072 |
| 1.0 | 0.212 | 0.041 | 0.176 | 0.110 |
| 1.5 | 0.225 | 0.043 | 0.172 | 0.121 |
| 2.0 | 0.251 | 0.043 | 0.174 | 0.130 |

## TABLE 12

### Photolysis of Hexaphenyl dilead in Cyclohexane

| $(Pb_2\emptyset_6)$ $\times 10^{-3}$ M | Quantum yield of | | | |
|---|---|---|---|---|
| | $C_6H_6$ | $C_6H_{10}$ | $(C_6H_{11})_2$ | Pb |
| 0.25 | 0.101 | 0.010 | 0.158 | 0.052 |
| 0.50 | 0.151 | 0.026 | 0.164 | 0.080 |
| 1.00 | 0.234 | 0.040 | 0.172 | 0.121 |
| 1.50 | 0.250 | 0.042 | 0.174 | 0.130 |
| 2.00 | 0.272 | 0.043 | 0.170 | 0.137 |

## TABLE 13

Photolysis of Triphenyl lead chloride in Cyclohexane

| $(\phi_3PbOH)$ × $10^{-3}$ M | Quantum yield of | | | |
|---|---|---|---|---|
| | $C_6H_6$ | $C_6H_{10}$ | $(C_6H_{11})_2$ | Pb |
| 0.25 | 0.097 | 0.019 | 0.159 | 0.049 |
| 0.50 | 0.151 | 0.029 | 0.168 | 0.076 |
| 1.00 | 0.226 | 0.041 | 0.176 | 0.115 |
| 1.50 | 0.242 | 0.043 | 0.172 | 0.124 |
| 2.00 | 0.264 | 0.043 | 0.174 | 0.131 |

## TABLE 14

Photolysis of Triphenyl lead hydroxide in cyclohexane

| $(\phi_3PbOH)$ × $10^{-3}$ M | Quantum yield of | | | |
|---|---|---|---|---|
| | $C_6H_6$ | $C_6H_{10}$ | $(C_6H_{11})_2$ | Pb |
| 0.25 | 0.099 | 0.018 | 0.158 | 0.051 |
| 0.50 | 0.156 | 0.026 | 0.164 | 0.078 |
| 1.00 | 0.231 | 0.040 | 0.172 | 0.119 |
| 1.50 | 0.250 | 0.042 | 0.174 | 0.126 |
| 2.00 | 0.254 | 0.043 | 0.176 | 0.130 |

## TABLE 15

$Co^{60}$ - $\gamma$ radiolysis of Tetraphenyl lead in cyclohexane

| $(Pb\phi_4)$ × $10^{-3}$ M | G value<br>$C_6H_6$ | $C_6H_{10}$ | $(C_6H_{11})_2$ | Pb |
|---|---|---|---|---|
| 0.00 | 0.60 | 2.95 | 1.45 | 0.00 |
| 0.25 | 1.65 | 2.97 | 1.45 | 0.52 |
| 0.50 | 2.50 | 3.00 | 1.45 | 0.94 |
| 1.00 | 4.90 | 3.05 | 1.45 | 2.18 |
| 1.50 | 5.80 | 3.04 | 1.45 | 2.63 |
| 2.00 | 6.20 | 3.06 | 1.45 | 2.89 |

## TABLE 16

$Co^{60}$ - $\gamma$ radiolysis of Hexaphenyl dilead in cyclohexane

| $(Pb_2\phi_6)$ × $10^{-3}$ M | G value<br>$C_6H_6$ | $C_6H_{10}$ | $(C_6H_{11})_2$ | Pb |
|---|---|---|---|---|
| 0.00 | 0.60 | 2.95 | 1.45 | 0.00 |
| 0.25 | 1.15 | 2.98 | 1.46 | 0.54 |
| 0.50 | 1.54 | 3.00 | 1.47 | 0.96 |
| 1.00 | 2.98 | 3.08 | 1.45 | 2.30 |
| 1.50 | 3.36 | 3.11 | 1.46 | 2.74 |
| 2.00 | 3.50 | 3.11 | 1.46 | 2.95 |

## TABLE 17

$Co^{60}$ - γ radiolysis of Triphenyl lead chloride in Cyclohexene

| $(\phi_3PbCl)$ × $10^{-3}$ M | G value |  |  |  |
|---|---|---|---|---|
|  | $C_6H_6$ | $C_6H_{10}$ | $(C_6H_{11})_2$ | Pb |
| 0.00 | 0.60 | 2.95 | 1.45 | 0.00 |
| 0.25 | 1.10 | 2.99 | 1.46 | 0.50 |
| 0.50 | 1.58 | 3.06 | 1.46 | 0.94 |
| 1.00 | 2.88 | 3.09 | 1.47 | 2.10 |
| 1.50 | 3.20 | 3.11 | 1.46 | 2.60 |
| 2.00 | 3.48 | 3.13 | 1.46 | 2.81 |

## TABLE 18

$Co^{60}$ - γ radiolysis of Triphenyl lead hydroxide in Cyclohexane

| $(\phi_3PbOH)$ × $10^{-3}$ M | G Value |  |  |  |
|---|---|---|---|---|
|  | $C_6H_6$ | $C_6H_{10}$ | $(C_6H_{11})_2$ | Pb |
| 0.00 | 0.60 | 2.95 | 1.45 | 0.00 |
| 0.25 | 1.10 | 2.97 | 1.46 | 0.50 |
| 0.50 | 1.50 | 2.99 | 1.46 | 0.95 |
| 1.00 | 2.76 | 3.05 | 1.45 | 2.14 |
| 1.50 | 3.19 | 3.10 | 1.46 | 2.55 |
| 2.00 | 3.33 | 3.10 | 1.47 | 2.80 |

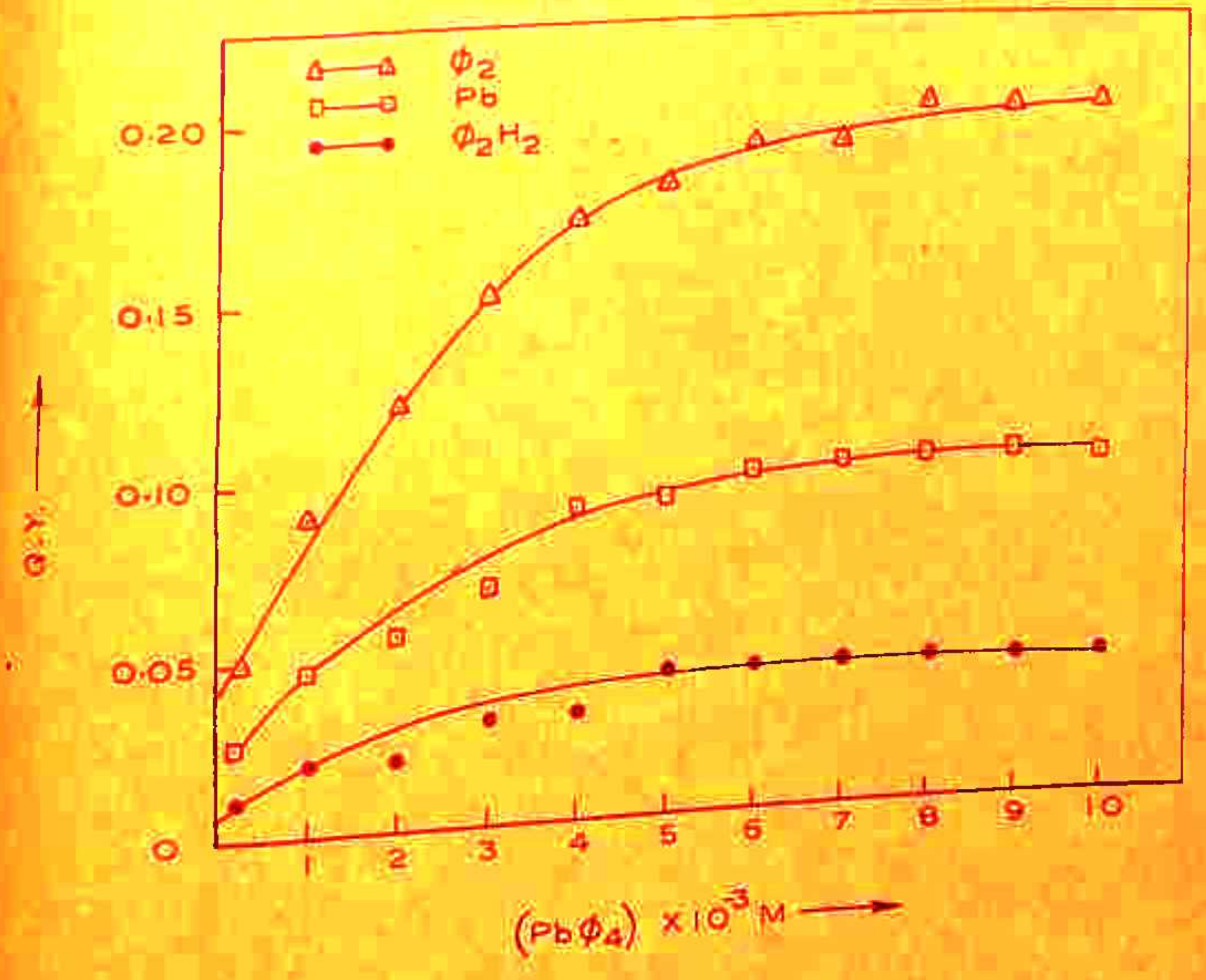

FIG. 4·1 PHOTOLYSIS OF LEAD TETRAPHENYL IN BENZENE.

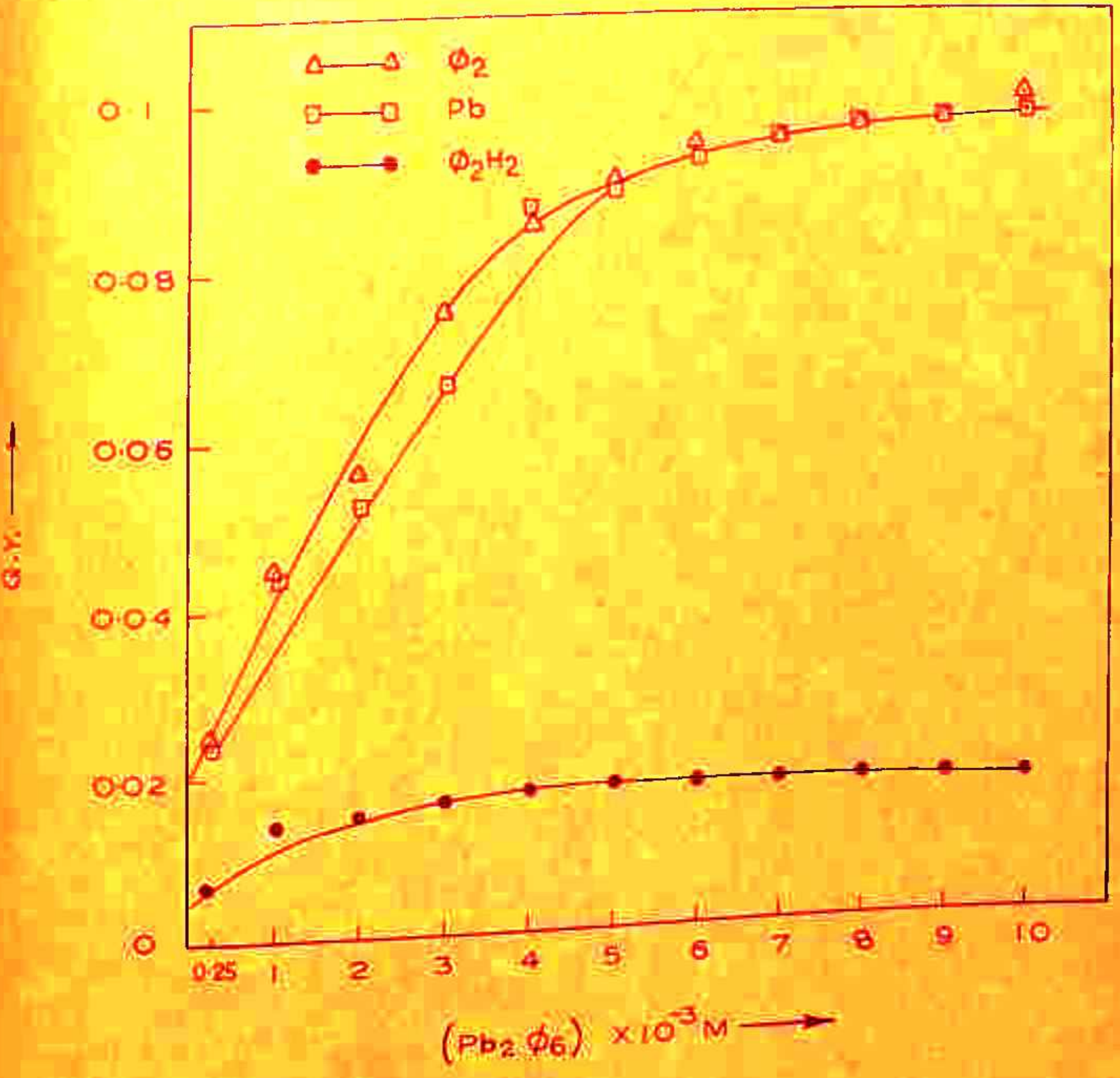

FIG. 4·2 PHOTOLYSIS OF HEXAPHENYL DILEAD IN BENZENE.

