IONS AND EXCITATIONS IN ORGANIC RADIATION CHEMISTRY

I. THE GAMMA RADIATION INDUCED REACTIONS OF 1,3-CYCLOHEXADIENE

II. THE RADIATION INDUCED ISOMERIZATION OF 1,2-DIPHENYLPROPENE IN CYCLOHEXANE

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ABSTRACTS

PART I. Irradiation of 1,3-cyclohexadiene with γ rays leads to dimerization, either in benzene solution or in the neat liquid. Relative amounts of the products vary widely with reaction conditions but the composition of the mixtures can be expressed as consisting of variable amounts of two groups. One set of products corresponds to those formed in thermal dimerization and the other has the distribution found in photodimerization induced by triplet sensitizers. Formation of the "thermal" dimers is inhibited by 2-propanol, a cation scavenger, and promoted by electron scavengers, so a cationic mechanism is postulated. The other, "photo" dimers, are presumably formed from triplet diene. Ring cleavage to give 1,3,5-hexatriene is also observed and attributed to an excited singlet state of 1,3-cyclohexadiene. Since ring opening is not affected by electron scavengers whereas "photo" dimers are quenched, it is inferred that excited singlets are formed in primary excitation processes and that triplets are largely produced by charge neutralization. In benzene solution charge and excitation transfer from the solvent are involved in the production of diene products. A chain dimerization also seems to be present in benzene solution.

PART II. The cis and trans isomers of 1,2-diphenylpropene are isomerized in cyclohexane by irradiation of solutions with γ radiation. At low solute concentrations both isomers appear to react through the triplet state of the 1,2-diphenylpropene which is formed by charge neutralization. At higher alkene concentrations and especially at low radiation doses a cationic chain reaction contributes to cis → trans isomerization. The value for isomerization of the trans isomer at high solute concentration gives a G for solute triplet of 4.4.

ABSTRACTS OF PROPOSITIONS

Proposition I

A flash photolysis apparatus capable of resolution on the picosecond time scale is described and proposed as a technique for the attempted study of the rate of internal conversion from higher singlet states to the first excited singlet (S_1) in aromatic hydrocarbons.

Proposition II

It is proposed to study the production of carbonium ions generated from alkyl halides by high energy radiolysis.

Proposition III

It is proposed to examine the effect of changing the nature of ionizing radiation on a number of charge scavenging reactions in an effort to observe whether the implications of charge scavenging models are experimentally valid.

Proposition IV

It is proposed to investigate the possibility of electronic effects due to β secondary hydrogen isotopic substitution through the study of an alkyl free radical by electron spin resonance spectroscopy.

Proposition V

It is proposed to study the possibility that radical intermediates are formed in the 2537 Å irradiation of benzene by an electron spin resonance trapping technique.

TABLE OF CONTENTS

TABLE OF CONTENTS
(con.)

TABLE OF CONTENTS
(con.)

LIST OF TABLES

LIST OF TABLES
(con.)

LIST OF FIGURES

LIST OF FIGURES
(con.)

PART I

GENERAL INTRODUCTION

The chemical effects induced by ionizing radiation have been known as long as the existence of the radiation itself. Indeed, the discovery of natural radioactivity by Becquerel in 1896 was made as a result of its chemical effect on a photographic emulsion. By the beginning of the 20th century reactions induced by radiation such as the decomposition of water (1), which has subsequently become the most studied radiation chemical process, and the reduction of mercuric salts (2), among others, had been observed. The field was an area of moderate research until after World War II when greater availability of radioactive isotopes increased activity in radiation chemistry. Within the past fifteen years, as a result of increasing scientific and technical sophistication in related fields such as photochemistry, free radical reactions, and mass spectrometry which can be applied to radiation chemical reactions, and new techniques such as pulse radiolysis, significant progress is being made toward clarifying the complex fundamental processes occurring in systems under high-energy irradiation.

No attempt will be made to review the large radiation chemical literature. Instead this General Introduction will give a brief description of the early events that are believed to occur upon the absorption of ionizing radiation. Pertinent specific literature will be included in the sections dealing with the two systems studied. Much of the picture presented here is based on experiments and theories concerning the gaseous state, and modifications, frequently of an unknown extent, are necessary for condensed media.

In the case of electromagnetic radiation the main interaction for

energies above approximately 0.1 Mev for materials of low atomic number (e.g. oxygen) is Compton scattering of the photon by a molecular electron. For incident photon energies of ca 1 Mev the electron receives approximately half this energy. Compton scattering cross sections are such that for a 1cm path length in a liquid essentially none of the scattered photons will undergo a second interaction. Thus the effect of the gamma ray is to generate a fast primary electron. This is borne out by the similarity of effects induced by γ rays and electrons accelerated to the Mev range.

The scattering interaction of high-energy electrons or energetic positive ions by molecular electrons imparts energy to the latter, causing excitation to various levels, including ionization, and a degradation of the energy of the incident primary particle. The secondary electrons produced in these ionizations can induce further ionizations and excitations. The number-energy spectrum of these secondary electrons will depend on the extent of collision experienced by the primary particle. It has been estimated that for electron irradiation the average energy of the secondary electrons is about 70ev although over 80% of the electrons probably have energies below 50ev (3). The reason for this is that there is a long "tail" of a few electrons at high energies in the distribution. Since for a given type of particle the rate at which it loses energy to the electrons with which it interacts is an inverse function of its energy, the number-energy spectrum of the secondary electrons will have a considerable influence on the spacial distribution. At energies below about 100ev, excitation and ionization will be caused by the secondary electron in a small spacial region

called a spur. At higher energies the secondary electron will have a greater range and proceed to produce tertiary energetic electrons which can create spurs. The picture is thus of a primary electron producing excitations and ionizations along its path at intervals which grow more closely spaced as it slows down, with a cluster of further ionizations and excitations around each secondary ionization, and a number of sub-branches similar to the primary track (called δ rays) branching off from it.

A similar situation applies to heavy positively charged ions except that the production of secondary electrons and excitation occur at much more closely spaced intervals than for electron irradiation due to the primary particle's greater interaction with the molecular electrons. By a cloud chamber technique, Wilson (4) estimated the number of ions produced in spurs by the secondary electrons and found that the average spur contained 2-3 ions. For α-particles or protons the spurs overlap and form a column of ions and excitation. For electrons of about 1 Mev, the production of secondary electrons has been estimated to occur at intervals of about 10^4 Å with spur sizes of about 20 Å produced (5). This spur separation will of course decrease as the primary electron slows down. For example, at 1 Kev the separation of secondary ionizations is only 50 Å (6). In addition, the spur sizes will not be uniformly 20 Å in diameter. They will vary in size from that of a single ion pair to δ rays which may well have ranges over 100 Å.

The above description is based largely on the gas phase situation. One exception is the calculation for spur sizes and separations which

are derived for the liquid state. It is generally felt that the situation described is applicable to the liquid state since the initial production of the various species is probably not too sensitive to the density. Of course, particle ranges and therefore the spacial distribution of ionized and excited molecules will be considerably affected. One of the consequences of this is that in the liquid state the interaction among species produced in spurs may be important in the same way that cage reactions can be important in free radical reactions in the liquid phase but not in the gaseous state.

One of the problems encountered in radiation chemical studies is that the species observed is dependent on the time scale at which the observation is made. This can be a serious problem because in many cases transient intermediates can have other short-lived species as precursors so that the assignment of a reaction to a particular intermediate may depend on the experimental conditions. For example, some secondary electrons will have just enough energy to ionize a molecule but not to separate the ion-electron pair appreciably. Recombination will occur within a time shorter than that required for the ion or electron to react. The recombination may lead to the formation of an excited state. This state is produced by ion neutralization but this neutralization cannot be distinguished experimentally from a directly excited molecule. If the secondary electron has a higher energy, recombination and ionic reaction may become competitive and the formation of the excited state from ions becomes observable through the use of additives. Yet there is no discontinuity between these cases. Thus the measure of the extent of such processes may be determined by

the time scale of the measuring technique employed.

An approximate time scale for some radiation chemical processes is indicated in Table 1. The times for ion recombination, in the absence and especially in the presence of electron scavengers, indicates that ion molecule reactions can be competitive with neutralization. Thus electron affinities, cation reactivity, electronic energy levels, and other properties of the irradiated liquid which influence these rates, not to mention added solutes, may affect the yields of the various intermediates and products formed.

The properties of the irradiated liquid can also affect initial spacial electron distributions. For example, if sub-ionizing electrons produced by the radiation do not encounter any low lying electronic energy levels to excite (e.g. in cyclohexane) they will lose their energy more slowly. They will thus have an increased range and will take longer to neutralize, thereby increasing the overall ionic lifetime.

Much of the early radiation chemical research involved the study of reactions induced in water and this probably remains the most frequently investigated compound. Until relatively recently most of the investigations involved studies of the products derived from a single irradiated component. Additives were used to observe their influence on the various products but the reactions of the additives themselves were not usually characterized. Systems studied in this way included in addition to water, benzene, saturated hydrocarbons, alcohols, and to a lesser extent other organic and inorganic compounds (10). More recently investigations have frequently involved the study of the reactions of a solute added to the main component in sufficiently

Table 1. Time Scale for Radiation Chemistry Processes

Time (sec)	Process
10^{-18}	1 Mev electron traverses a molecule (6).
10^{-16}	5ev Electron traverses a molecule (6).
10^{-15}	Vertical excitation (6).
10^{-14}	Molecular vibration. Possible dissociation (6).
10^{-14}-10^{-13}	Electron Thermalization (7). Earliest possibility for recapture in liquid spur (8).
10^{-13}	Collision time in liquid. Internal conversion of excitation (6).
$5x10^{-12}$-10^{-11}	Ion jump time in diffusion (7).
10^{-11}	Dielectric relaxation (6).
$5x10^{-10}$	Half-life of cations recombining in cyclohexane under electron irradiation (9).
10^{-10}-10^{-8}	Radiative lifetime of singlets.
10^{-8}	Half-life of cations recombining in cyclohexane under electron irradiation when all negative species have been converted to anions through scavenging (9).
10^{-8}-10	Radiative lifetime of triplet state.

small quantities so that the primary energy is localized in the solvent; that is, a study of solvent sensitized solute reactions. In this way, by observing reactions which have been characterized photochemically or by some other means, it may be possible to obtain an indication of the presence and yield of the intermediate species formed in the solvent. Often, of course, it becomes necessary to identify these solute reactions more thoroughly under radiation chemical conditions and for this the use of added quenchers becomes important.

In addition to these techniques, pulse radiolysis (11), the analog to flash photolysis has made a considerable contribution to radiation chemistry in recent years and promises to become even more valuable as techniques are improved (12, 13). Our concern with the method will only be to the extent that it has provided information with a direct bearing on the problems at hand.