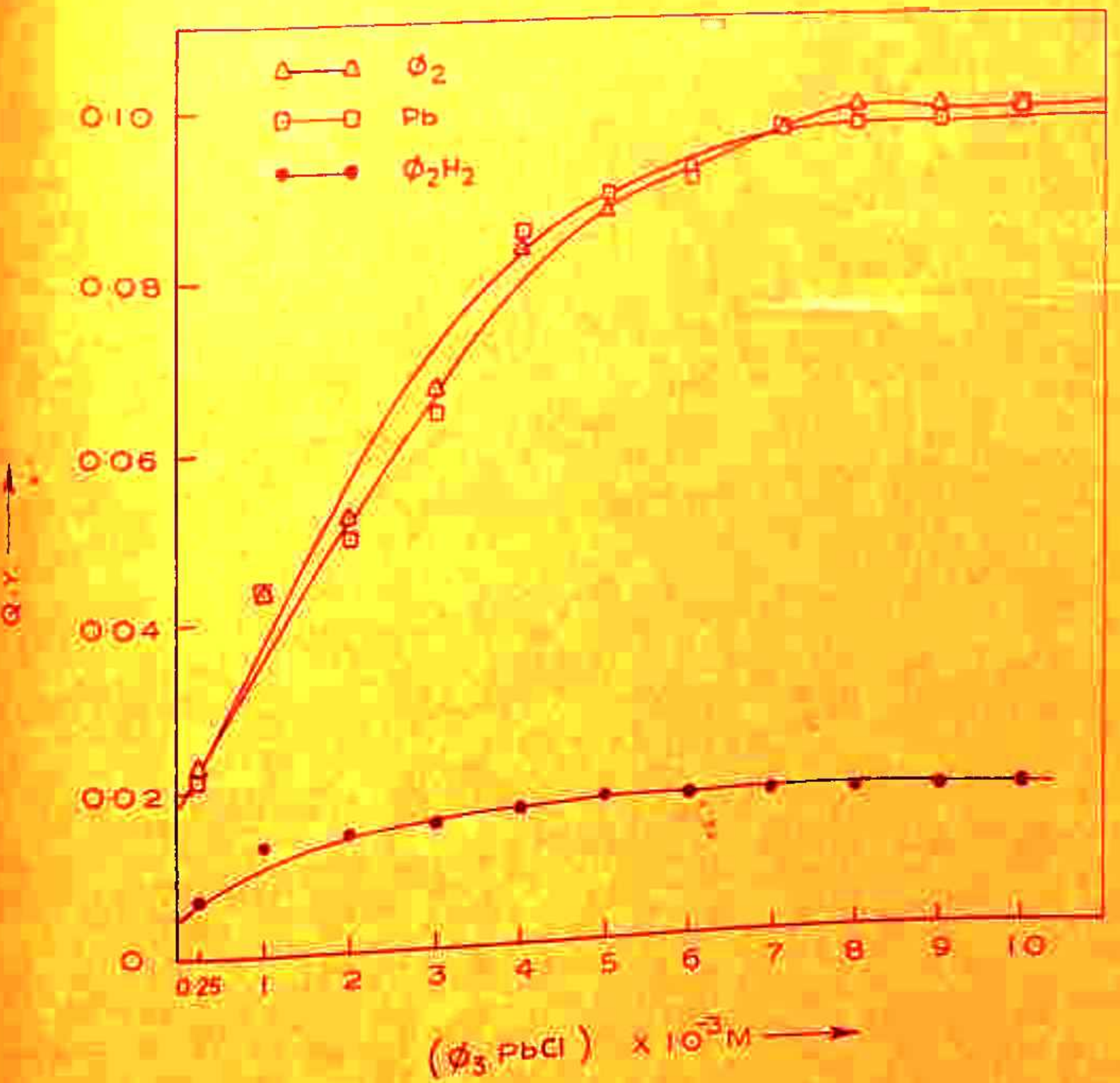

FIG.4·3 PHOTOLYSIS OF LEAD TRIPHENYL CHLORIDE IN BENZENE.

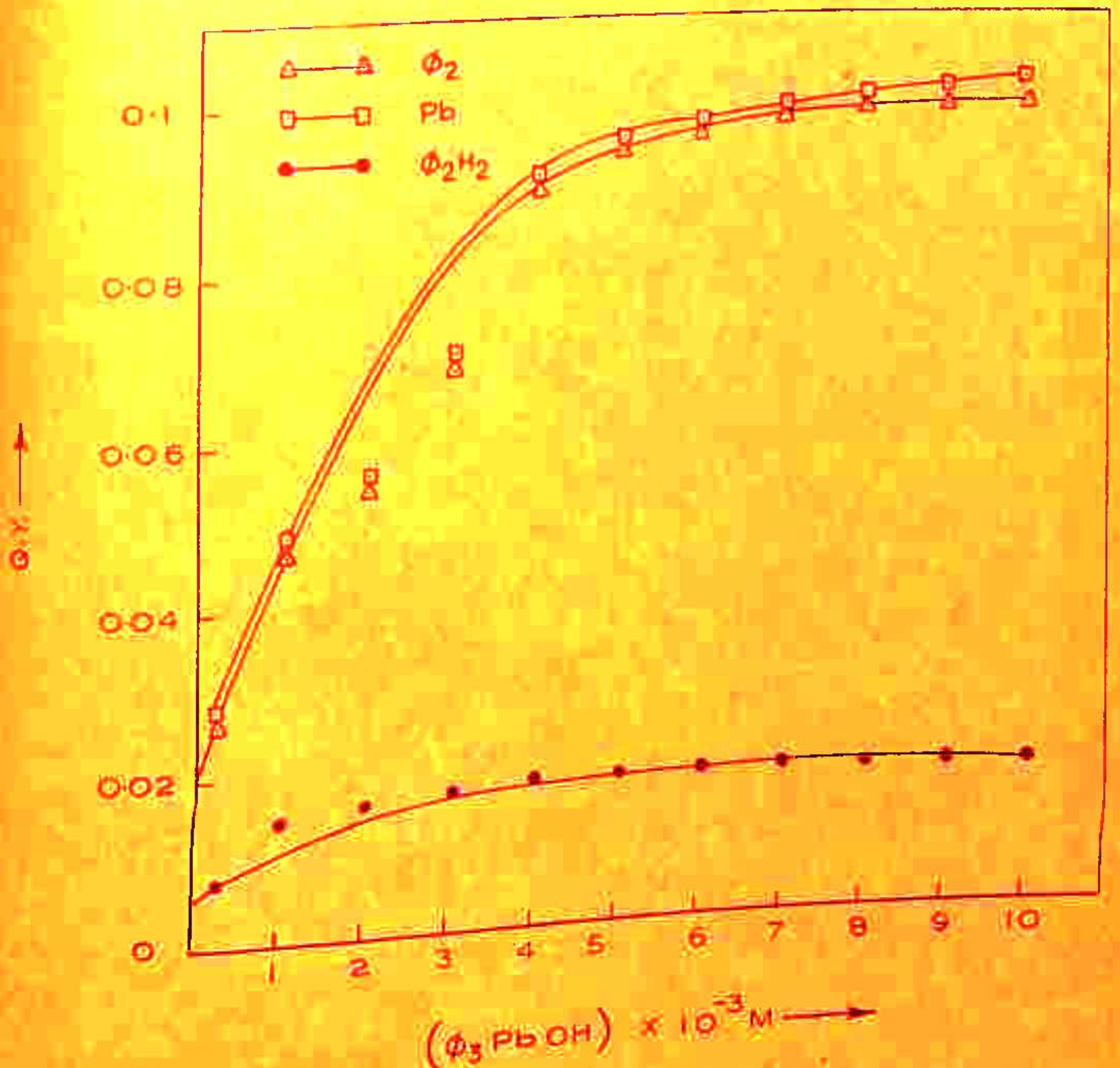

FIG 4·4 PHOTOLYSIS OF TRIPHENYL LEAD HYDROXIDE IN BENZENE.

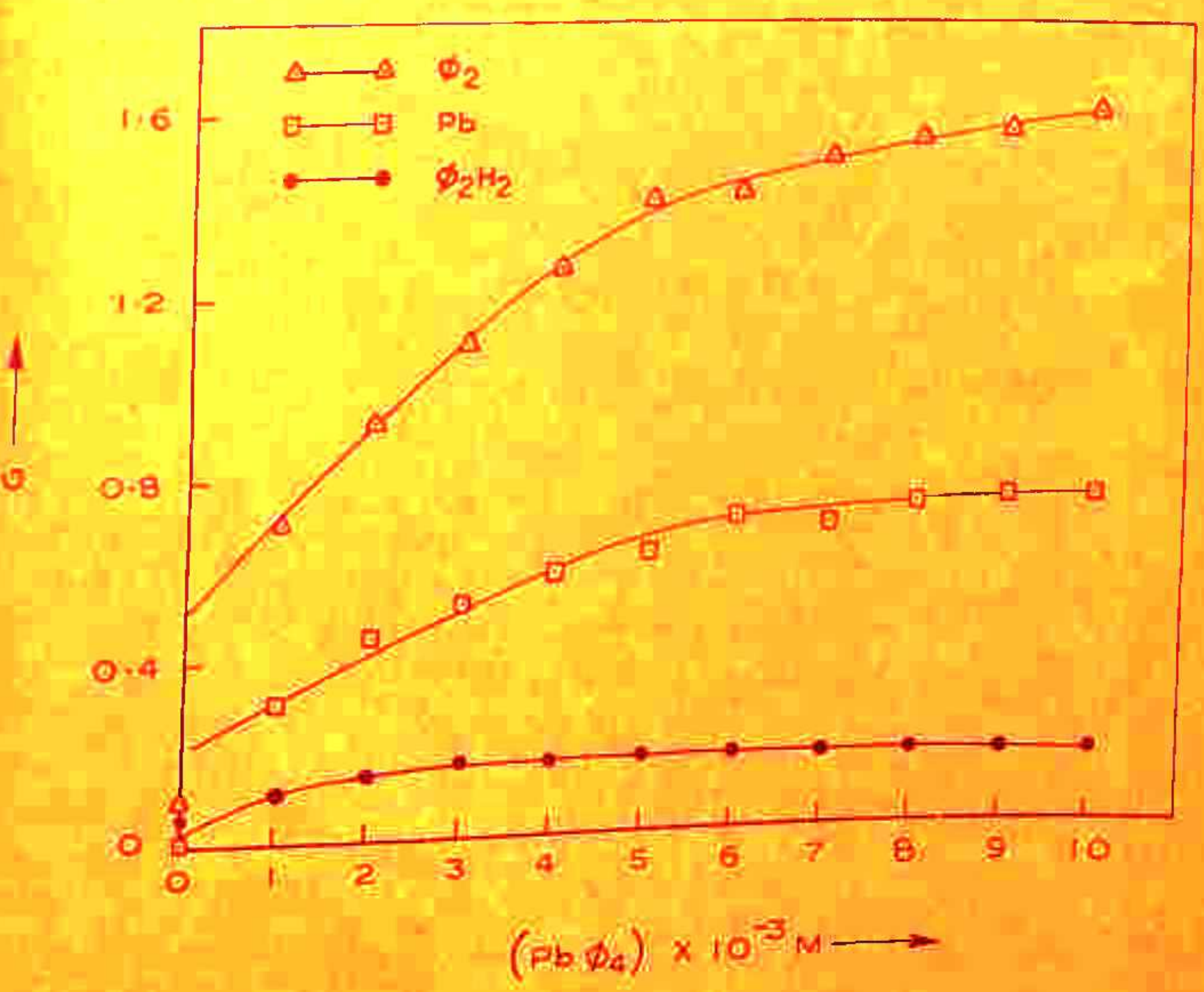

FIG. 4·5 RADIOLYSIS OF LEAD TETRAPHENYL IN BENZENE.