By convention radiation chemical yields are reported as G values. G is the yield of a particular substance in molecules per 100 ev of energy absorbed.

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PART II

THE GAMMA RADIATION INDUCED REACTIONS OF 1,3-CYCLOHEXADIENE

INTRODUCTION

As mentioned in the General Introduction, radiation chemical studies using solute reactions to characterize intermediates formed in a solvent have become fairly common within the past few years (1-8). The present work began as a continuation of such a study originated in 1965 by D. G. Whitten using the photochemically characterized solute 1,3-cyclohexadiene in an attempt to measure the yields of benzene triplets formed by gamma irradiation.

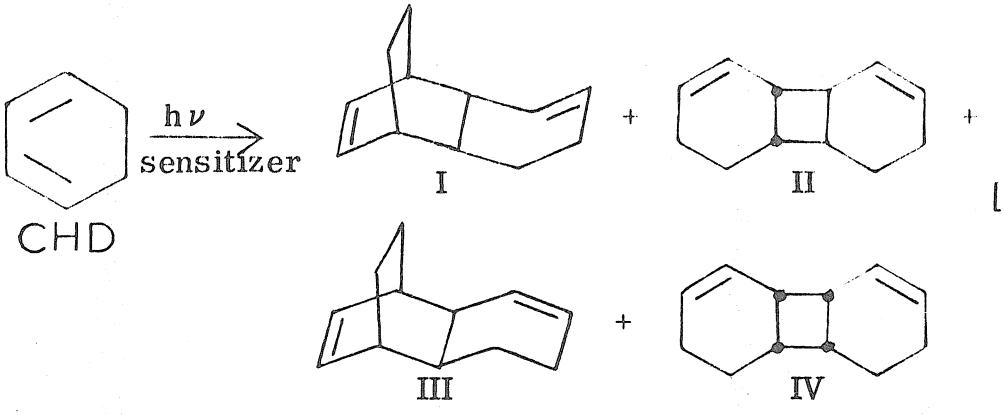
Evidence based on a number of experiments involving pulse radiolysis (9-12) and scintillation studies (13-16) as well as solute reactions has demonstrated the formation of excited and ionized molecules in organic liquids under electron or gamma irradiation. These studies have also demonstrated charge or excitation energy transfer to solutes under energetically favorable conditions. One of the main research objectives of most groups using solute reaction techniques in radiation chemistry has been the measurement of benzene triplet yields. This has been done almost exclusively by measuring the yields of isomerization induced in stilbenes (3,4,17,18) and other alkenes (4,19,20). Although complications arise in some reactions because of superimposed non-triplet isomerization, it is generally agreed that the yield of solvent triplets is ~ 5.

The original aim of the 1,3-cyclohexadiene work as envisioned by Whitten was to provide a measure of benzene triplets using a solute reaction other than alkene isomerization. When reactions in addition

to those known to originate from a triplet state were observed it became of interest to investigate their origin in greater detail. It is this investigation that forms the basis of the present research. It has proved to be true that much of the more definitive information has been obtained from solutions in which no benzene was present, although experiments using it as a solvent were also conducted.

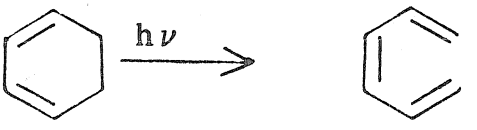
At the time this investigation was being concluded, a report appeared in the literature concerning the reaction of 1,3-cyclohexadiene under γ irradiation in a number of solvents, including benzene (21). There is overlap with some of these experiments, with general agreement concerning the identity of the intermediates responsible for those reactions which both groups investigated. Differences in mechanistic interpretations do exist, based partially on discrepancies in experimental results. Comparisons with this paper will be drawn in the discussion of the present results where the two works overlap. There was communication between the two groups prior to publication.

The photochemical reactions of 1,3-cyclohexadiene taking place through the triplet state are well characterized (22,23). The dimers I-IV are formed. Dimer I is only formed in trace amounts but dimers II-IV are produced in a fixed ratio independent of the sensitizer used as long as its triplet energy is greater than that of the diene, 52.5 kcal/mole. The values found, based on a series of triplet sensitizers were 0.59:0.23:0.18 for the ratios II:III:IV. At 1 M diene, the dimerization quantum yield is 0.98 (23). No other products are formed from the triplet cyclohexadiene. In addition to this sensitized reaction, unsensitized ultraviolet radiation reactions of 1,3-cyclohexadiene have



[1]

also been observed. In solution, ring opening to form 1,3,5-hexatriene is a major reaction (25,26). This is generally accepted to proceed



[2]

via the singlet state of the diene (26,27). In addition, the formation of dimers has been reported in the direct irradiation of 1,3-cyclohexadiene in the liquid phase. Distributions of dimers different from those formed by sensitized reaction were reported (28). Irradiation at $\lambda < 258$ nm lead to equal portions of dimers II, III, and IV. However, dimerization constituted only a small portion of the total product. Benzene formation was also reported, but this has been disputed (27). A distribution of 44:33:23 was observed when light of > 330 nm was used. No quantum yields were reported. In the gas phase, unsensitized irradiation of 1,3-cyclohexadiene leads to benzene, H_2, C_2H_2, and C_2H_4 as well as 1,3,5-hexatriene (26). These additional products probably arise from a vibrationally excited ground state. The 1,3,5-hexatriene produced can also undergo reactions, including dimerization

(29). In addition to the photochemical reactions indicated above, 1,3-cyclohexadiene can also undergo a dimerization reaction when heated to 200°C in the absence of air (22). The dimers produced are I and III in a reported ratio of 4:1.

In addition to the recent paper of Schutte and Freeman (21) already mentioned, a small number of investigations involving γ radiation initiated reactions of 1,3-cyclohexadiene have been reported in the literature. Freeman and co-workers (30,31) observed the formation of uncharacterized dimers when the diene was used as a quencher in gamma irradiated aliphatic solutions. Schenck et al. (28) reported that exclusively dimer III was formed in the ^{60}Co γ radiolysis of benzene solution of 1,3-cyclohexadiene but that in neat diene only polymer was formed.

In view of the characteristic reaction of triplet 1,3-cyclohexadiene, with essentially no intersystem crossing from the singlet, and the literature indications that dimerization reactions could be induced in the diene under γ irradiation, this appeared to be a favorable compound to use as a new indicator of the yield of benzene triplets formed by ionizing radiation.

Since Whitten's work (32) provides the early results upon which the present study is based, a general indication of his main observations and conclusions will be given here. Details of and comparisons with the results of this work will be included at the appropriate places in the Discussion section.

Whitten observed that dimers I-IV were all produced in the gamma radiolysis both in solutions of benzene and in neat diene. The

proportions of the dimers did not vary greatly in solutions of concentrations between 0.2M and 1 M diene although overall yields did. However, in pure cyclohexadiene the relative amounts of the four dimers had definitely changed. A very significant observation was that the product dimers could be factored into two groups, one of which contained dimers I and III in a 4:1 ratio. The other consisted of dimers II, III, and IV in the same distribution as exhibited by these dimers when formed by photosensitization. This was true both in benzene solution and in neat diene although the yields of the two groups, (referred to hereafter as "thermal" and "photo" dimers respectively,) was different in the two cases. This observation indicated that two processes probably occur and that one of them involves 1,3-cyclohexadiene triplets. He further observed that, for 0.2 M diene in benzene, 2-propanol quenched the thermal group of dimers almost completely, leaving the photo dimers unaffected. That is, dimer I was almost entirely quenched and dimer III was quenched to the extent that II:III:IV exhibited the triplet induced dimer distribution. On this basis he suggested a cation precursor for the thermal dimers. It was also reported that carbon tetrachloride, a commonly used electron scavenger, had no effect on the dimer yield. The yield of triplets as measured by the yield of the photo dimer group in benzene appeared to be much lower than that measured by alkene isomerization.

It was with the goal of elucidating these proposed mechanisms, especially the ionic one, and to establish the dimer factoring characteristic more fully, as well as to obtain additional information on

the yields of the various dimers as a function of diene concentration in benzene that the present work was undertaken.

RESULTS AND DISCUSSION

Dimer Distribution. As mentioned in the Introduction, it was observed by Whitten that the yields of the various dimers formed from 1,3-cyclohexadiene by γ radiation could be factored into two groups, one of which contained dimers I and III in their thermal ratio. In the second group, dimers II, III, and IV are found in the triplet sensitized distribution. Since this observation has a major implication concerning the dimerization mechanism, some emphasis has been placed on establishing it more firmly beyond the two or three previous occasions for which the conditions had been rather similar. As a prerequisite, the distribution of dimers produced under thermal conditions previously reported as 4:1 for the ratio I:III was remeasured. Heating 1,3-cyclohexadiene to 200°C for 12 hours in sealed tubes under vacuum gave dimers I and III in the ratio 4.6:1. In order to test the dimer distribution under radiation chemical conditions, the value 1/4.6 G(I), representing the "thermal" contribution to G(III), was subtracted from G(III). If the factoring process is correct, G(II): G(III) - 1/4.6 G(I): G(IV) should exhibit the triplet sensitized distribution of 0.59:0.23:0.19 established for II:III:IV (23). During the course of the present experiments, dimer yields were obtained under a number of different conditions of diene concentration, quenchers, and irradiation, leading to widely varying yields of the individual dimers. In all cases the "factoring test" described above was applied and found to hold true. Table 1 gives

Table 1. Dimer Distribution Factoring Process

Solution	G(thermal)	G(photo)	G(II)/G(photo)	[G(III)-1/4.6G(I)]/G(photo)	G(IV)/G(photo)
Neat 1,3-Cyclohexadiene	2.06	3.19	0.57	0.22	0.21
0.35 $MCCl_4$ in 1,3-Cyclohexadiene	3.4	1.8	0.59	0.22	0.19
0.20 $MCCl_4$ plus 0.21 M 1,3-Cyclohexadiene in Benzene	5.71	0.84	0.55	0.30	0.15
Neat 1,3-Cyclohexadiene, Alpha Radiolysis	not known absolutely	1.5xG (thermal)	0.59	0.19	0.21
0.21 M 1,3-Cyclohexadiene in Pyridine	0.05	0.51	0.57	0.22	0.21

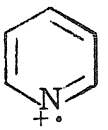
a number of representative examples obtained under the conditions indicated. Only in cases where G(I) was much larger than G(II) so that G(III) - 1/4.6 G(I) was only a small fraction of G(III) and the error in the difference was large, did the photo dimer distribution deviate appreciably from the triplet sensitized value. Thus, this factoring appears to be genuine and there is justification in speaking of two pathways. In the remainder of this discussion, dimer yields will be treated in this context. 5.6/4.6 G(I) will be referred to as G(thermal) and G(II) + G(III) - 1/4.6 G(I) + G(IV) will be referred to as G(photo). Table 1 includes values of G(thermal) and G(photo) in order to indicate the wide range of dimer distribution for which the factoring process was tested.

Since other works referred to in the Introduction indicated that dimers are formed photochemically under unsensitized conditions, this was investigated more fully to determine if processes not involving 1,3-cyclohexadiene triplets could be involved. Irradiation of neat 1,3-cyclohexadiene at 2537 Å produced dimers, but at a very low quantum yield: < 0.02. These could possibly have arisen via singlet-triplet intersystem crossing. Even if they are produced by some alternative manner, the quantum yield is too low for this process to contribute appreciably to the γ radiation results. At 3130 Å, dimers are produced at a higher efficiency, with a quantum yield of 0.11. Of these, 66% are dimers I-IV. However, the distribution is entirely different from that found by triplet sensitization. It is 0.10:0.18:0.15:0.58 for I:II:III:IV. These dimers may be produced by dimerization of the 1,3,5-hexatriene produced

by the photolysis, since this compound does dimerize (29), or perhaps by reaction of excited triene with 1,3-cyclohexadiene. In any case, the distribution of the dimers and the presence of appreciable quantities of at least 6 other products separable on a capillary vapor phase chromatography column indicates that the reactions present under 3130 Å irradiation do not enter into the γ radiolysis.

Thermal Dimer Formation. It was felt that the alcohol quenching results (32) were insufficient to establish diene cations as the immediate precursors of the thermal dimers. It was quite possible that cations were involved but lead to some other species that actually dimerized. An example of such a possibility is indicated in the discussion below.

In an effort to determine the precursors of the thermal dimers more certainly an attempt was made to carry out the dimerization under conditions made more favorable to the formation of ionic species. It has been shown by Tsuji et al. (33) that when pyridine is subjected to gamma irradiation at -196°C, one of the species formed, although in small yield, is the parent radical cation:



V

The addition of even small amounts of I_2 enhances the yield of this specie greatly. Whitten observed a G(total dimer) of 0.56 for 0.21 M 1,3-cyclohexadiene in pyridine but reported that this was

all photo dimer although the ionization potential of pyridine is greater than that of the diene (9.2 ev (34) and 8.4 ev (35) respectively). Repetition of this experiment indicated that some thermal dimer was formed, although the amount was small. As seen in Table 2, addition of I_2 to the system increased the thermal fraction of the dimer composition rather dramatically. This seems to be a fairly good indication that radical cations are involved in the thermal dimer production. However, the results are not entirely unambiguous since Tsuji observed that the addition of iodine also enhanced the yield of non-ionic radicals. There is thus the possibility that free radicals are involved in thermal dimer formation. The effect of the alcohol quencher could be explained as a quenching of ions involved in reactions such as:

$$A^+ + e \longrightarrow A^* \qquad [3]$$

$$A^* \longrightarrow B\cdot + C\cdot \qquad [4]$$

where ion recombination leads to the formation of a thermally excited ground state A^* which dissociates into free radicals.

That the 1,3-cyclohexadiene radical cation (CHD^+) can dimerize, at least in the gas phase was demonstrated by experiments using the technique of ion cyclotron resonance (icr) spectroscopy (36). As used in the present experiments the instrument was employed essentially as a mass spectrometer with the analyzing chamber at a pressure high enough to permit ion-molecule collisions. The results are indicated in Figure 1. At a pressure of 10^{-7} torr of 1,3-cyclohexadiene and a 10 volt ionizing potential only the parent

Table 2. The Effect of Iodine on the Dimer Distribution from Gamma Irradiated 0.21 M 1,3-Cyclohexadiene in Pyridine

I_2 (M)	$\frac{G(\text{thermal})}{G(\text{total dimer})}$
0.0	0.08
≈0.01	0.42
0.28	0.69

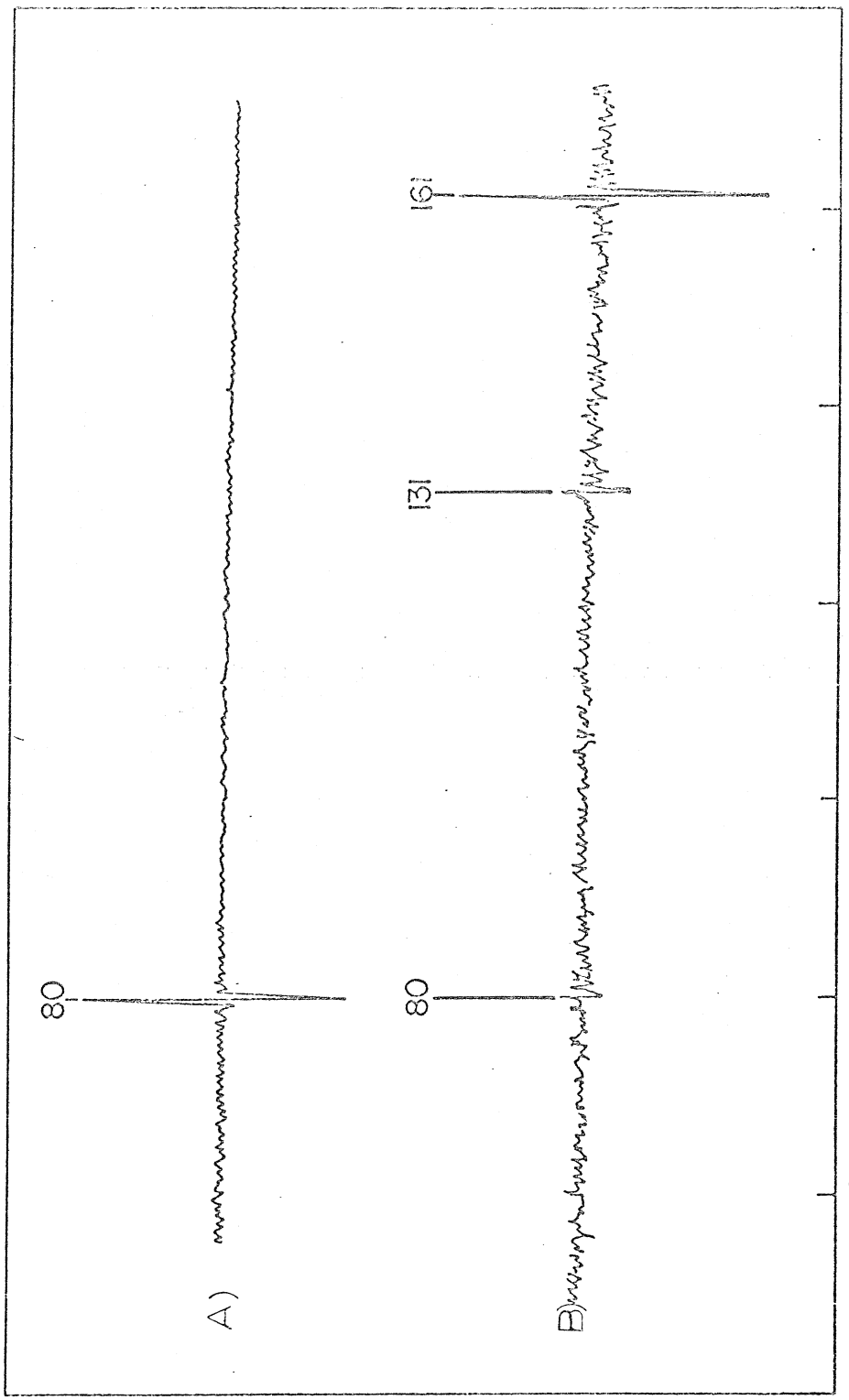


Figure 1. Ion Cyclotron Resonance Spectra of 1,3-Cyclohexadiene.
A) 10^{-7} Torr pressure B) 2×10^{-6} Torr pressure

ion of mass 80 is present as indicated by the upper spectrum in Figure 1. The lower trace, run at the same ionizing potential but at 2×10^{-6} torr indicates that the parent ion has almost all reacted, producing dimers and a small amount of fragmentation product. The extra hydrogen present in the dimer probably arises from stabilization of the hot dimeric ion by hydrogen abstraction from diene. In condensed phase the excess energy resulting from dimer formation would be rapidly dissipated by nonchemical paths.

Alcohol quenching was carried out in neat 1,3-cyclohexadiene to complement that found by Whitten (32). At 0.1 M 2-propanol no quenching of dimers could be observed. At 1.2 M alcohol both photo and thermal dimers were quenched, overall quenching being 54%, based on the primary energy absorbed by the diene alone. This suggests that in neat diene both types of products are ionically derived. It also appears that there is a competition between alcohol and 1,3-cyclohexadiene for these cations since at 0.1 M alcohol Whitten had already observed extensive quenching at 0.21 M diene in benzene.

Carbon Tetrachloride Electron Scavenging in Neat 1,3-Cyclohexadiene. The observation by Whitten that the electron scavenger carbon tetrachloride had no effect on dimer yields in benzene solution of 1,3-cyclohexadiene would appear to rule out the initiation of dimerization by free radicals formed by reactions such as [3] and [4] since there should have been a quenching effect. However, it would also argue against cationic precursors to thermal dimers since these should be enhanced by electron scavengers. Electron

scavengers are considered to increase cation lifetimes by decreasing the mobility of the negatively charged entity (37). Since 84% of the dimers produced by γ radiation of 0.2 M 1,3-cyclohexadiene in benzene are already of the thermal type it appeared possible that any enhancement of this by CCl_4 might be small. In neat diene only 42% of the dimer is thermal so that there is considerably greater potential for an enhancing effect to occur.

Figure 2 illustrates the effect of carbon tetrachloride on G(total dimer), G(thermal) and G(photo). Because of the manner of product analysis in which absolute G values were determined mainly on a vpc column which did not separate the dimers, and dimer distribution was obtained under conditions where absolute yields were not usually measured, the values for G(thermal) and G(photo) were determined from G(total dimer) in Figure 2 and a graph giving the per cent of the dimer which was of the thermal group as a function of the scavenger concentration (Figure 3). All data points on these and subsequent Figures are the mean of the results obtained from a minimum of 2 samples.