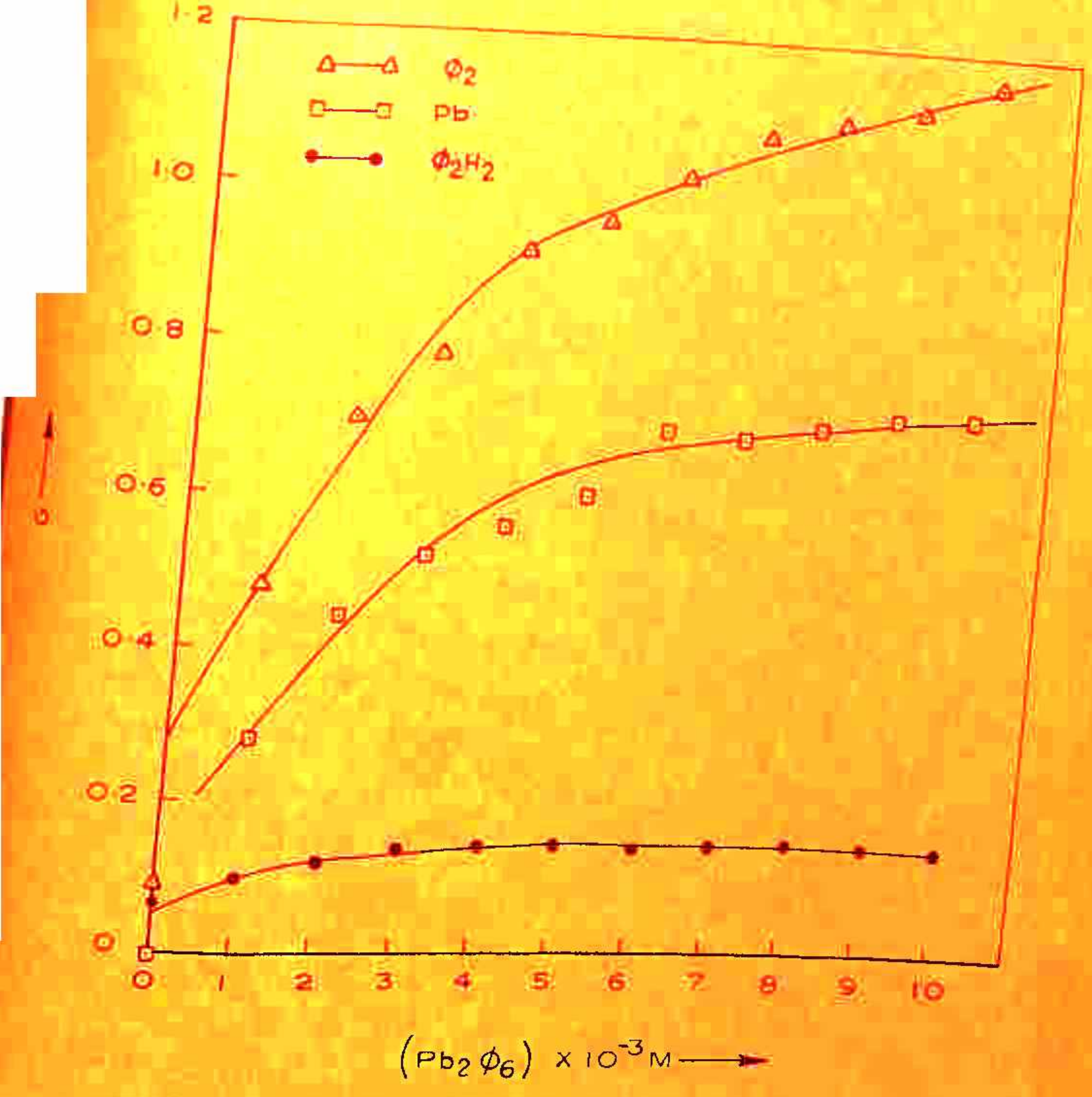

FIG. 4.6 RADIOLYSIS OF HEXAPHENYL DILEAD IN BENZENE.

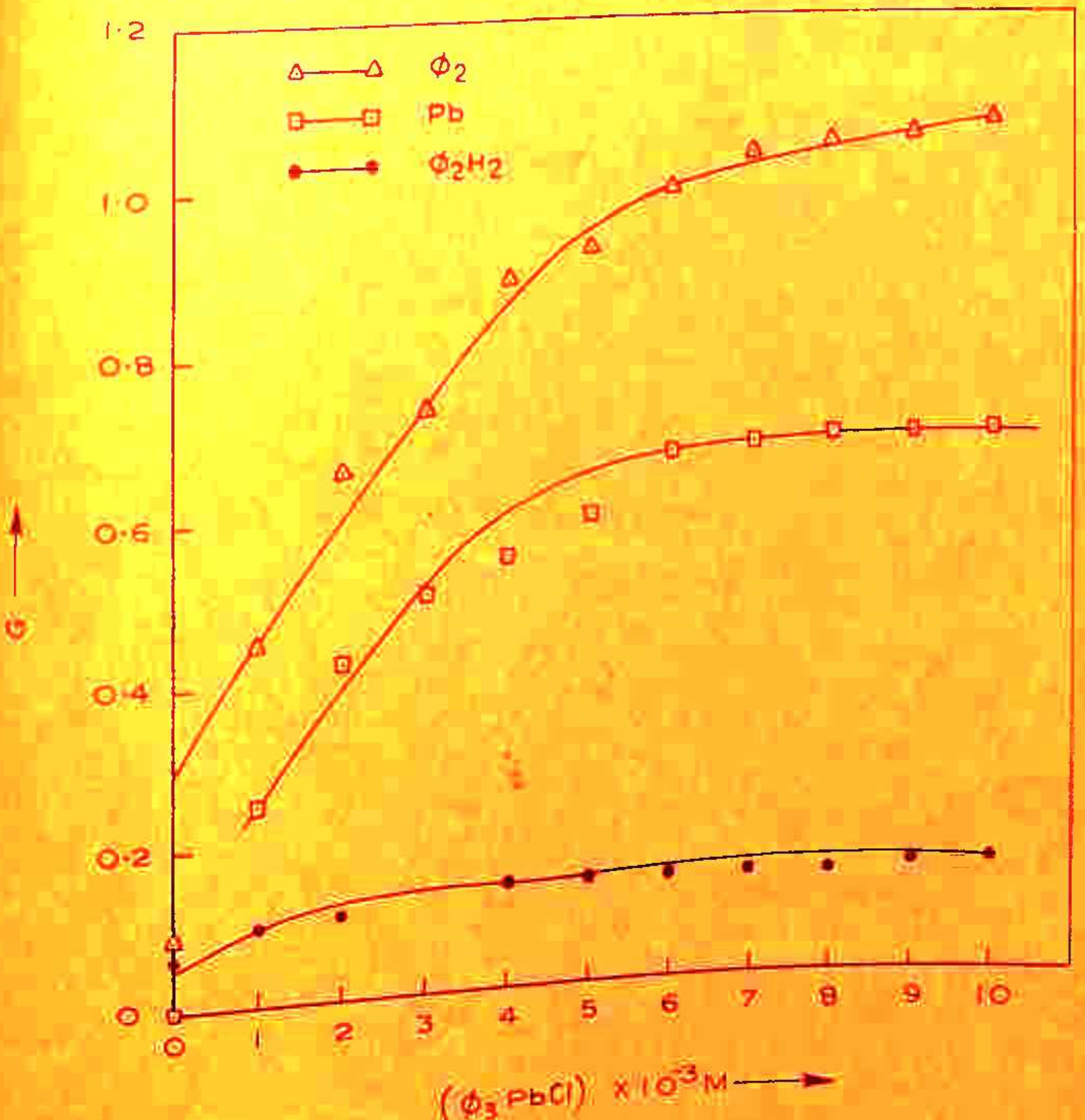

FIG.4·7 RADIOLYSIS OF TRIPHENYL LEAD CHLORIDE IN BENZENE.

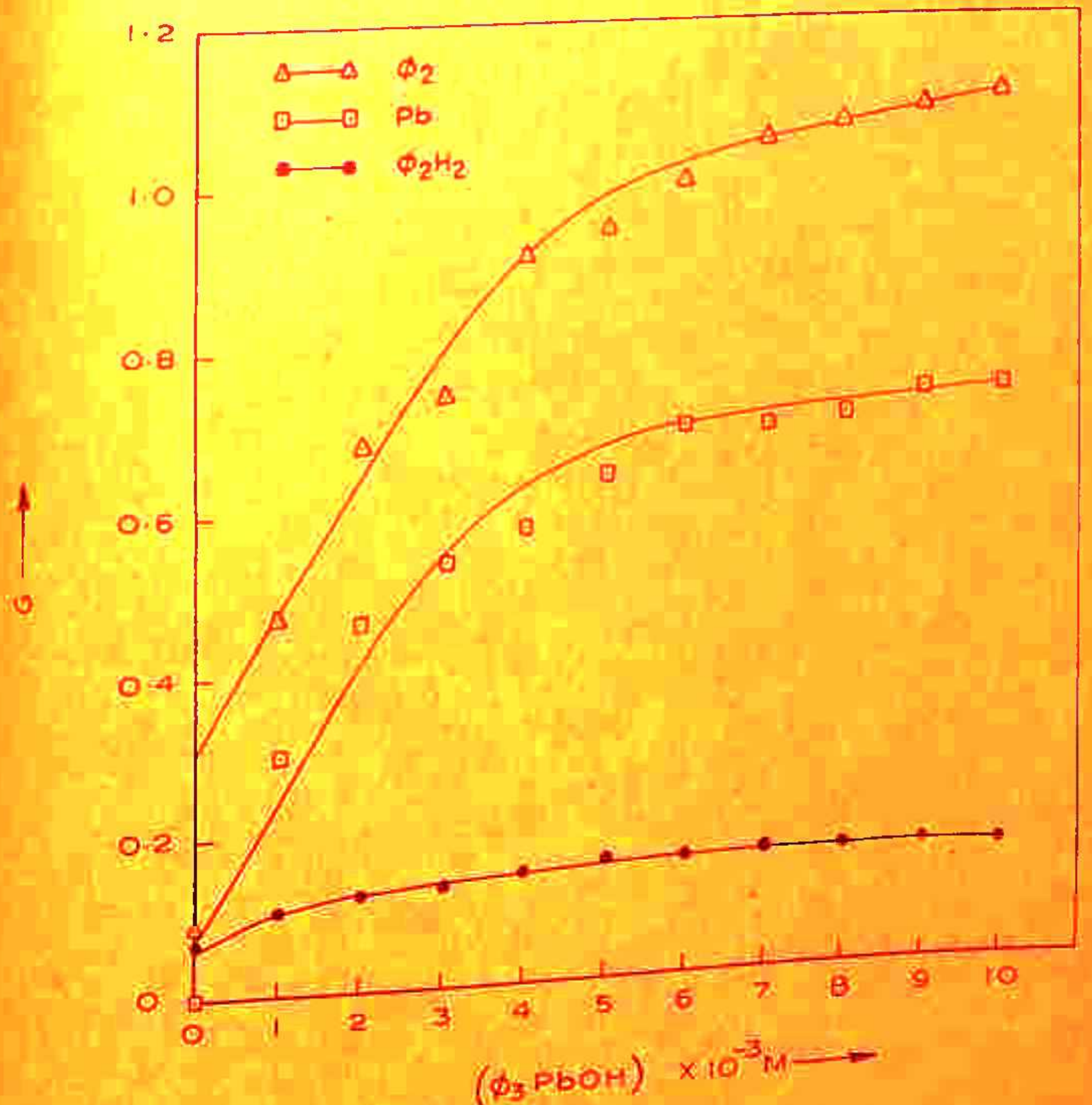

FIG. 4·8 RADIOLYSIS OF TRIPHENYL LEAD HYDROXIDE IN BENZENE.