As a preliminary test to this electron scavenging experiment it was determined that CCl_4 in concentrations up to 0.6 M had no effect on the quantum yield of benzophenone sensitized dimer formation in neat 1,3-cyclohexadiene. Also, there was no change in the dimer distribution. In particular, no formation of dimer (I), the only purely thermal dimer, was observed beyond the minute trace observed in the photochemical dimerization. Thus the results in Figure 2 are not the result of any effect of CCl_4 on diene excited

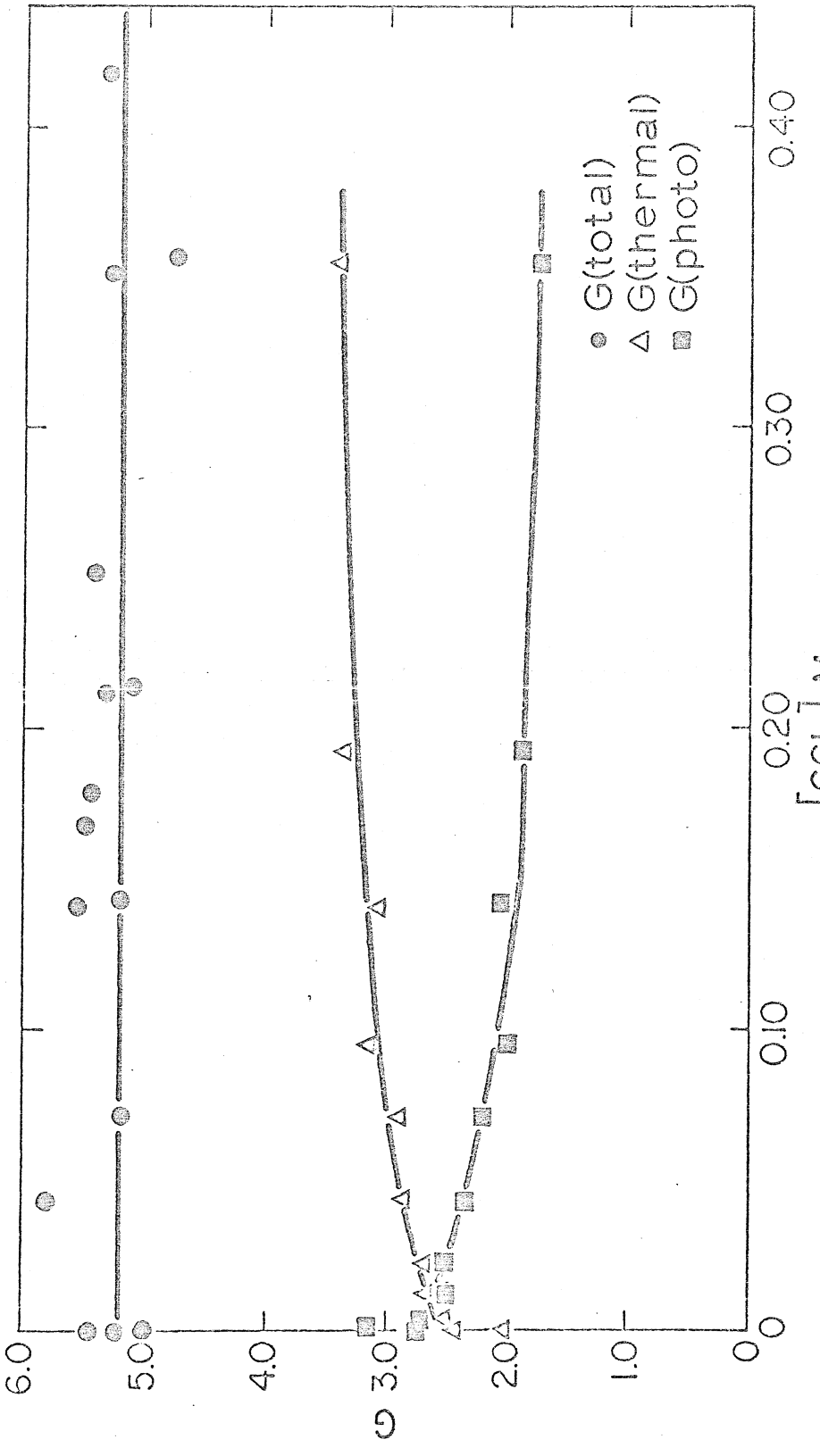


Figure 2. The Effect of Carbon Tetrachloride on G(total dimer), G(photo), and G(thermal) in Neat 1,3-Cyclohexadiene.

Table 3. Effect of Carbon Tetrachloride on G(total dimer), G(photo), and G(thermal) in neat 1,3-Cyclohexadiene. Data for Figure 2.

CCl_4,(M)	G(total dimer)	CCl_4,(M)	G(thermal)*	G(photo)*
0.0	5.19	0.0	2.06	3.19
0.042	5.80	0.0004	2.49	2.76
0.071	5.20	0.0022	2.53	2.72
0.141	5.52	0.011	2.61	2.64
0.142	5.47	0.022	2.73	2.52
0.167	5.33	0.044	2.88	2.37
0.178	5.12	0.071	3.02	2.23
0.211	5.41	0.096	3.13	2.12
0.214	5.25	0.142	3.27	1.98
0.251	4.72	0.193	3.37	1.88
0.352	5.33	0.356	3.48	1.77
0.356	4.72			
0.418	5.33			

* G(thermal) and G(photo) were calculated using the straight line for G(total dimer) = 5.25 in Figure 2 and the values for fraction thermal group from the curve in Figure 3.

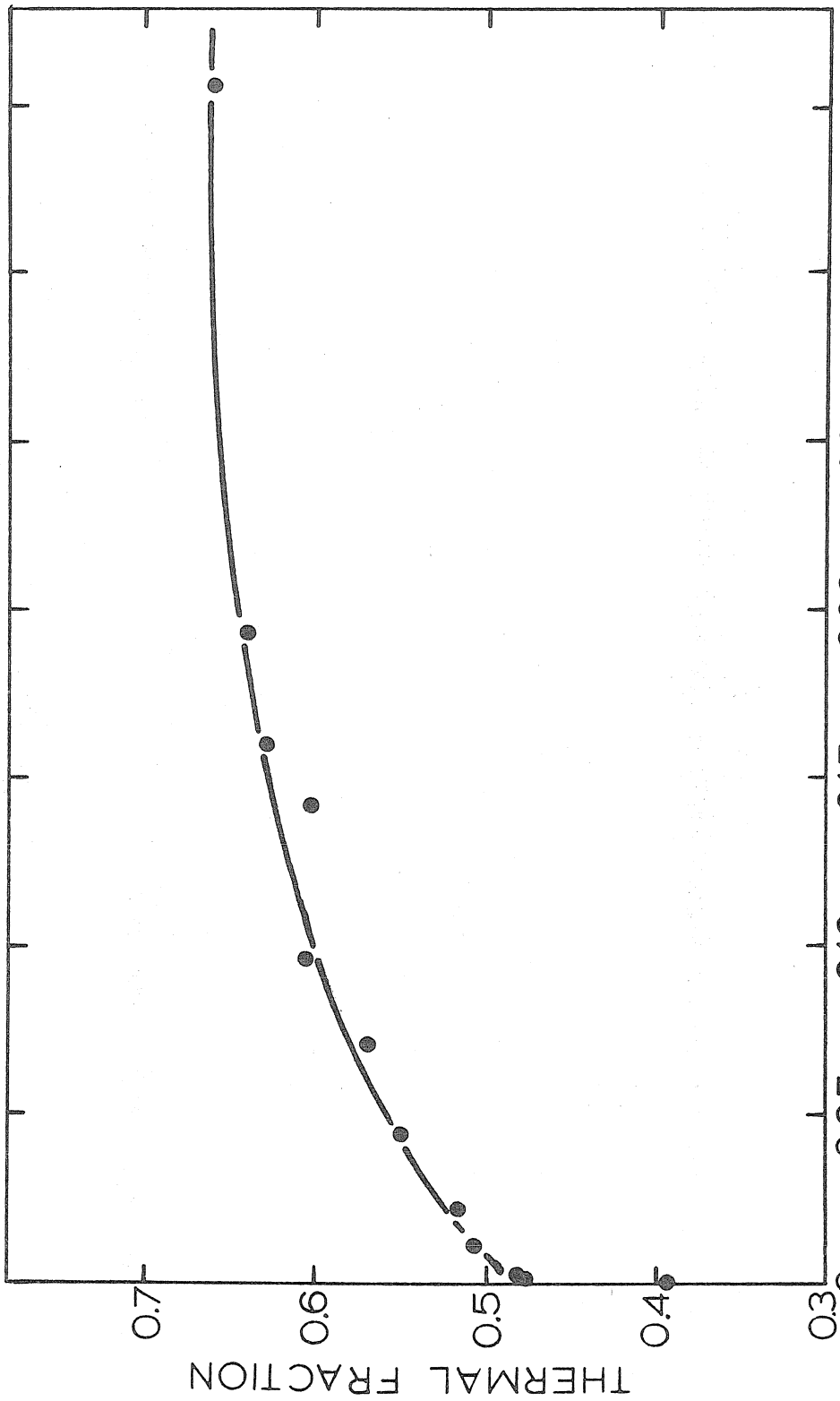


Figure 3. The Effect of Carbon Tetrachloride on the Fraction of Thermal Group Dimers in Neat 1,3-Cyclohexadiene.

Table 4. Effect of Carbon Tetrachloride on the Fraction of the Thermal Group Dimers in Neat 1,3-Cyclohexadiene. Data for Figure 3.

CCl_4,(M)	Fraction Thermal Group
0.0	0.393
0.00044	0.475
0.0022	0.482
0.011	0.506
0.022	0.516
0.044	0.549
0.071	0.570
0.096	0.607
0.142	0.604
0.193	0.642
0.356	0.662

states.

Figure 2 indicates that the effect of carbon tetrachloride on G(thermal) is that which would be expected from an electron scavenger on a cationic process. Somewhat unexpectedly there is also a quenching effect on the photo dimers. Significantly G(total dimer) is unaffected by the scavenger so that the enhancement of the process forming thermal dimers is equal to the quenching of the photo dimer production. In view of the implications of this observation the measurement of total dimer yield was repeated several times using independently prepared samples in separate irradiations. Such a 1:1 correspondence of enhancing and quenching effects indicates strongly that the processes leading to the two types of dimers are not independent. Since the dimer distribution indicates diene triplets as the photo dimer precursors,and the electron scavenging results together with the previous evidence provides strong evidence for diene cations as the intermediate in thermal dimer production, these two species must be related. The photochemical experiments show that CCl_4 does not induce thermal dimer formation from triplets so the cations do not originate by electron abstraction from excited 1,3-cyclohexadiene. Thus the triplets must be produced from diene radical cations by charge neutralization. A mechanism such as that indicated in reactions [5] - [10] appears to be operative:

$$CHD \overset{h\nu}{\longrightarrow} CHD^{+} + e^{-} \qquad [5]$$

$$CHD \overset{h\nu}{\longrightarrow} CHD^{3} \qquad [6]$$

$$CHD^{+} + e^{-} \longrightarrow CHD^{3} \qquad [7]$$

$$CHD^{+} + CHD \longrightarrow CHD_2^{+} \qquad [8]$$

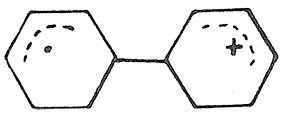
$$CHD_2^{+} + e^{-} \longrightarrow \text{thermal dimers} \qquad [9]$$

$$CHD_2^{+} + e^{-} \rightarrow CHD_2 \longrightarrow \text{thermal dimers} \qquad [9']$$

$$(CHD)_2^{+} \longrightarrow D_2^{+} \xrightarrow{e^{-}} \text{thermal dimers} \qquad [9'']$$

$$CHD^{3} + CHD \longrightarrow \text{photo dimers} \qquad [10]$$

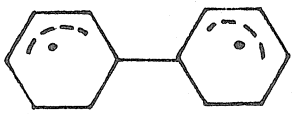
The symbol $\overset{h\nu}{\longrightarrow}$ indicates a process induced directly by the radiation. The symbol CHD represents 1,3-cyclohexadiene. There is no information available concerning the details of the formation of thermal dimers from $(CHD)_2^{+}$ which is envisioned as a non-fused two ring system such as :