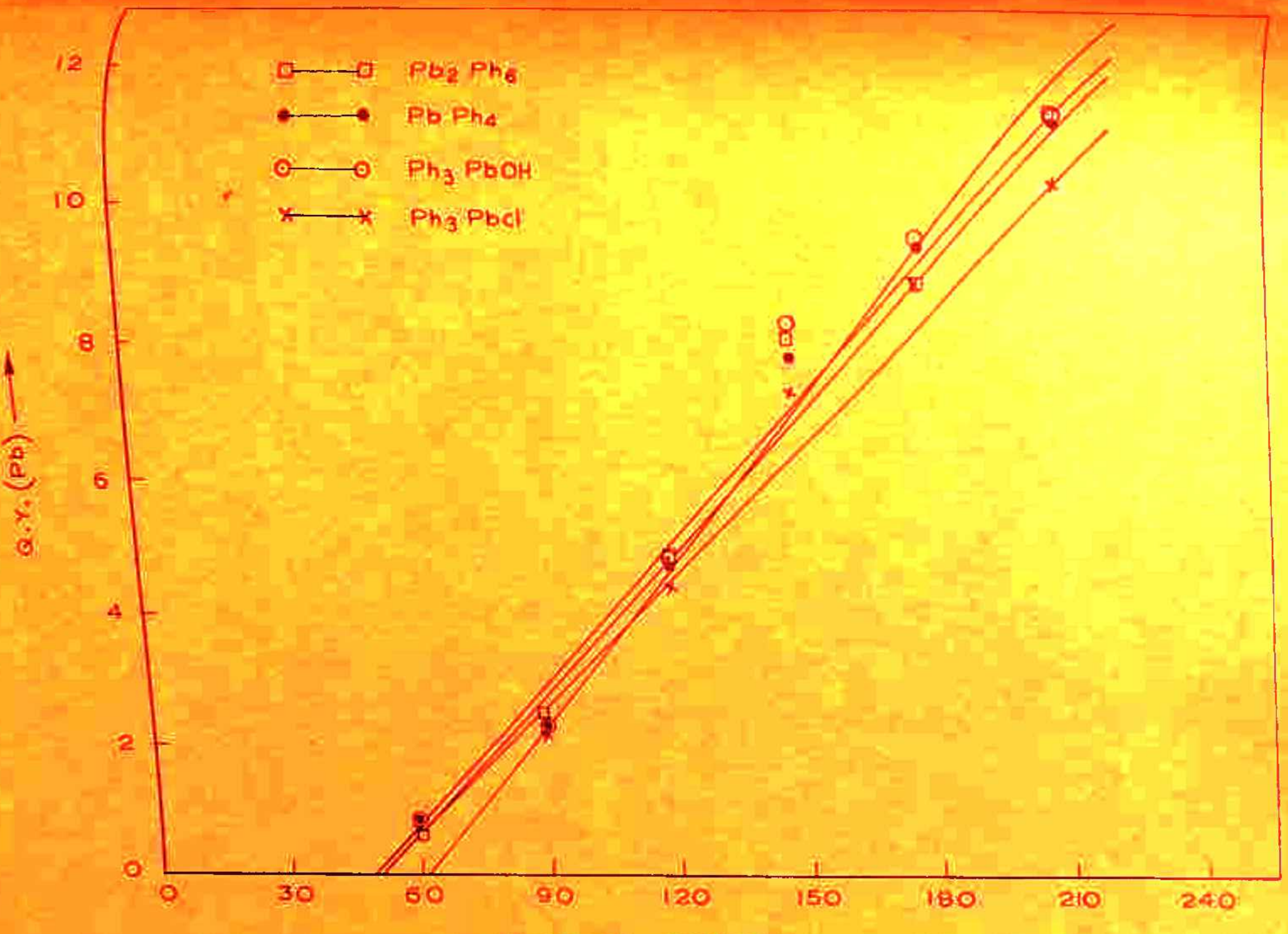

FIG 4·9 EFFECT OF DOSE ON THE PHOTOLYSIS OF LEAD ARYLS IN BENZENE

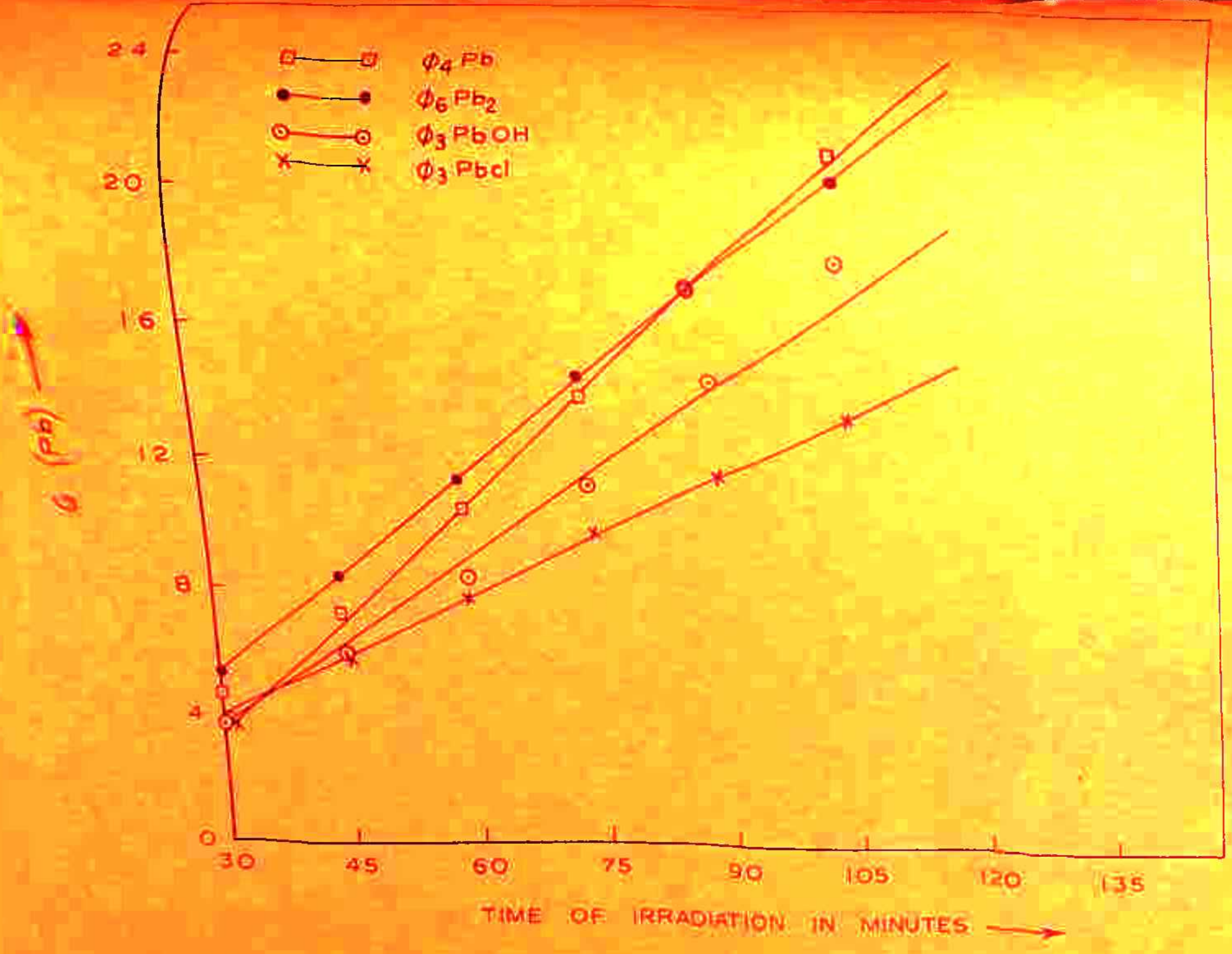

FIG. 4.10 EFFECT OF DOSE ON RADIOLYSIS OF LEAD ARYLS IN BENZENE.