VI

The ring closure could occur either from the ionic state or following charge neutralization to an active ground state. Since the ratio of dimers I and III formed by the dimerization of radiation induced cations is the same as that found in the thermal dimerization at 200°C, it would seem reasonable if the same type of intermediate were involved in both processes. Although the intermediate involved in the thermal dimerization is not known, Valentine et al. suggested

a biradical such as VII, indicated below, as an intermediate in the thermal isomerization of II and IV to I and III respectively. It is



VII

possible that such a species is formed in both thermal and γ radiation processes, in the latter case from VI by electron capture. Alternatively VI may ring close prior to neutralization to give the same I:III distribution as VII. These alternative radiation chemical processes are represented by reactions [9'] and [9''] respectively. D_2^+ is the representation for a cationic Diels-Alder species produced by ring closure of intermediate VI. Lacking evidence, these proposed possible reaction pathways are only conjecture.

If an electron scavenger S is added to the diene, additional reactions become possible.

$$e^- + S \rightarrow S^- \qquad [11]$$

$$CHD^+ + S^- \rightarrow CHD^3 + S \qquad [7a]$$

$$(CHD)_2^+ + S^- \rightarrow \text{thermal dimers} \qquad [9a]$$

Since reaction [10] proceeds from CHD^3 with 100% efficiency as

indicated by a quantum yield of 1 (23), the equality of enhancing and quenching effects of CCl_4 means that reactions [8] + [9] must also proceed with no non-reactive decay of the cations.

The formation of triplets by ion neutralization has been proposed previously in radiation chemical systems. There are pulse radiolysis (9) and electron scavenging (38) experiments which indicate that it is a major process in the formation of benzene triplets. The generation of solute triplets in solvents with no known triplet states, such as cyclohexane, has also been attributed to such a mechanism (39, 40).

A property of considerable interest concerning the basic processes of generating excited states in radiation chemistry is the relative importance of different modes of producing a particular state. In the present case, electron scavengers can give an indication of the relative importance of reactions [6] and [7] since the former is unaffected by electron scavengers. The results of Figure 2 show that at $\approx 0.35\,M CCl_4$ 45% of the initial yield of photo dimers are quenched in favor of thermal dimer formation. Therefore at least that percentage of the triplets are formed by reaction [7].

m-Dinitrobenzene Quenching in Neat 1,3-Cyclohexadiene. The extent to which an electron scavenger can quench triplets produced by reaction [7] will depend on the relative rates of [7], [7a], [8], and [11]. In addition, there is a limitation to the extent of quenching dependent on the relative mobilities of e^- and S^-. Even if S can scavenge all the electrons, reaction [7a] may still produce triplets. Even so, a more powerful electron scavenger than CCl_4 should be

able to provide a better indication of the fraction of triplets formed by charge neutralization.

m - Dinitrobenzene has been found to be one of the strongest electron scavengers in a test of the relative scavenging ability of the normally used compounds (41). The effect of this scavenger on the G values of total, thermal, and photo dimer is given in Figure 4. Figure 5 gives the curve for dimer distribution used in calculating G(photo) and G(thermal). The photo dimer quenching effect of m - dinitrobenzene is complicated by the fact that, unlike carbon tetrachloride, it quenches dimer formation in the xanthone sensitized 3130Å irradiation of neat 1,3-cyclohexadiene. It is important to note, however, that this quenching is not accompanied by any formation of thermal dimer. Thus in the γ radiation chemical case there are two mechanisms of triplet, and therefore photo dimer, quenching. One of these is electron scavenging which the CCl_4 results have shown leads to an increase in G(thermal)/G(photo) but does not change G(total dimer). The other process is a direct quenching of 1,3-cyclohexadiene triplets by m - dinitrobenzene, resulting in an equal quenching of G(photo) and G(total dimer). Thus the decrease in G(total dimer) in the presence of m -dinitrobenzene seen in Figure 4 is a measure of this triplet quenching. Therefore reaction [12] must be included in the reaction scheme when S is m- dinitrobenzene. S^3 does not lead to dimers. This was

$$CHD^3 + S \longrightarrow CHD + S^3 \qquad [12]$$

confirmed by an unsuccessful attempt to sensitize diene dimerization

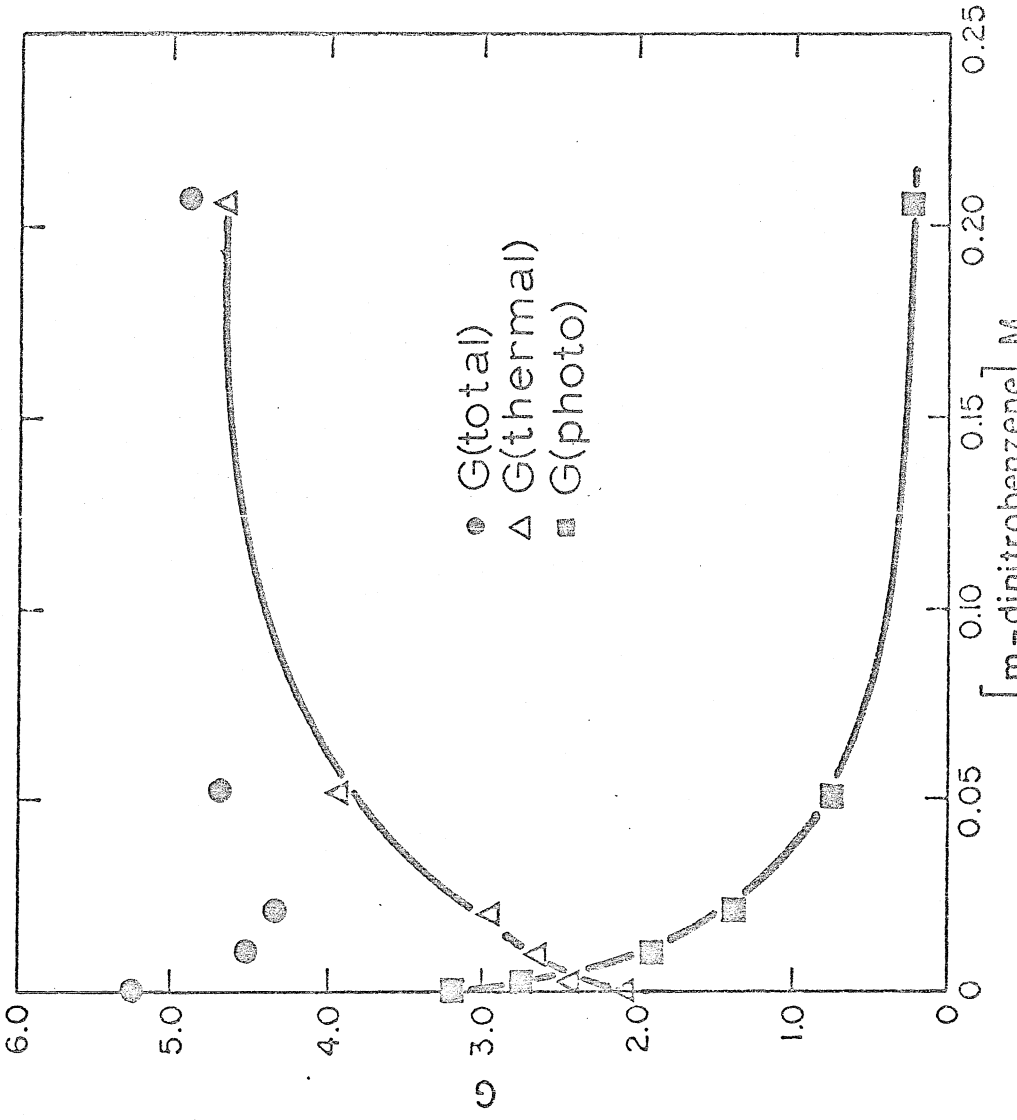


Figure 4. Effect of m-Dinitrobenzene on G(total dimer), G(photo), and G(thermal) in Neat 1,3-Cyclohexadiene.

Table 5. Effect of m-Dinitrobenzene on G(total dimer), G(photo), and G(thermal) in Neat 1,3-Cyclohexadiene. Data for Figure 4.

m-Dinitrobenzene, M.	G (total dimer)	G(photo)	G(thermal)
0.0	5.28	3.22	2.06
0.002	5.18[a]	2.75	2.43
0.01	4.56	1.92[b]	2.64[b]
0.021	4.36	1.40[b]	2.96[b]
0.052	4.72	0.78[b]	3.94[b]
0.21	4.94	0.25	4.69

a. Obtained by interpolation of G(total dimer) between 0.01 M m-dinitrobenzene and neat diene.

b. The fraction thermal group used to calculate these values of G(photo) and G(thermal) was obtained from the curve in Figure 5 rather than the data points.