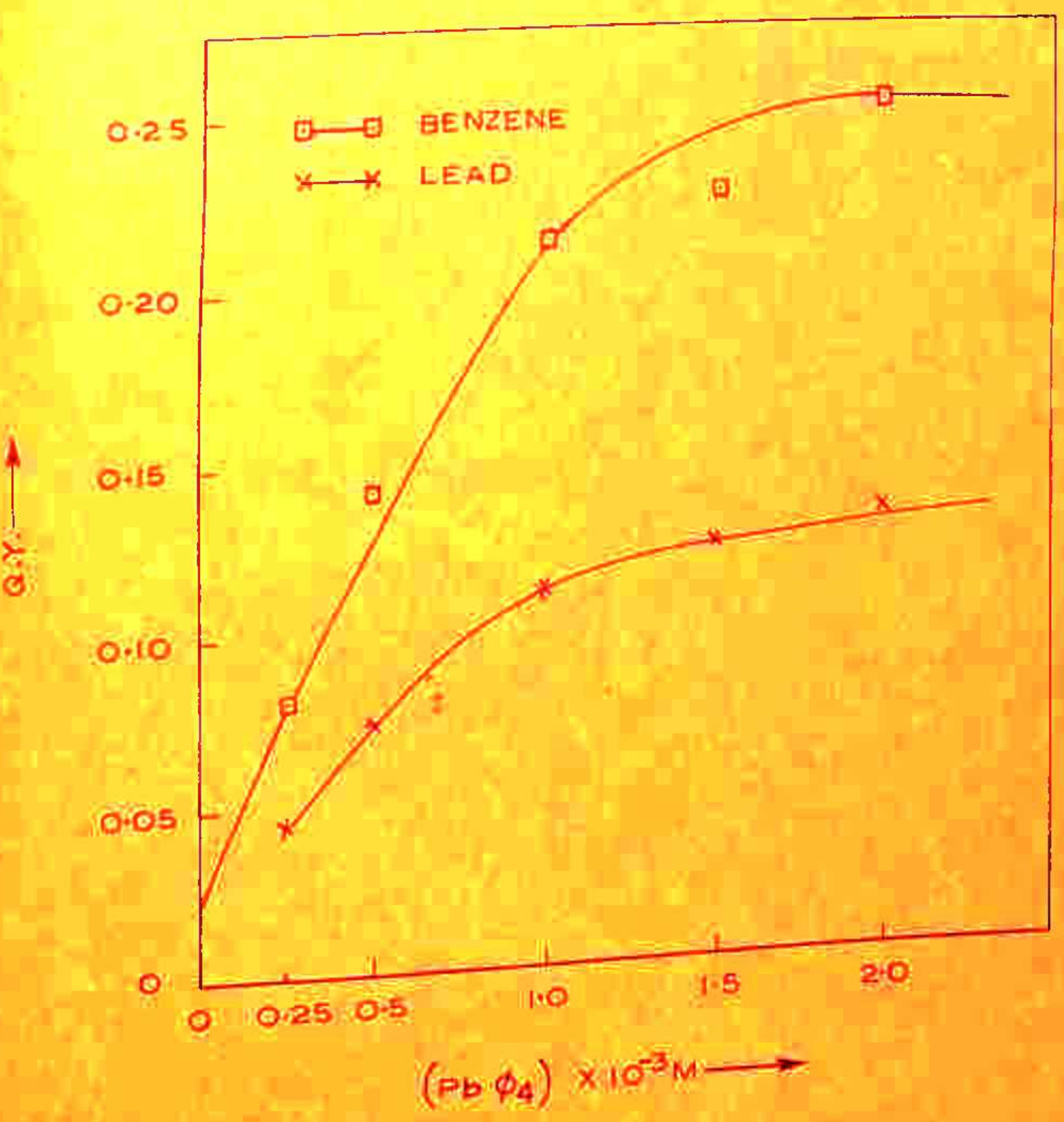

FIG. 4·11 PHOTOLYSIS OF TIN TETRAPHENYL IN CYCLOHEXANE

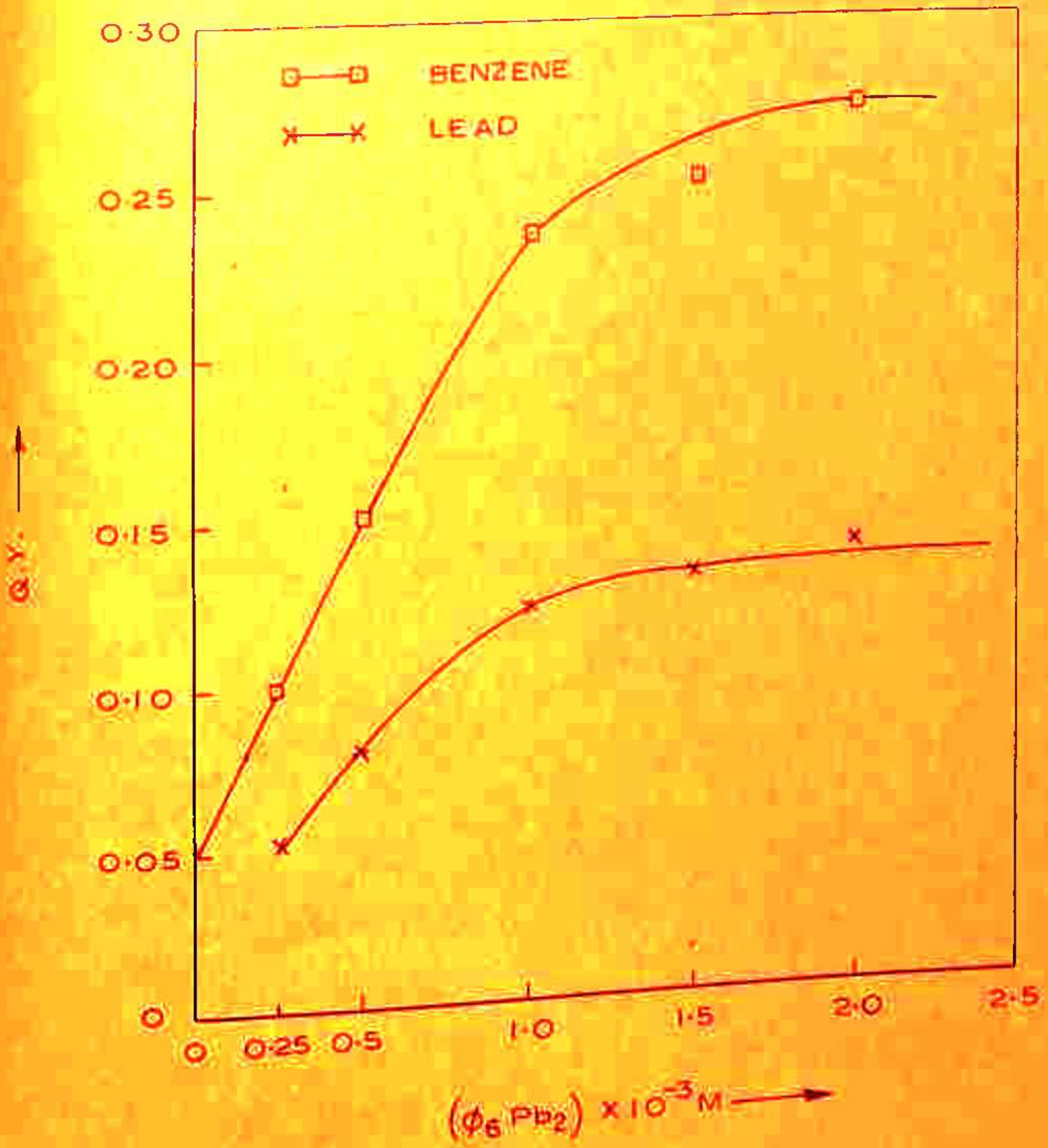

FIG 4·12 PHOTOLYSIS OF HEXAPHENYL DILEAD IN CYCLOHEXANE.

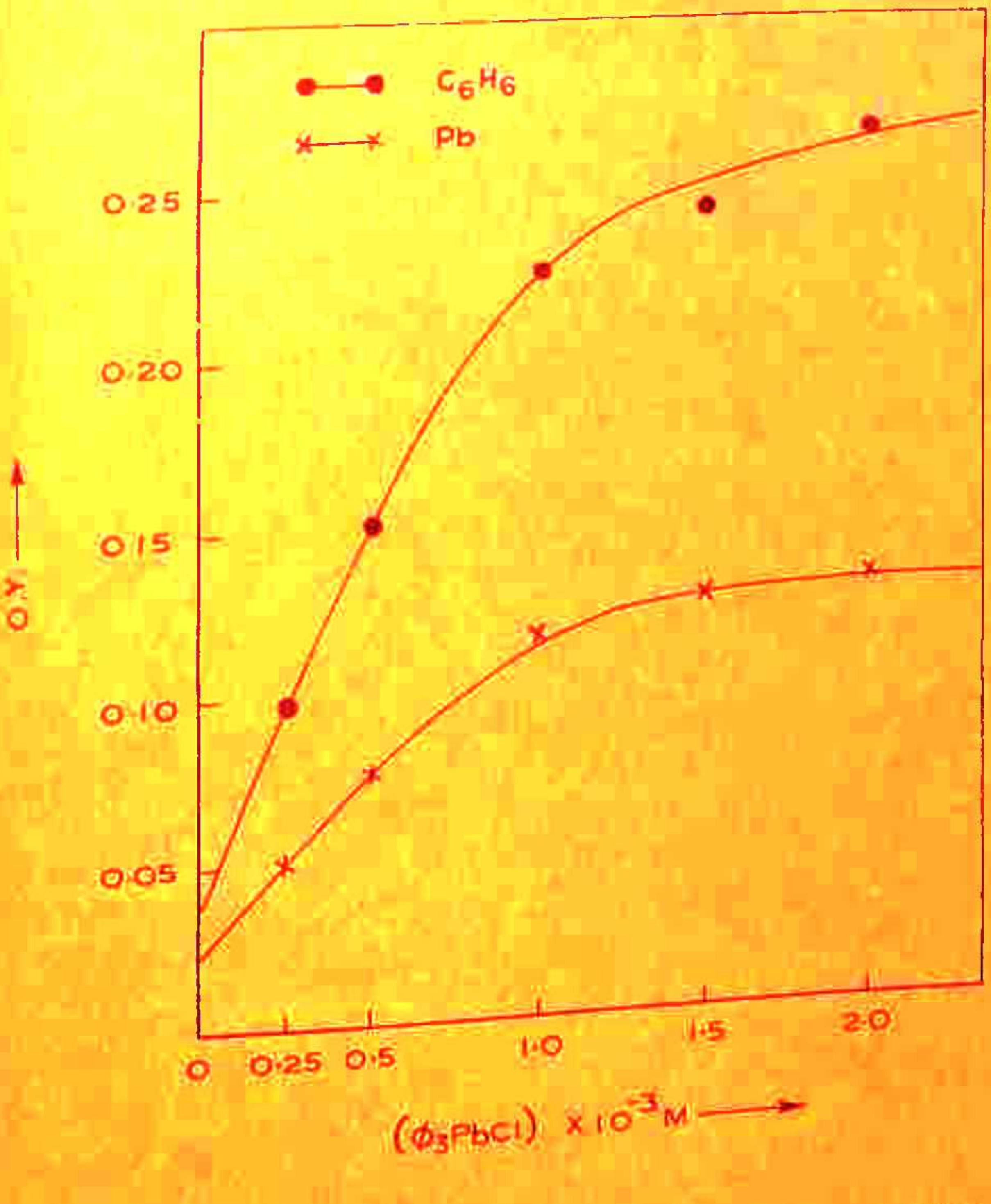

FIG. 4.13 PHOTOLYSIS OF TRIPHENYL LEAD CHLORIDE IN CYCLOHEXANE.

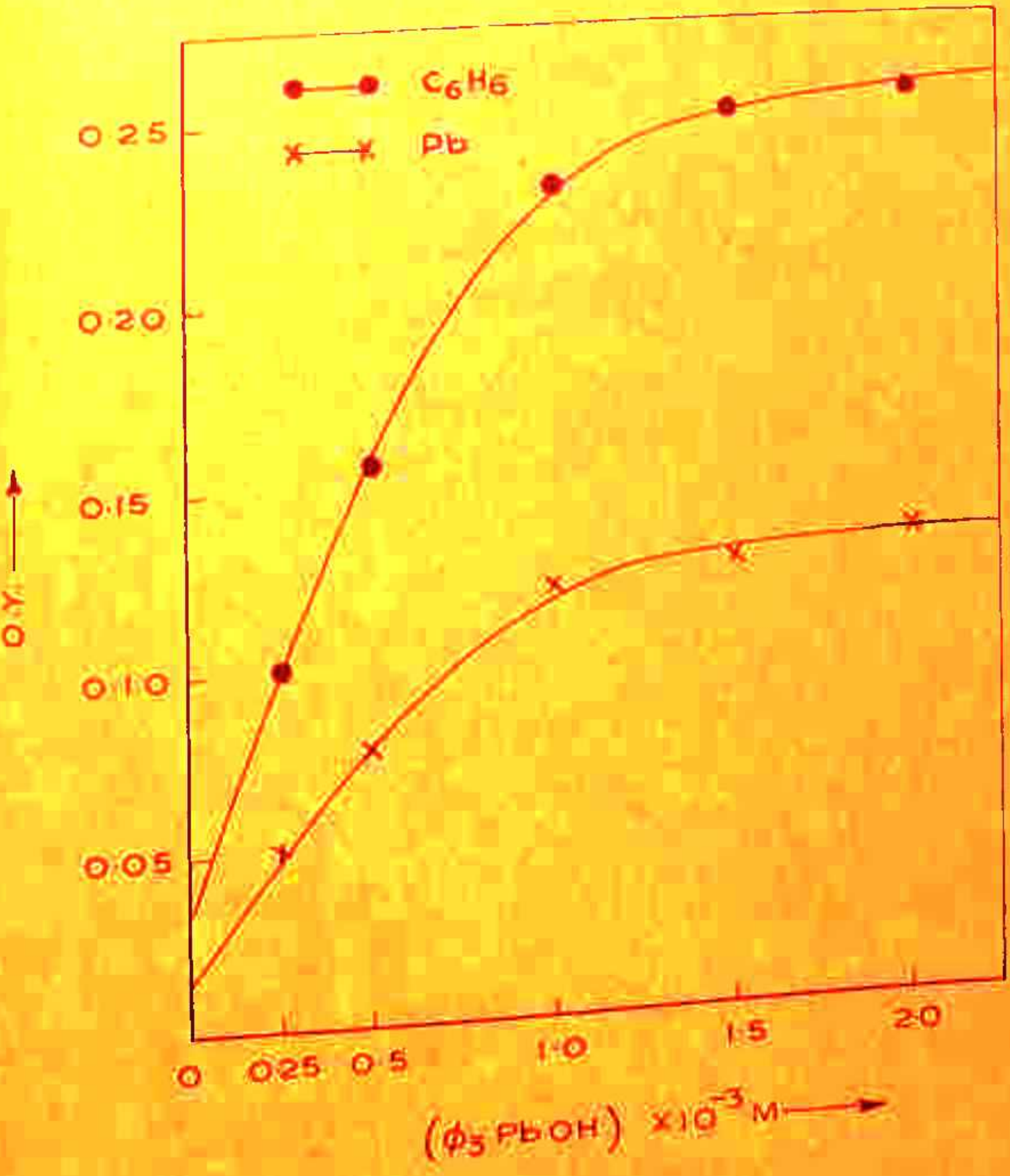

FIG. 4.14 PHOTOLYSIS OF TRIPHENYL LEAD HYDROXIDE IN CYCLOHEXANE.

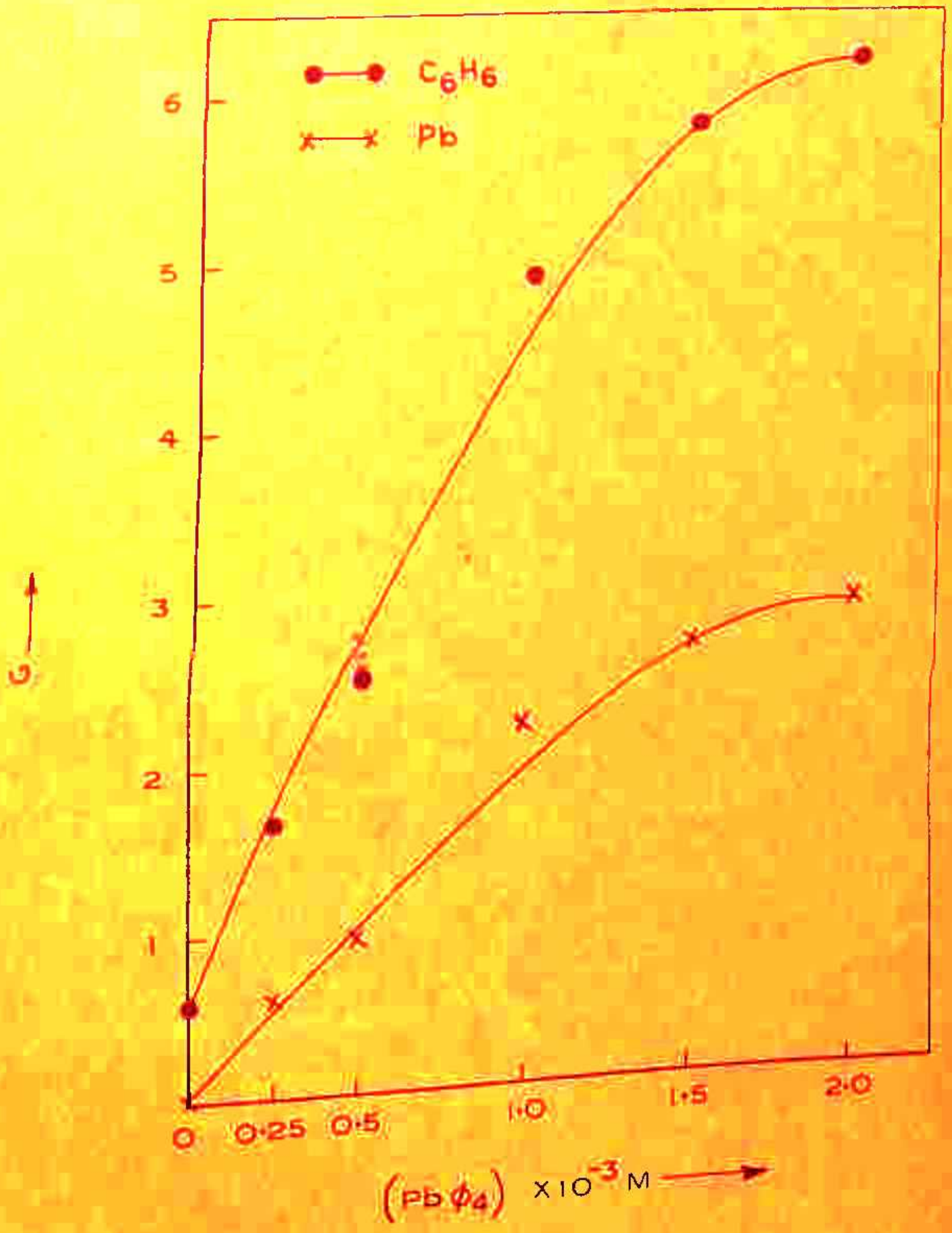

FIG. 4·15 RADIOLYSIS OF LEAD TETRAPHENYL IN CYCLOHEXANE.

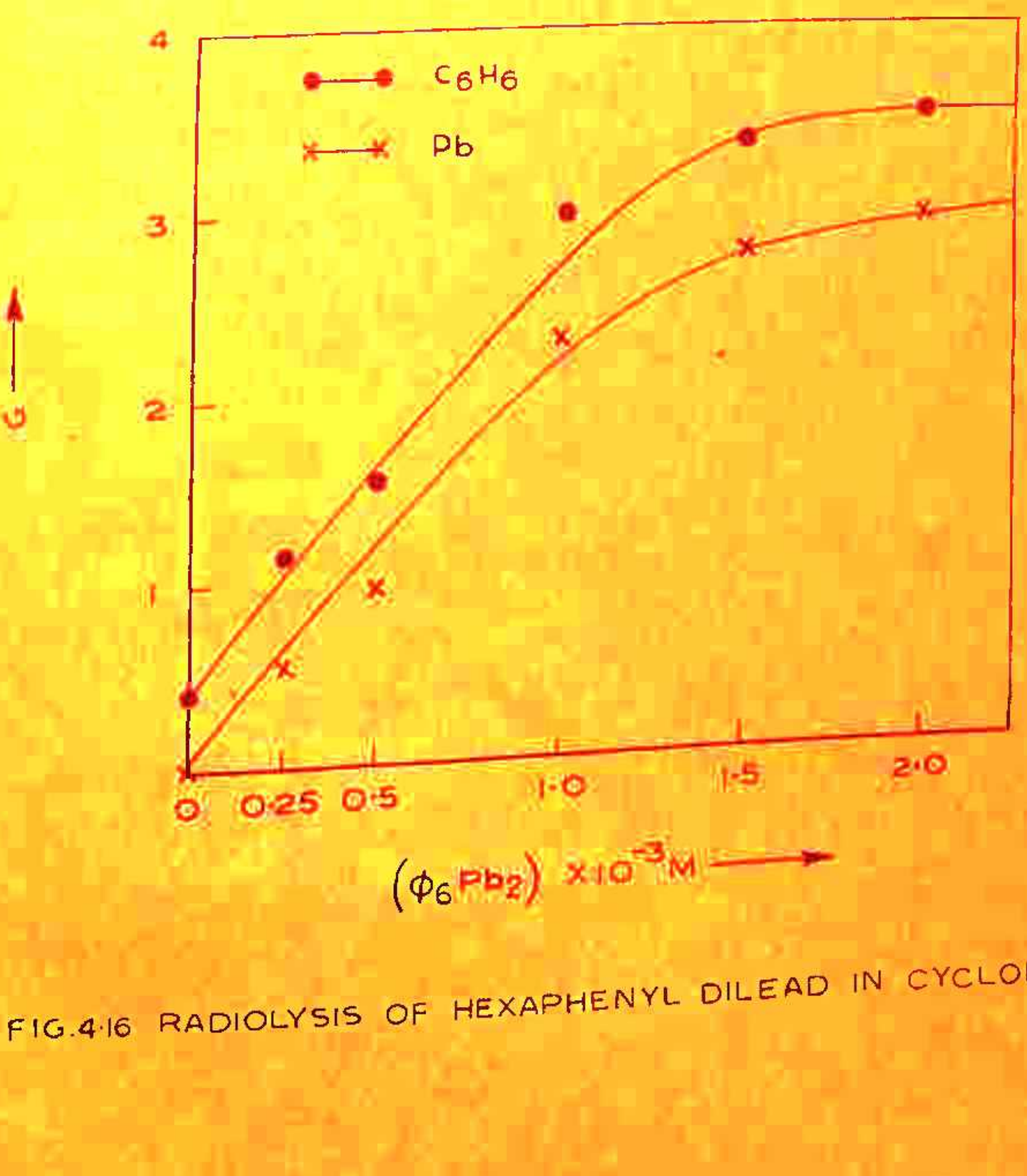

FIG. 4.16 RADIOLYSIS OF HEXAPHENYL DILEAD IN CYCLOHEXANE.

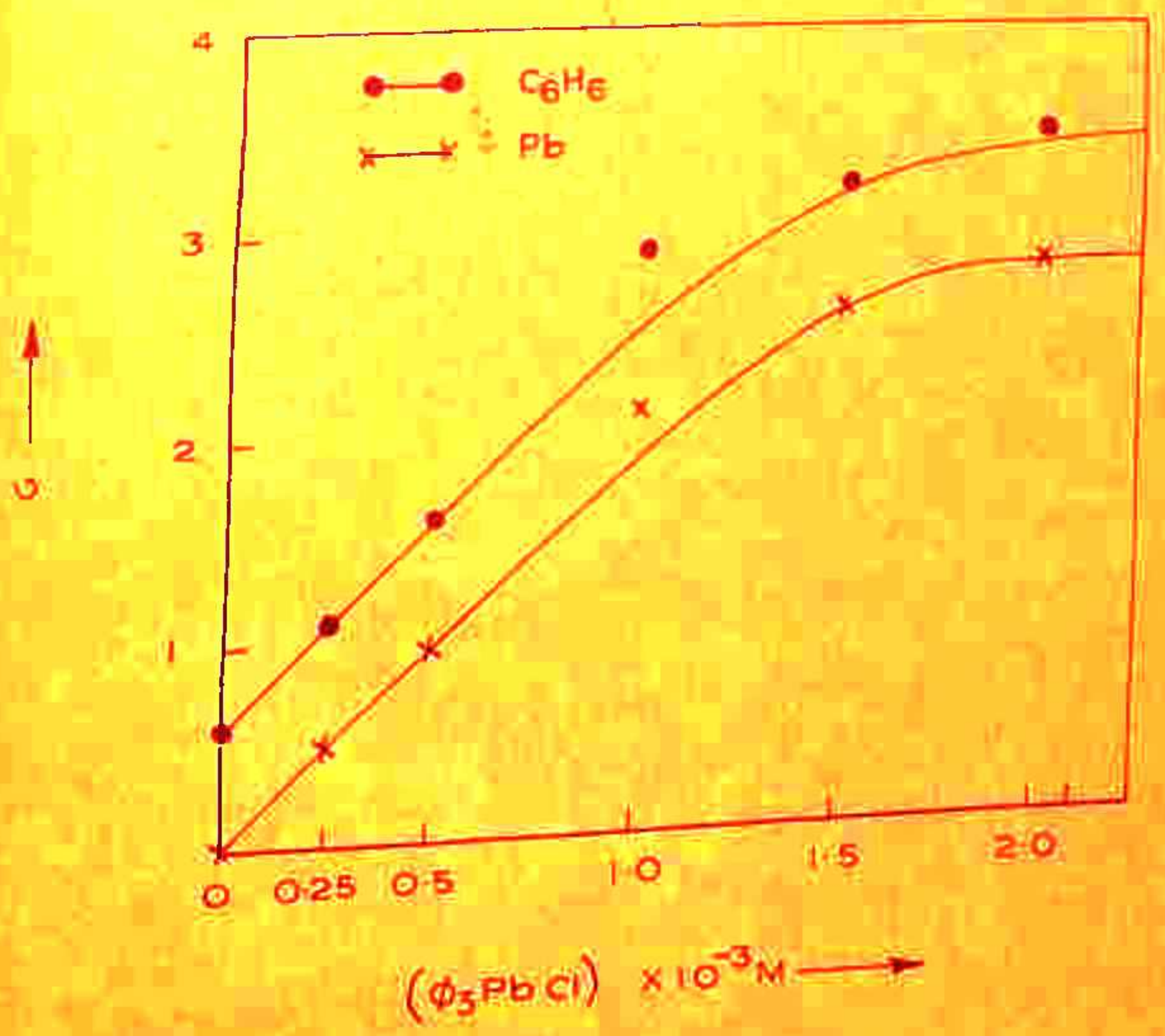

FIG. 4·17 RADIOLYSIS OF TRIPHENYL LEAD CHLORIDE IN CYCLOHEXANE.

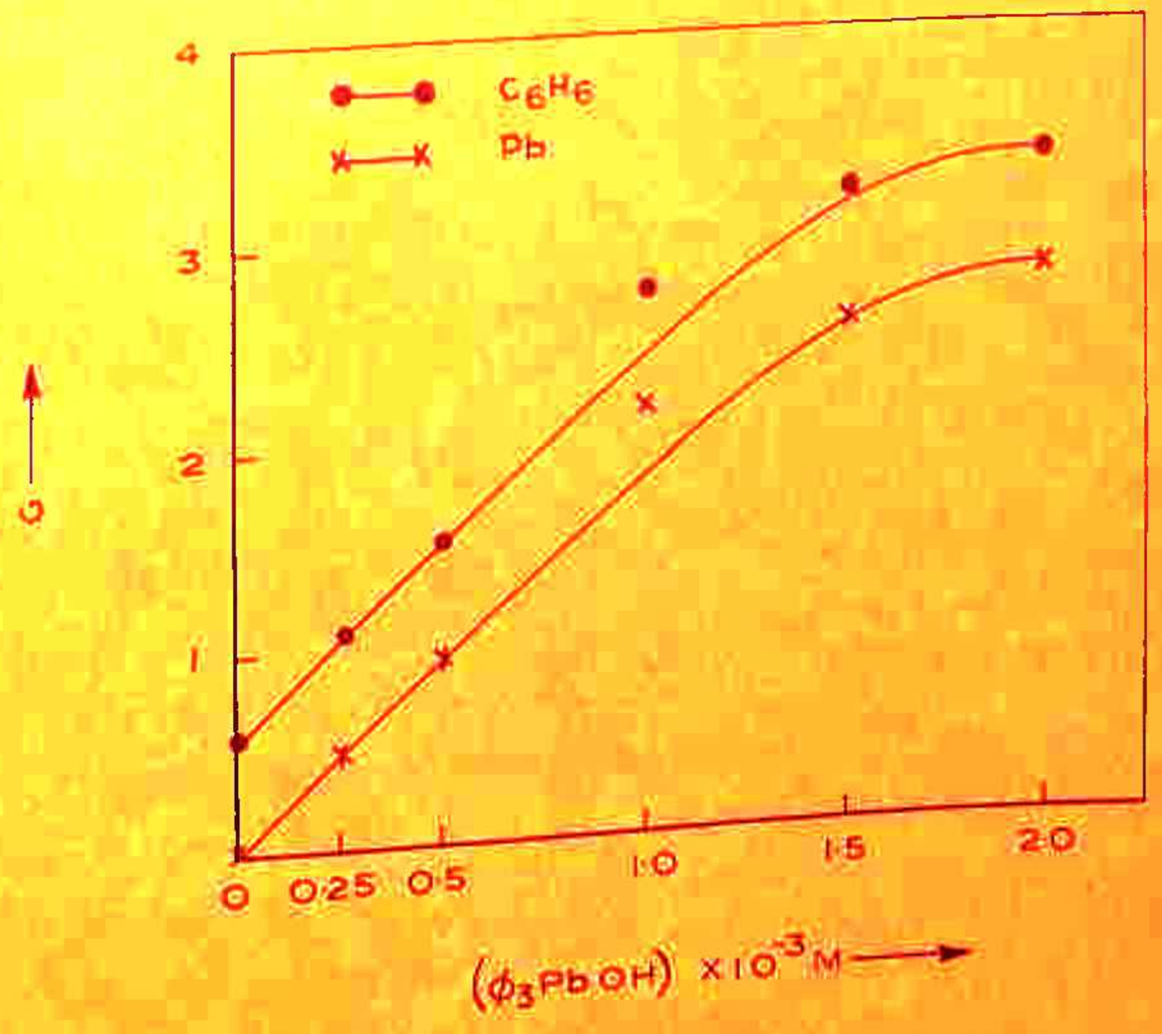

FIG. 4·18 RADIOLYSIS OF TRIPHENYL LEAD HYDROXIDE IN CYCLOHEXANE.

layer is bright red and the upper layer is colorless, there is probably too much lead in the sample. Enough of carbon tetrachloride layer is carefully transferred to fill the experimental cell and optical density is determined at 520 mμ. The optical density is also determined by 1% nitric acid standard lead solution.