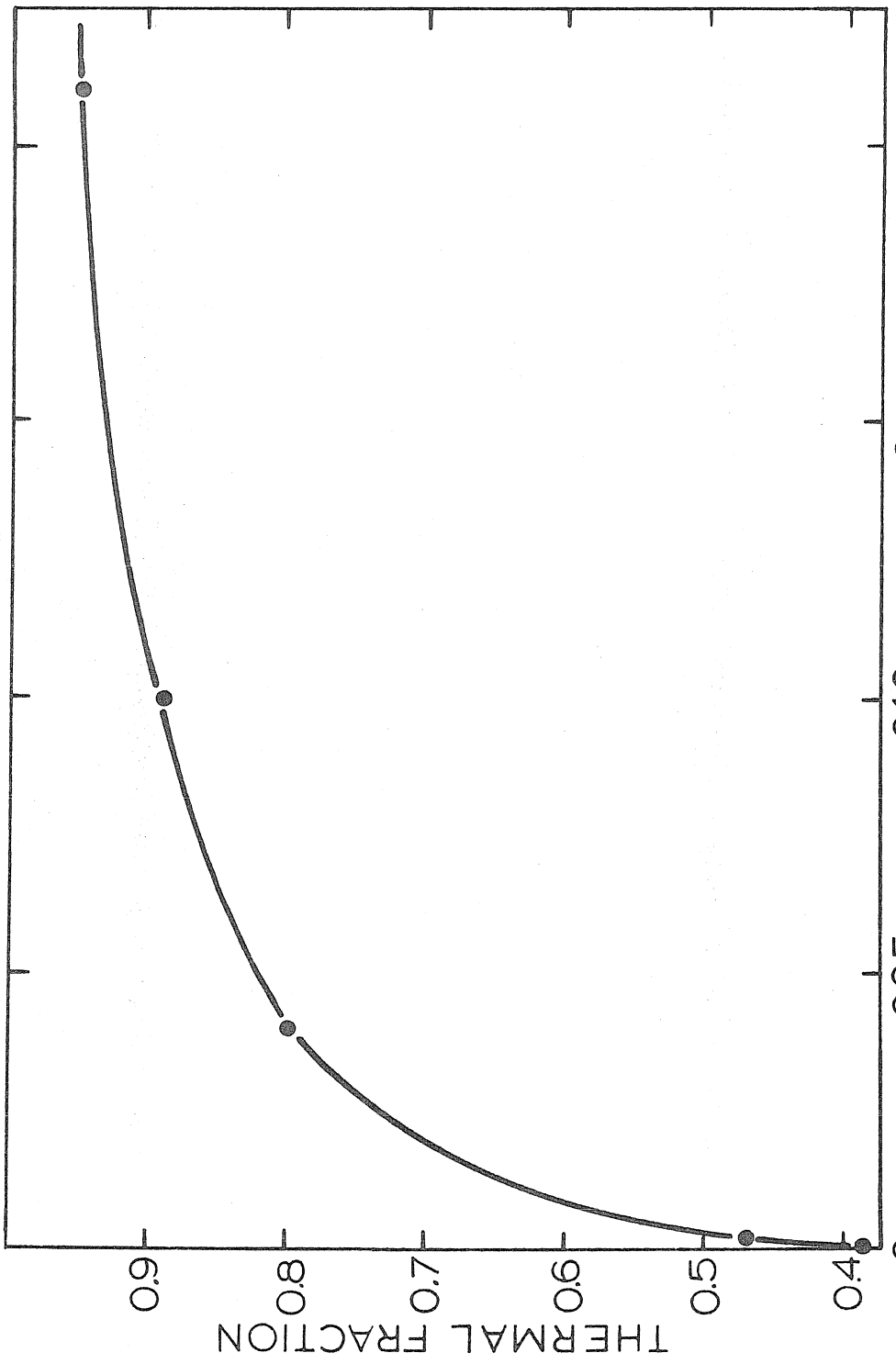


Figure 5. Effect of m-Dinitrobenzene on the Fraction of Thermal Group Dimers in Neat 1,3-Cyclohexadiene.

Table 6. Effect of m-Dinitrobenzene on the Fraction of the Thermal Group Dimers in Neat 1,3-Cyclohexadiene. Data for Figure 5.

m-Dinitrobenzene (M)	Fraction Thermal Group
0	0.39
0.002	0.47
0.04	0.80
0.10	0.89
0.21	0.95

with m - dinitrobenzene at 3130 Å.

That G(total dimer) can pass through a minimum is reasonable in view of the two mechanisms operative in the m-dinitrobenzene quenching. At high quencher concentration most of the cations form thermal dimers rather than triplets. Since the triplet yield is therefore small, the absolute G value for triplet quenching is also small even though most of the triplets formed are quenched. On the other hand, at intermediate m-dinitrobenzene concentrations more of the cations form triplets and the G value for their quenching is larger than at high quencher concentration, although the fraction quenched is smaller. At quite low concentrations quenching by reaction [12] can only compete with dimerization of the diene triplet to a small extent so that, although the triplet yield is fairly high, G for triplet quenching is quite small.

To the limited extent that a comparison is possible, the data of Figure 4 and the extent of photochemical dimer quenching are consistent with the concept of two quenching mechanisms. At 0.04 M m-dinitrobenzene G(thermal) is 3.70, an increase of 1.65 over the value in the absence of quencher. Thus the quenching of photodimers by electron scavenging is also 1.65. Since G for photo dimers (and triplets) in the absence of m-dinitrobenzene is 3.22 this leaves 3.22 - 1.65 = 1.57 as the G value for triplet formation by reaction [7] in the presence of 0.04 M quencher. However, G for photo dimers is 0.85 under these conditions so that a G of 0.72 of the triplets have been quenched by reaction [12]. This is a quenching of 46% of the triplets. The extent of quenching

of xanthone sensitized photodimerization of neat 1,3-cyclohexadiene by 0.044M m-dinitrobenzene was 52%. In view of the errors in analysis and interpolation in Figure 4 this is very good agreement.

It can be seen from Figure 4 that at 0.21 M m-dinitrobenzene, G(thermal) is 4.7 so that 81% of the photo dimers formed in the absence of quencher have been converted into thermal dimers. This is therefore the minimum fraction of cyclohexadiene triplets that are formed by charge recombination and direct triplet excitation accounts for a G of 0.6 or less.

The Electron Scavenging and Ion Recombination Processes. Although the theories of the kinetics of ion-recombination and electron scavenging are at present the subject of considerable literature discussion and active research and are not quantitatively rigorous, some insight can be gained concerning ion recombination to form triplets observed in the present system on the basis of these theories.

The model of Samuel and Magee estimates that the time for recapture of a thermalized electron by a geminate cation would be about 10^{-13} seconds (42) in a liquid of low dielectric constant. This is much too fast for a reaction such as electron scavenging or cationic reactions to compete appreciably with neutralization. However, ionic reactions have been observed in solvents such as cyclohexane and more recent theoretical attempts to correlate the observed yields with competing neutralization and ionic reactions indicate that the average lifetime of ions that undergo geminate

recombination must be of the order of 10^{-9} seconds (37,43). This is possible if the mobility of the negatively charged entity is much lower than that of the free electron (44). Hummel's semi-empirical treatment (37) found that the effect of an electron scavenger on cation lifetimes, as indicated by increased cationic reaction in cyclohexane, could be explained if the anionic diffusion coefficient in the presence of the electron scavenger CCl_4 is 1/25 that in the absence of the scavenger. Since the mobility of a free electron is approximately $10^{5\pm1}$ that of a cation (44), and the diffusion coefficient of Cl^-, the probable negative scavenger in the presence of CCl_4, is approximately equal to that of the cyclohexane cation, the negative species in the absence of scavenger represents an intermediate situation, resembling that of the anion but about an order of magnitude more mobile. This has been suggested to be a trapped or solvated electron (44,45). The work of Hummel indicates a bimolecular rate constant of 2.4×10^{10} l mole^{-1}sec^{-1} for the reaction of unscavenged negative species with carbon tetrachloride. This rate constant, combined with the half-life for ions (or electrons) of 6×10^{-10} seconds, which gives a first order rate constant of 1.1×10^{9}sec^{-1} for ion recombination, gives an indication of the fraction of electrons which should be scavenged at any CCl_4 concentration:

$$Go/G = 1 + 22\,[S]$$

The scavenging of electrons as indicated by the decrease in G(photo) in Figure 2 is considerably larger than the prediction below 0.01 M and smaller at concentrations of $CCl_4 > 0.02$ M. In fact the photo

dimers are 18% quenched at 0.002M CCl_4 instead of the calculated 6%. This sensitivity to low quencher concentrations indicates that the quenching here is not competing with geminate ion recombination, but is probably a scavenging of electrons which have escaped their cationic field. Just what fraction of the electrons do escape to be scavenged in this way is difficult to say. Hummel's rate constants would predict essentially no quenching at 4×10^{-4}M CCl_4 whereas photo dimer formation is quenched by G = 0.5. It is probable that this is due to the quenching of free negative charge. Values for free ion yields for saturated hydrocarbons ranging up to 0.74 have been found (46).

Most of the theoretical treatments of charge recombination kinetics have used single ion-electron pairs as the model. This reflects both the view that most of the ions in a spur undergo fast recombination with electrons because of a higher effective charge than that of an isolated ion (47), and is also a result of a simplification to avoid the necessity of including the behavior of charged particles in the fields of other ions in already complex theories (44,48). In effect these theories equate a spur with a single ion-electron pair, so that a spur reaction is equivalent to geminate recombination. In reality there are interactions in spurs which arise from the presence of more than one ion pair in close proximity (49). Since the electrons obtain essentially all the kinetic energy during ionization, the spur consists of a core of positively charged ions in a distribution not much different from that of the initial spur with the initially unthermalized electrons surrounding

it. The larger the spur, the greater the effective Coulombic force exerted on the electrons for recombination (50). Thus a reaction such as [7] which occurs by ion neutralization would be expected to be enhanced relative to reaction [8] by increasing the spur size. The size of the spurs produced by a given type of radiation is determined by the linear rate at which energy is deposited in the solution as measured by the linear energy transfer (L.E.T.) in ev/Å. For 2 Mev α-particles the L.E.T. is approximately 1000 times that of ^{60}Co γ rays (49,51).

In order to determine the importance of spur neutralization reactions in the production of 1,3-cyclohexadiene triplets, irradiation of neat diene with α particles from ^{210}Po was carried out. Using the irradiation cell diagramed in Figure 12, the energy of the α particles entering the solution was estimated to be ~ 2 Mev from the stopping power of mica (52) and aluminum (51). Of course straggling will broaden the energy spectrum of the initially monoenergetic 5.3 Mev particles. The spurs from the α radiation will be entirely overlapped producing cylindrical tracks where spur reactions should be enhanced relative to γ radiation.

Although absolute G values for dimers were not obtained, the dimer distribution was. It was found that now 54% of the dimers were photo dimers whereas in the case of γ radiation the value is 60%. This is only a very small difference in view of the differences in irradiation conditions and effective dose rates. Also, the small L.E.T. effect that is observed is in the opposite direction to that predicted. This may be due to quenching of diene triplets by small

residual amounts of oxygen not removed by the N_2 displacement procedure used. Alternatively it might be due to annihilation of triplets by free radicals in the spurs as has been suggested for the stilbene-benzene system (53). In any case the effect is very small and indicates that at least the difference in spur effects between α and γ radiation on reaction (7) is small. In view of the large differences in spur conditions it is difficult to see how this could be so if the actual spur contributions were appreciable. This conclusion is supported by the extent of electron quenching at low concentrations already discussed. Thus a large percentage of the electrons and ions probably escape from the spurs prior to recombination or capture.