The results of the analysis are presented in Tables 1-18 and are summarized in Figs. 4.1-4.18.

## RESULTS

The major condensable products formed during the photolysis of lead tetraphenyl, hexaphenyl dilead, triphenyl lead chloride and triphenyl lead hydroxide in benzene by ultraviolet light are diphenyl, phenyl cyclohexadiene ($\phi_2H_2$) and metallic lead. The quantum yield of diphenyl increases regularly with the concentration of the solute and reaches a plateau. The quantum yield of diphenyl is nearly double that of metallic lead in case of lead tetraphenyl and nearly equal in the case of other lead compounds.

The radiolysis of lead tetraphenyl, hexaphenyl dilead, triphenyl lead chloride and triphenyl lead hydroxide in benzene by $Co^{60}$ - γ rays gives diphenyl, phenylcyclohexadiene and lead as major condensable products.

The ratio of the yield of diphenyl to metallic lead is almost two in the case of lead tetraphenyl. However this ratio is approximately greater than one in case of other lead compounds.

To observe the effect of dose on dilute solutions of lead phenyls, some concentrations were taken in benzene and irradiated by ultraviolet and gamma radiation. It is observed that the quantum yield and the G value of lead increases linearly with dose of radiation (Figs. 4.9 and 4.10).

The major condensable products formed in the photolysis of lead tetraphenyl, hexaphenyl dilead, triphenyl lead chloride and triphenyl lead hydroxide in cyclohexane by ultraviolet light are benzene, cyclohexene, bicyclohexyl and metallic lead. The quantum yields of cyclohexene and bicyclohexyl increase regularly with concentration. The ratio of the quantum yield of benzene to metallic lead is nearly two in each case.

The major condensable products formed in the radiolysis of dilute solutions of lead tetraphenyl, hexaphenyl dilead, triphenyl lead chloride and triphenyl lead hydroxide in cyclohexane are benzene, cyclohexene, bicyclohexyl and metallic lead. The yield of cyclohexene and bicyclohexyl per 100 ev are almost the same in each compound and the G values practically remain constant. The yield of diphenyl is double with respect to lead in the case of lead tetraphenyl. However, the yield of diphenyl in other lead phenyls is almost equal to the yield of lead.

## DISCUSSION

### Photolysis and Radiolysis of Lead Tetraphenyl in Benzene

#### Lead Tetraphenyl

The large yield of diphenyl and dihydrodiphenyl cannot be explained by the direct dissociation of lead tetraphenyl by absorption of energy directly, because solution is very dilute and therefore the electron fraction of the solute is very small. Further no diphenyl production has been noted in the radiolysis of lead tetraphenyl in cyclohexane, although considerable amount of benzene has been found out. Therefore decomposition of lead tetraphenyl by an attack of phenyl radical is ruled out. Further tetraphenyl lead is decomposed thermally[1], or photochemically[2] or by high energy radiation[3,4]. Since no dihydrodiphenyl or lead yield is reported in the photolysis of lead tetraphenyl in benzene and the data are not precise[3,4], an attempt has been made to improve it and to provide more information on the yield of lead and dihydrodiphenyl since diphenyl is produced almost twice in comparison to lead, the following mechanism is suggested, which is quite consistent, with that discussed in the Chapter 3. Since different excited states are involved in the photochemistry and radiation chemistry, therefore the yield must be different.

$$\phi H \longrightarrow \phi H^{*}, \phi H^{**} \qquad (0)$$

$$\phi H^{**} \longrightarrow \phi + H \qquad (1)$$

$$\phi H^{*} + Pb\phi_4 \longrightarrow \phi H + Pb\phi_4^{*} \qquad (2)$$

$$Pb\phi_4^{*} \longrightarrow Pb + 4\phi \qquad (3)$$

$$\phi + \phi H \longrightarrow \phi_2 H \qquad (4)$$

$$2\ \phi_2 H \longrightarrow \phi_2 + \phi_2 H_2 \qquad (5)$$

$$Pb\phi_4^{*} + Pb\phi_4 \longrightarrow 2\ Pb\phi_4 \qquad (6)$$

Here in step (0) at least two different excited states of benzene are formed. The higher excited state forms phenyl and hydrogen as in step (1) and the lower excited state transfers its energy to the solute, which consequently undergoes photosensitized decomposition into phenyl radical and lead. It has been already discussed that the chances of the formation of diphenyl from phenyl radicals are remote. Hence the products are formed via step (5). According to this diphenyl and dihydrodiphenyl must be present in equal amount. A notable difference in the values and higher yields for diphenyl can be given by the following reaction. Here the attack of phenyl radical

$$\phi + \phi\,2H \longrightarrow \phi H + \phi_2 \qquad (7)$$

from benzene on $\phi_2H$ give diphenyl. Thus from stocnio-metric consideration the yield of $\phi_2$ is twice of lead. Another possible reaction for the formation of dihydro-diphenyl can be given by the reaction of hydrogen radical with $\phi_2H$.

$$H + \phi_2H \longrightarrow \phi_2H_2 \qquad (8)$$

If step (8) is operative, the yield of $\phi_2$ and $\phi_2H_2$ must be equal. It is contrary to the experimental data. Hence the only possibility of this reaction is in "spurs".

Steps (0) and (1) replaced in the radiolysis of benzene because several excited states of benzene are involved. Therefore steps (0) and (1) is replaced by the following:

$$\phi H \longrightarrow \phi H^{*},\ \phi H^{**},\ \phi H^{***} \qquad (0)$$

$$\phi H^{**} \longrightarrow \phi^{\cdot} + H^{\cdot} \qquad (1)$$

$$\phi H^{***} \longrightarrow \text{gaseous products} \qquad (2)$$

<u>Hexaphenyl dilead</u>

The following mechanism in photochemistry is suggested.

$$\phi H \longrightarrow \phi H^{*} + \phi H^{**} \qquad (0)$$

$$\phi H^{**} \longrightarrow \phi^{\bullet} + H^{\bullet} \qquad (1)$$

$$\phi H^{*} + Pb_2\phi_6 \longrightarrow \phi H + Pb_2\phi_6^{*} \qquad (2)$$

$$Pb_2\phi_6^{*} \longrightarrow 2\ Pb\phi_3^{\bullet} \qquad (3)$$

$$2\ Pb\phi_3^{\bullet} \longrightarrow Pb\phi_4 + Pb\phi_2 \qquad (4)$$

$$Pb\phi_2 \longrightarrow Pb + 2\phi^{\bullet} \qquad (5)$$

$$\phi + \phi H \longrightarrow \phi_2 H \qquad (6)$$

$$2\ \phi_2 H \longrightarrow \phi_2 + \phi_2 H_2 \qquad (7)$$

$$2\ Pb\phi_3 + \phi H \longrightarrow \phi_3 PbC_6H_4\ Pb\phi_3 \qquad (8)$$

In this mechanism triphenyl lead radical disproportionates into lead tetraphenyl and lead diphenyl, which yields metallic lead and phenyl radical by fragmentation. The yield of lead and diphenyl are equal and the above mechanism supports it. However lead tetraphenyl is formed as a product and it should dissociate to give lead and diphenyl resulting a high quantum yield. It is contrary to the experimental observations. Hence it is certain that the energy from benzene is directly transferred to hexaphenyl dilead and not to the product. Lead triphenyl radical can further react with benzene to form hexaphenyl diplumbyl benzene as in step (8). This product is soluble in benzene. Therefore it could not be isolated from hexaphenyl dilead and lead tetraphenyl.

It has been reported that benzene forms acetylene during γ-radiolysis. Therefore triphenyl lead might react with acetylene to form hexaphenyl diplumbyl acetylene ($\phi_3PbC \equiv CPb\phi_3$).

Triphenyl Lead Chloride

Following mechanism is suggested on the basis of equal lead and diphenyl.

$$\phi H \longrightarrow \phi H^*,\ \phi H^{**} \tag{0}$$

$$\phi H^{**} \longrightarrow H^\bullet + \phi^\bullet \tag{1}$$

$$\phi H^* + \phi_3PbCl \longrightarrow \phi H + \phi_3PbCl^* \tag{2}$$

$$2\ \phi_3PbCl^* \longrightarrow \phi_2PbCl^\bullet + Pb + 4\phi^\bullet + Cl^\bullet \tag{3}$$

$$\phi_2PbCl^\bullet + Cl^\bullet \longrightarrow \phi_2PbCl_2 \tag{4}$$

$$2\ \phi^\bullet + 2H^\bullet \longrightarrow 2\ \phi H \tag{5}$$

$$2\ \phi^\bullet + 2\ \phi H \longrightarrow 2\ \phi_2H \tag{6}$$

$$2\ \phi_2\ H \longrightarrow \phi_2 + \phi_2H_2 \tag{7}$$

The phenyl radicals formed in step (3) react with hydrogen to form benzene and thus it is depleted resulting in the formation of equal lead and diphenyl. Further diphenyl lead dichloride formed in step (4) could not be isolated, because it is soluble in benzne along with triphenyl lead chloride.

Triphenyl Lead Hydroxide

Since the amount of lead and diphenyl is equal, the following mechanism is suggested.

$$\phi H \longrightarrow \phi H^{*} + \phi H^{*} \qquad (0)$$

$$\phi H^{**} \longrightarrow \phi^{\bullet} + H^{\bullet} \qquad (1)$$

$$\phi H^{*} + \phi_3PbOH \longrightarrow \phi_3PbOH^{**} + \phi H \qquad (2)$$

$$\phi_3PbOH^{*} \longrightarrow \phi_3Pb^{\bullet} + OH^{\bullet} \qquad (3)$$

$$2\ \phi_3Pb^{\bullet} \longrightarrow Pb\phi_4 + Pb\phi_2 \qquad (4)$$

$$Pb\phi_2 \longrightarrow Pb + 2\phi^{\bullet} \qquad (5)$$

$$Pb\phi_2 + OH^{\bullet} \longrightarrow OPb\phi_2 + H^{\bullet} \qquad (6)$$

$$\phi^{\bullet} + \phi H \longrightarrow \phi_2H \qquad (7)$$

$$2\ \phi_2 H \longrightarrow \phi_2 + \phi_2H_2 \qquad (8)$$

The compound formed in step (6) could not be isolated, because of its solubility in benzene. All compounds of lead mentioned here in the mechanism have been reported[5]. The plateau in the curves has been attributed to the phenomenon of self quenching.

## Photolysis and Radiolysis of Lead Aryls in Cyclohexane

### Lead Tetraphenyl

The formation of different products in the photolysis of cyclohexane in the presence of tin tetraphenyl has been explained by suitable mechanism in the Chapter 3. Some products are formed with lead tetraphenyl. Metallic lead is an additional product and benzene yield is twice the yield of lead. Therefore a mechanism quite analogous to the previous one has been suggested, while due consideration has been given to the stoichiometric formation of lead and benzene.

$$C_6H_{12} \longrightarrow C_6H_{11}^{\bullet} + H^{\bullet} \qquad (1)$$

$$C_6H_{12} \longrightarrow C_6H_{12}^{+} + e^{-} \qquad (2)$$

$$C_6H_{12}^{+} + e^{-} \longrightarrow C_6H_{12}^{\pm} \longrightarrow C_6H_{12}^{\circ} \qquad (3)$$

$$C_6H_{12}^{\circ} + Pb\emptyset_4 \longrightarrow C_6H_{12} + Pb\emptyset_4^{\circ} \qquad (4)$$

$$Pb\emptyset_4^{\circ} \longrightarrow Pb + 4\emptyset^{\bullet} \qquad (5)$$

$$3\emptyset^{\bullet} + 3C_6H_{12} \longrightarrow 3C_6H_{11}^{\bullet} + 3\emptyset H \qquad (6)$$

$$2C_6H_{11}^{\bullet} \longrightarrow C_6H_{10} + C_6H_{12} \qquad (7a)$$

$$2C_6H_{11}^{\bullet} \longrightarrow (C_6H_{11})_2 \qquad (7b)$$

$$H^{\bullet} + \emptyset H \longrightarrow C_6H_7^{\bullet} \qquad (8)$$

$$C_6H_7^{\bullet} + \emptyset^{\bullet} \longrightarrow \text{Polymer} \qquad (9)$$

In this process the phenyl radicals formed can react with the solvent forming benzene. Since the amount of benzene is double the amount of lead, it is postulated that 'polymer' is formed, which reduces the yield of benzene. Schoepfle and Fellows has shown[6] that benzene acts as a scavenger for active hydrogen liberated from cyclohexane. It has also been confirmed by Burr[7]. It has been shown by Gordon[8] and coworkers that the polymer contains a number of $C_{12}$- and $C_{18}$- fractions and high molecular weight material, which cannot be separated from each other. The yield of cyclohexene is twice the yield of bicyclohexyl. Hence the reaction (7a) is twice as fast as (7b).