Production of 1,3,5-Hexatriene in Neat 1,3-Cyclohexadiene. As mentioned in the Introduction, excited states of 1,3-cyclohexadiene also lead to ring cleavage to 1,3,5-hexatriene. The quantum yield for production of the cis isomer was measured to be 0.46 at 2537Å. Prolonged irradiation also produced the trans isomer, which is probably formed by absorption of a second photon by the cis triene. No benzene or cyclohexene was formed.

Radiation chemical experiments in neat 1,3-cyclohexadiene also indicated the formation of cis and trans 1,3,5-hexatriene. Identification of these products is described in the experimental section. The G value of the cis triene was measured to be 1.58. The trans isomer was detectable but could not be measured with any reliability because of interference from diene in the vpc analysis. Its G value was estimated to be approximately 5% that of the cis.

The G value for cis-1,3,5-hexatriene together with the 2537Å quantum yield gives an upper limit of 3.4 for 1,3-cyclohexadiene singlets. This value is an upper limit because the radiation may produce singlet states higher than the first excited state which might very well undergo ring opening with a quantum yield higher than that measured at 2537Å. No information is available on the yield of 1,3,5-hexatriene at wavelengths below 2537Å. The minimum G for diene excited singlets is 1.58.

The effect of cation and electron scavengers on the yield of cis-1,3,5-hexatriene was determined since it was obviously desirable to obtain a comparison of the modes of singlet and triplet production in 1,3-cyclohexadiene. The results of these experiments are given in Table 7. The values under the heading g(cis-triene) are G values based on the energy absorbed by the diene alone and omit the energy absorbed directly by the quencher. In most of the experiments conducted with scavengers the concentrations are so small that it makes no appreciable difference whether the energy they absorb is included or not. However, at concentrations near 1 M the quencher receives an appreciable fraction of the energy which may not be transferred to the diene and thus gives a spurious quenching effect. The values in Table 7 are not accurate to better than 10% and are therefore only given to 2 significant figures. Table 7 indicates that there is very little, if any, quenching by the additives, even up to ca. 1 M, at least on the basis of g(cis-triene). If the triene were formed in a manner similar to the photo dimers, carbon tetrachloride and m-dinitrobenzene should have a quenching effect, even

Table 7. Effect of Cation and Electron Scavengers on cis - 1,3,5-Hexatriene Yields in Neat 1,3-Cyclohexadiene.

Scavenger	Conc. Scavenger (M)	G(cis-triene)	g(cis-triene)
		1.6	1.6
CCl_4	0.006	1.5	1.5
	0.06	1.5	1.5
	0.10	1.3	1.4
	0.20	1.4	1.5
	0.42	1.3	1.4
	1.04	1.2	1.4
m-Dinitrobenzene	0.02	1.5	1.5
2-Propanol	0.09	1.4	1.5
	1.20	1.1	1.3

at low concentrations. Since the alcohol must compete with 1,3-cyclohexadiene for CHD^+, its quenching effect might not be expected to appear at low concentrations. But we have already seen that 1.2M 2-propanol quenches at least 52% of all dimers and should therefore have a similar effect on triene yield if the singlets were produced by the same process of charge recombination that generates the diene triplets. The conclusion is that the 1,3-cyclohexadiene singlets formed by γ radiation are produced by different processes than the charge neutralization which generates the majority of the diene triplets. This is consistent with the results of Figure 2. The equality of the photo dimer quenching and the thermal dimer enhancement precludes the formation of any other species by a process involving neutralization of scavengable electrons. If such a process did occur, electron scavenging would cause an increase in thermal dimers not matched by a corresponding decrease in photo dimers.

Comparison of Triplet and Singlet Production Processes. It is rather surprising that the two excited species are formed by processes which are mutually exclusive, or at least nearly so. There are not a great many examples available where the mechanisms of both singlet and triplet production in an organic liquid by high energy radiation are known. One system for which such information has recently been obtained is that of benzene. Cooper and Thomas (9) in a nanosecond pulse radiolysis study conclude on the basis of charge scavenging effects that G values of 1.6 and 1.8 observed for the lowest excited benzene singlet and triplet states are both formed by neutralization of benzene cations.

The high fraction of triplets produced in this same manner in 1,3-cyclohexadiene is consistent with this finding and is not incompatible with theories of excitation by electron impact. These predict, and in the gas phase it has been confirmed, that to a good approximation electrons with more than ca. 100 ev energy create the various excited states in proportion to the optical oscillator strengths of the states (54). This means that electrons of such energies will cause almost no direct triplet excitation. At energies a few tens of ev above the ionizing threshold a new mechanism of excitation, electron exchange, becomes important and can lead to the formation of optically forbidden states such as singlet triplet transitions (55). This process can be regarded as a momentary capture of the exciting electron. The ejected electron can have the same or opposite spin as that of the incoming one. It is just at these lowest energies where the flux of electrons is likely to be greatest, although the number-energy spectrum is rather uncertain (44). Thus the "expected" singlet and triplet yields formed directly by electron impact cannot be estimated with any certainty. The low yield ($G \leq 0.6$) found for unscavengable triplets does not contradict the theories.

The formation of higher yields of singlet states than triplets by direct excitation is also compatible with these ideas. It is rather surprising, however, that no singlets are formed by ion-electron recombination. It has been shown by Magee (56) that the triplet: singlet ratio expected from neutralization would be dependent upon spur conditions. If only an isolated ion-electron pair are present in a spur, recombination will lead only to singlets. Totally homo-

geneous distribution of ions would lead to a 3:1 triplet:singlet distribution. This should be the highest percentage of triplets possible by ion recombination.

One possible reason for the lack of singlet production by charge neutralization concerns the energetics of the neutralization process. As already mentioned, the evidence of Hummel (48) seems to indicate that the electron involved in recombination with cyclohexane cations is already partially trapped or solvated, giving it a lower mobility than the free electron. It has also been shown that only extreme purification and degassing procedures allow species with the mobilities expected for free electrons ($\geq 10^3$ x mobility of cations) to be observed in n-hexane (57). In most solutions sufficient impurities exist to form species with lower mobilities. Since it appears that usually some trapped or solvated negative species are involved in the ion recombination process, the energy released will be less than the ionization potential. Whether it will be too low to allow formation of the first excited singlet is difficult to say since it depends on the solvation energy of the cation as well as that of the negative entity and also on the singlet energy of the 1,3-cyclohexadiene. It has been reported previously that the diene is a fairly good electron scavenger (30) so it may form a relatively stable negative species. It has been calculated that such a process may be responsible for the selective excitation of a low electronic state by charge recombination in some organic molecules (58).

In summary, most 1,3-cyclohexadiene triplets are formed

by ion neutralization although a maximum G of 0.6 may be formed by direct excitation. Excited singlets are produced by an essentially unquenchable process. This may involve primarily direct excitation by secondary electrons. The electron recapture process responsible for triplet formation does not seem to be involved, possibly because the electrons are solvated and the neutralization does not provide sufficient energy for singlet excitation.

Dimers of 1,3-Cyclohexadiene in Benzene Solution. The radiation chemical reactions of 1,3-cyclohexadiene in benzene were also studied. It is under these conditions that comparison with Schutte and Freeman's recently published results is possible. On the basis of Whitten's observed selective quenching of thermal dimers by 2-propanol, the fact that the dimers can be factored into the two groups in benzene solutions of diene as well as in neat solution, and the small but real effect of carbon tetrachloride on the dimer distribution (Figures 6 and 7), the precursors of the thermal and photo dimers in benzene are probably the same as in neat diene, namely CHD^+ and CHD^3. Figure 7, the dependence of the fraction of the thermal group on CCl_4 concentration probably shows the effect of this quencher better than Figure 6 since in the latter case there is an obscuring variation in G(total dimer) which is probably not real. Whitten's conclusion that CCl_4 had no quenching effect is not surprising since it was based on an examination of G(total dimer).

The variation of the G values for total, thermal, and photo dimers with diene concentration in benzene is given in Figure 8. The latter two G values have been obtained from G(total dimer) and the

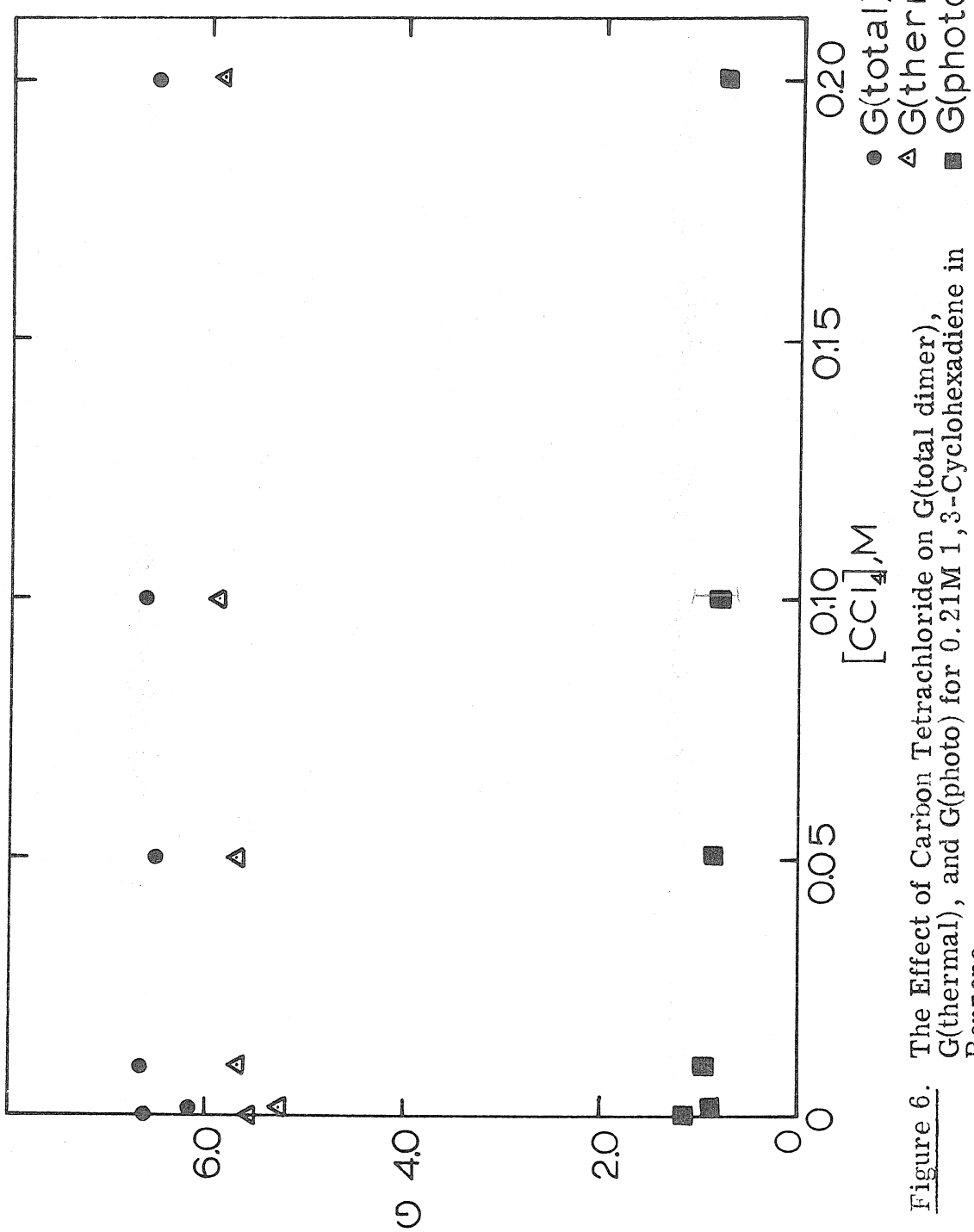


Figure 6. The Effect of Carbon Tetrachloride on G(total dimer), G(thermal), and G(photo) for 0.21M 1,3-Cyclohexadiene in Benzene.