### Hexaphenyl dilead

The mechanism suggested for the formation of almost equal amount of lead and benzene in this reaction is given below.

$$C_6H_{12} \longrightarrow C_6H_{11}^{\bullet} + H^{\bullet} \tag{1}$$

$$C_6H_{12} \longrightarrow C_6H_{12}^{+} + e^{-} \tag{2}$$

$$C_6H_{12}^{+} + e^{-} \longrightarrow C_6H_{12}^{\pm} \longrightarrow C_6H_{12}^{*} \tag{3}$$

$$C_6H_{12}^{*} + \phi_6Pb_2 \longrightarrow C_6H_{12} + Pb_2\phi_6^{*} \tag{4}$$

$$Pb_2\phi_6^{*} \longrightarrow 2\ Pb\phi_3^{\bullet} \tag{5}$$

$$2\ Pb\phi_3^{\bullet} \longrightarrow Pb\phi_4 + Pb\phi_2 \tag{6}$$

$$Pb\phi_2 \longrightarrow Pb + 2\phi^{\bullet} \tag{7}$$

$$2\ \phi^{\bullet} + 2\ C_6H_{12} \longrightarrow 2\ \phi H + 2\ C_6H_{11}^{\bullet} \tag{8}$$

$$2\ C_6H_{11}^{\bullet} \longrightarrow C_6H_{10} + C_6H_{12} \tag{9a}$$

$$2\ C_6H_{11}^{\bullet} \longrightarrow (C_6H_{11})_2 \tag{9b}$$

$$H^{\bullet} + \phi H \longrightarrow C_6H_7^{\bullet} \tag{10}$$

$$C_6H_7^{\cdot} + C_6H_{11}^{\cdot} \longrightarrow \text{Polymer} \qquad (11)$$

$$\phi H + 2\,Pb\phi_3^{\cdot} \longrightarrow \phi_3Pb\,C_6H_4\,Pb\phi_3 + H_2 \qquad (12)$$

Lead tetraphenyl is formed in the step (6). It is not reacted, because the energy is transferred from excited cyclohexane to hexaphenyl di lead. Benzene can be depleted by two ways. The first probability is the formation of polymer and the second one is the formation of hexaphenyl diplumbyl benzene. The polymer and the other compound is soluble in cyclohexane and cannot be easily isolated from it.

## Triphenyl Lead Chloride

The stoichiometric considerations regarding lead and benzene has tempted to suggest the following mechanism.

$$C_6H_{12} \longrightarrow C_6H_{11}^{\cdot} + H^{\cdot} \qquad (1)$$

$$C_6H_{12} \longrightarrow C_6H_{11}^{+} + e^{-} \qquad (2)$$

$$C_6H_{12}^{+} + e^{-} \longrightarrow C_6H_{12}^{\pm} \longrightarrow C_6H_{12}^{*} \qquad (3)$$

$$C_6H_{12}^{*} + \phi_3PbCl \longrightarrow C_6H_{12} + \phi_3PbCl^{*} \qquad (4)$$

$$2\phi_3PbCl^{*} \longrightarrow \phi_2PbCl^{\cdot} + Pb + 4\phi^{\cdot} + Cl^{\cdot} \qquad (5)$$

$$\phi_2PbCl + Cl^{\cdot} \longrightarrow \phi_2PbCl_2 \qquad (6)$$

$$3\phi^{\cdot} + 3C_6H_{12} \longrightarrow 3\phi H + 3C_6H_{11}^{\cdot} \qquad (7)$$

$$\begin{tikzcd}
 & C_6H_{10} + C_6H_{12} & (8a) \\
2C_6H_{11}^{\cdot} \arrow[ur] \arrow[dr] & & \\
 & (C_6H_{11})_2 & (8b)
\end{tikzcd}$$

$$H^{\cdot} + \phi H \longrightarrow C_6H_7^{\cdot} \qquad (9)$$

$$C_6H_7^{\cdot} + \phi^{\cdot} + \phi H \longrightarrow \text{Polymer} \qquad (10)$$

The formation of step (10) has been proved by Gordon and coworkers[8]. Diphenyl lead dichloride formed in step (6) is soluble in cyclohexane and has not been separated from the polymer and triphenyl lead chloride. The yield of $C_6H_{10}$ is almost double the yield of $(C_6H_{11})_2$. Therefore step (8a) is faster than (8b).

Triphenyl Lead Hydroxide

The stoichiometric consideration has lead to suggest the following mechanism.

$$C_6H_{12} \longrightarrow C_6H_{11}^{\cdot} + H^{\cdot} \qquad (1)$$

$$C_6H_{12} \longrightarrow C_6H_{12}^{+} + e^{-} \qquad (2)$$

$$C_6H_{12}^{+} + e^{-} \longrightarrow C_6H_{12}^{\pm} \longrightarrow C_6H_{12}^{*} \qquad (3)$$

$$C_6H_{12}^{*} + \phi_3PbOH \longrightarrow C_6H_{12} + \phi_3PbOH^{*} \qquad (4)$$

$$\phi_3PbOH^{*} \longrightarrow \phi_3Pb + OH^{\cdot} \qquad (5)$$

$$2\phi_3Pb \longrightarrow Pb\phi_4 + Pb\phi_2 \qquad (6)$$

$$Pb\phi_2 \longrightarrow Pb + 2\phi^{\cdot} \qquad (7)$$

$$Pb\phi_2 + OH^{\cdot} \longrightarrow OPb\phi_2 + H^{\cdot} \qquad (8)$$

$$2\phi^{\cdot} + 2C_6H_{12} \longrightarrow 2C_6H_{11}^{\cdot} + 2\phi H \qquad (9)$$

$$H^{\cdot} + \phi H \longrightarrow C_6H_7^{\cdot} \qquad (10)$$

$$C_6H_7 + C_6H_{11}^{\bullet} \longrightarrow \text{Polymer} \qquad (11)$$

$$H^{\bullet} + C_6H_{12} \longrightarrow C_6H_{11}^{\bullet} + H_2 \qquad (12)$$

$$2C_6H_{11}^{\bullet} \left\langle \begin{array}{ll} \longrightarrow C_6H_{10} + C_6H_{12} & (13a) \\ \\ \longrightarrow (C_6H_{11})_2 & (13b) \end{array} \right.$$

The mechanism given here for all the lead aryls show that metal aryls are directly involved in the formation of products, through energy transfer process from excited cyclohexane.

The yield of cyclohexene is practically the same as with pure cyclohexane and it is not affected by benzene. Similarly the yield of bicyclohexyl is equal to the yield from pure solvent. The yield of cyclohexene is twice to bicyclohexyl.

Lead is capable to form a number of products with cyclohexyl radical. If these compounds were formed at all, phenyl radical must be given out which consequently will increase benzene yield. Since the yield of benzene is either double the lead or slightly higher than lead, the formation of substituted cyclohexyl compounds is ruled out.

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# CHAPTER V

## SUMMARY OF THE MAIN RESULTS ACHIEVED

In this work the Radiation Chemistry and Photochemistry of Benzene and Cyclohexane solutions of Tin tetraphenyl, Lead tetraphenyl, Hexaphenyl dilead, Triphenyl lead chloride and Triphenyl lead hydroxide have been presented. An attempt has been made to elucidate the mechanism of sensitized decomposition of metal perphenyls in Benzene and Cyclohexane. Further the study is aimed at to illustrate further the kinetic peculiarities of reactions of atoms and free radicals in liquid state.

Since different products are likely to be formed during thermolysis, photolysis and radiolysis, therefore thermal, photochemical and radiation induced reactions have been studied with these compounds.

The nature of decomposition of $Pb\phi_4$ has been studied thermally and free radicals and metallic lead are formed. This takes place between 250°-350°C. Similar decomposition pattern as observed in the case of $Pb\phi_4$ was found with $\phi_6Pb_2$. It is possible that $Pb\phi_4$ and $Pb\phi_2$ are formed. $Pb\phi_2$ is very reactive and it is either converted into $\phi_6Pb_2$ and lead. Triphenyl lead chloride does not show any loss on heating up to 230°C and after that a rapid loss between 240° to 300°C has been observed. The possible compound formed can be diphenyl lead dichloride and lead tetraphenyl. Diphenyl lead dichloride can form triphenyl lead chloride and phenyl lead trichloride. Lead tetraphenyl have been isolated. Lastly triphenyl lead hydroxide showed a loss in weight between 150° to 190°C corresponding to the loss of one molecule of water. This can be attributed to the formation diphenyl lead oxide, $Pb\phi_4$ and $H_2O$.

The photolysis and radiolysis of $Sn\phi_4$ in benzene give diphenyl and dihydrodiphenyl as the major condensable products. The quantum yield and G-value increase for both the products and the values are higher for diphenyl. These values are concentration dependent. The formation of diphenyl and dihydrodiphenyl has been given by excited solute molecule, which absorbs the energy from the solvent. Since the electron fraction of the solute is very small, all the energy should be absorbed by the solvent molecule. The first excited singlet state of benzene transfers the energy to $Sn\phi_4$. The excited $Sn\phi_4$ forms either the phenyl radical or is self quenched. The phenyl radical is added to benzene and this addition is very fast leading to the formation of cyclohexadienyl radical, which disproportionates to diphenyl and dihydrodiphenyl. Another possibility is the formation of tetrahydroquaterphenyl and other high molecular weight products. These were not isolated. A plot of quantum yield of diphenyl or dihydrodiphenyl$^{-1}$ versus concentration of $Sn\phi_4^{-1}$ is linear. In the same manner $\Delta G$ (diphenyl) and $\Delta G$ (dihydrodiphenyl) is directly or inversely proportional to the concentration of $Sn\phi_4$.

Photolysis and radiolysis of $Sn\phi_4$ in cyclohexane give benzene, cyclohexene, bicyclohexyl, cyclohexanol and cyclohexanone as the major condensable products. Benzene is not formed during the photolysis and radiolysis of cyclohexane. Therefore it is assumed that $Sn\phi_4$ is directly involved in its formation. Excited $Sn\phi_4$ react with cyclohexane forming benzene, and cyclohexyl radical. Two cyclohexyl radical can disproportionate to form cyclohexene and cyclohexane or can form an additional product bicyclohexyl. Quantum yield$^{-1}$ versus $(Sn\phi_4)^{-1}$ is linear. Similarly $\frac{1}{\Delta G}$ (Benzene) versus $(Sn\phi_4)^{-1}$ is linear. The yield of cyclohexene and bicyclohexyl is not effected in the presence of $Sn\phi_4$. This is explained by the reaction of cyclohexyl radical with hydrogen.

The photolysis and radiolysis of lead tetraphenyl, $\phi_6Pb_2$, $\phi_3PbCl$ and $\phi_3PbOH$ in benzene give diphenyl, dihydrodiphenyl and lead as major condensable products. The yield of diphenyl is nearly double of metallic lead in the case of $Pb\phi_4$ and almost equal in the case of other lead phenyl compounds. The quantum yield of diphenyl increases and finally reaches a plateau. Similarly G values also follow the same path. The photolysis and radiolysis of $Pb\phi_4$, $\phi_6Pb_2$, $\phi_3PbCl$ and $\phi_3PbOH$ in cyclohexane give benzene, cyclohexene, bicyclohexyl and lead as the major condensable products. The quantum yield of cyclohexene and bicyclohexyl increase regularly with concentration of lead phenyls. The quantum yield of benzene is double the quantum yield of lead in case of lead tetraphenyl. The G-value in this case is also double but with other lead phenyls. G (diphenyl) is slightly higher than G (lead).

Suitable mechanisms have been suggested for the formation of these products. The product formation has been explained via the energy transfer process from excited cyclohexane to metal phenyls. Several products of lead are likely to be formed during the irradiation. These are known products and have been already reported by other workers. The amount of benzene in dilute cyclohexane solutions has been attributed to the depletion of benzene by reacting with hydrogen and finally reacting with either phenyl radical and benzene or cyclohexyl radical. The yield of cyclohexene is practically the same as in pure cyclohexane. It is not affected by benzene. Similarly the yield of bicyclohexyl is equal to the yield from pure solvent. The yield of cyclohexene is twice to bicyclohexyl. It is reported that lead is capable to form a number of products with cyclohexyl radical. If these compounds were formed at all phenyl radical must be given out which will increase the yield of benzene. It is contrary to observation. Hence the formation of substituted cyclohexyl lead phenyl compounds is ruled out.

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