Table 8. The Effect of Carbon Tetrachloride on G(total dimer), G(photo), and G(thermal) for 0.21 M 1,3-Cyclohexadiene in Benzene. Data for Figure 6.

CCl_4,(M)	G(total dimer)	G(photo)*	G(thermal)*
0.0	6.66	1.07	5.59
0.002	6.19	0.91	5.28
0.01	6.68	0.96	5.72
0.05	6.54	0.86	5.68
0.10	6.66	0.80	5.88
0.20	6.55	0.73	5.82

* These G values were obtained from G(total dimer) and the curve for the Fraction of Thermal Group Dimers in Figure 7.

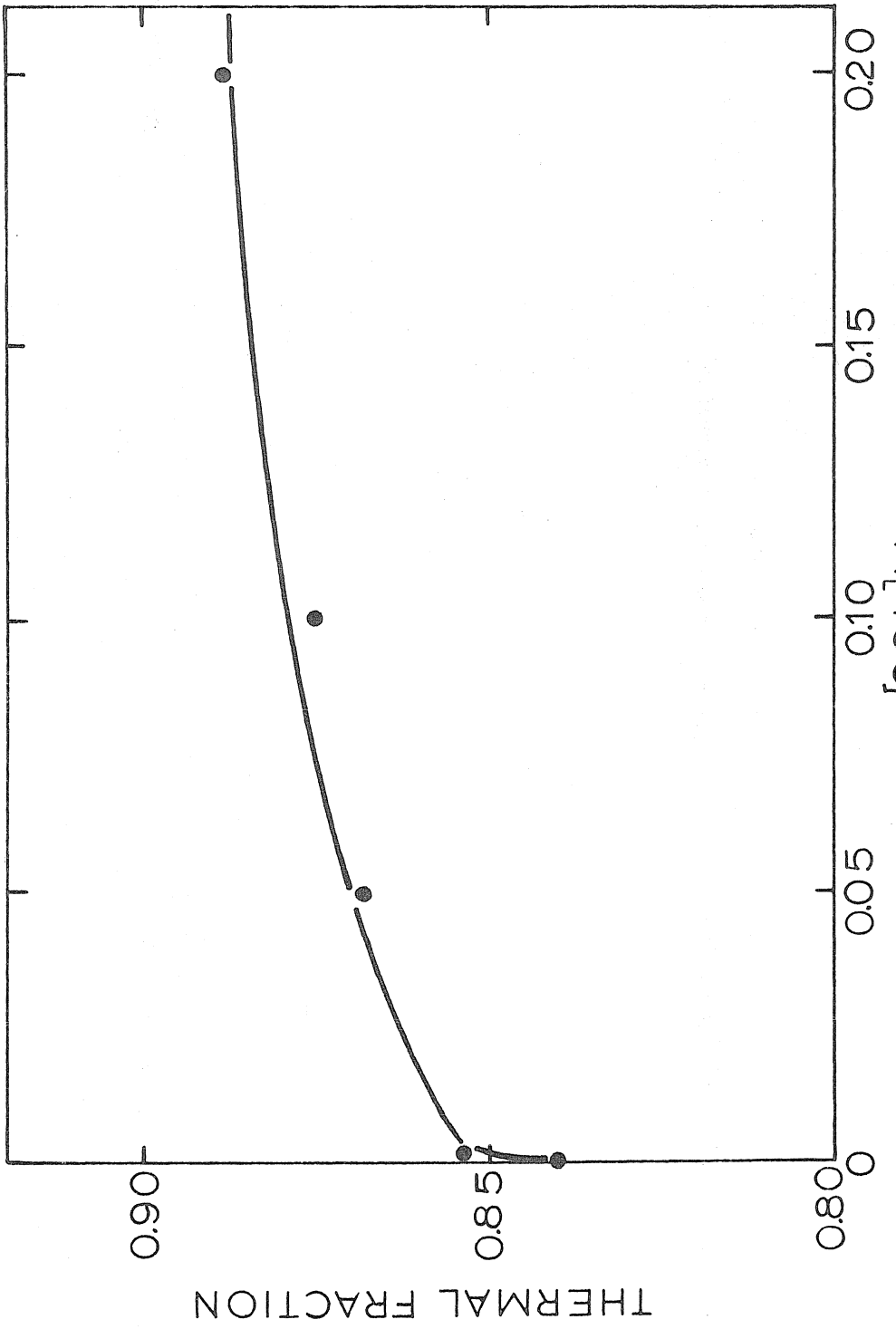


Figure 7. The Effect of Carbon Tetrachloride on the Fraction of Thermal Group Dimers for 0.21M 1,3-Cyclohexadiene in Benzene.

Table 9. The Effect of Carbon Tetrachloride on the Fraction of Thermal Group Dimers for 0.21 M 1,3-Cyclohexadiene in Benzene. Data for Figure 7.

CCl_4,(M)	Fraction Thermal Group
0.0	0.840
0.002	0.854
0.05	0.868
0.10	0.875
0.20	0.889

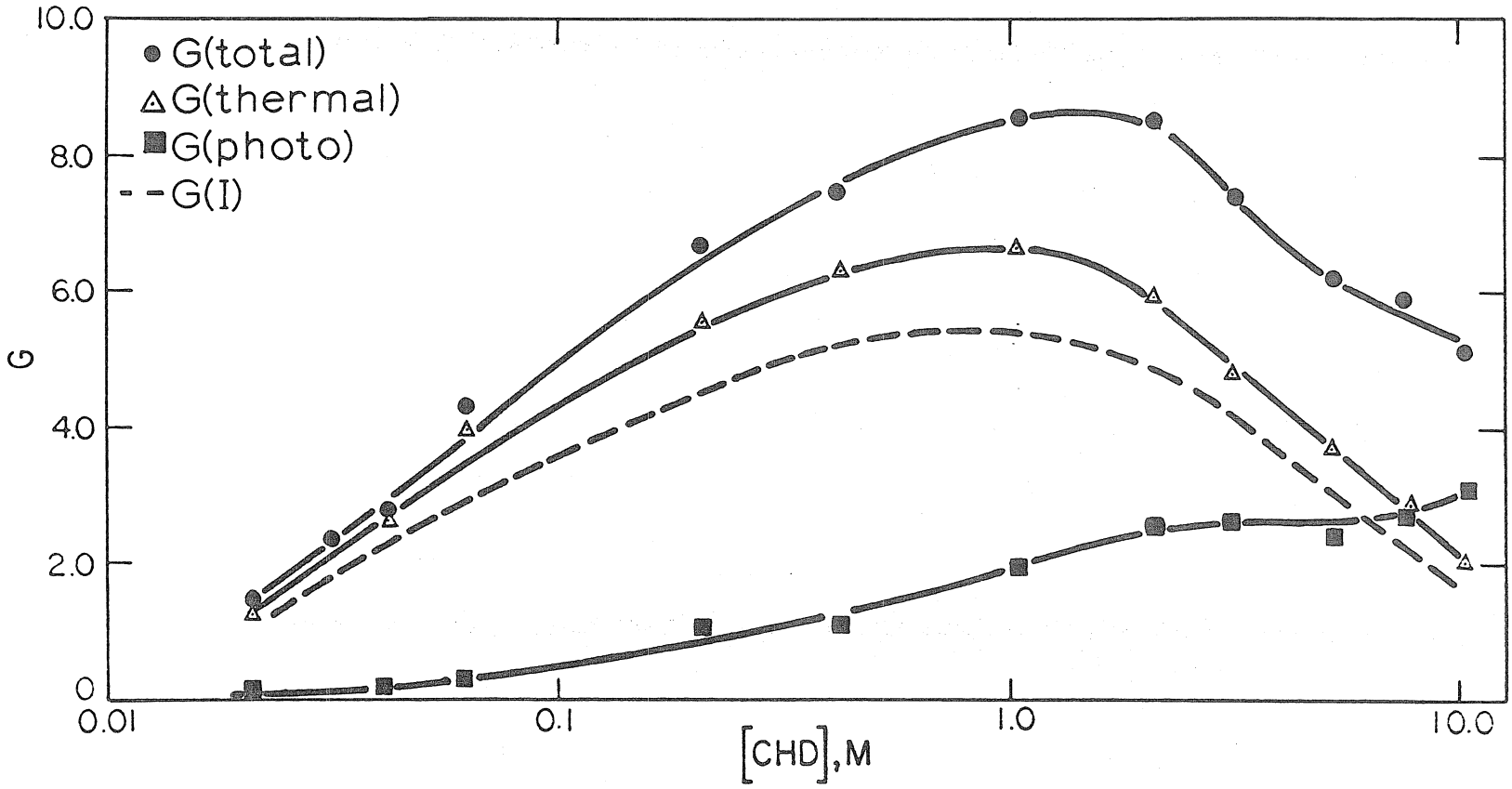


Figure 8. The Variation of G(total dimer), G(thermal) and G(photo) with the Concentration of 1,3-Cyclohexadiene in Benzene. G(I) included for Comparison with Ref. 21.

Table 10. The Variation of G(total dimer), G(photo), and G(thermal) with the Concentration of 1,3-Cyclohexadiene in Benzene Solution. Data for Figure 8.

1,3-Cyclohexadiene,(M)	G(total dimer)	G(photo)*	G(thermal)*
10.40	5.24	3.18	2.06
7.34	5.90	2.93	2.97
5.24	6.20	2.64	3.56
3.15	7.37	2.58	4.79
2.10	8.54	2.57	5.97
1.05	8.60	2.00	6.60
0.420	7.50	1.18	6.32
0.210	6.66	1.07	5.59
0.063	4.34	0.35	3.99
0.042	2.72	0.18	2.54
0.032	2.38	0.15	2.23
0.021	1.38	0.08	1.30

* These G values were obtained from G(total dimer) in this Table and the Fraction Thermal Group curve, Figure 9.

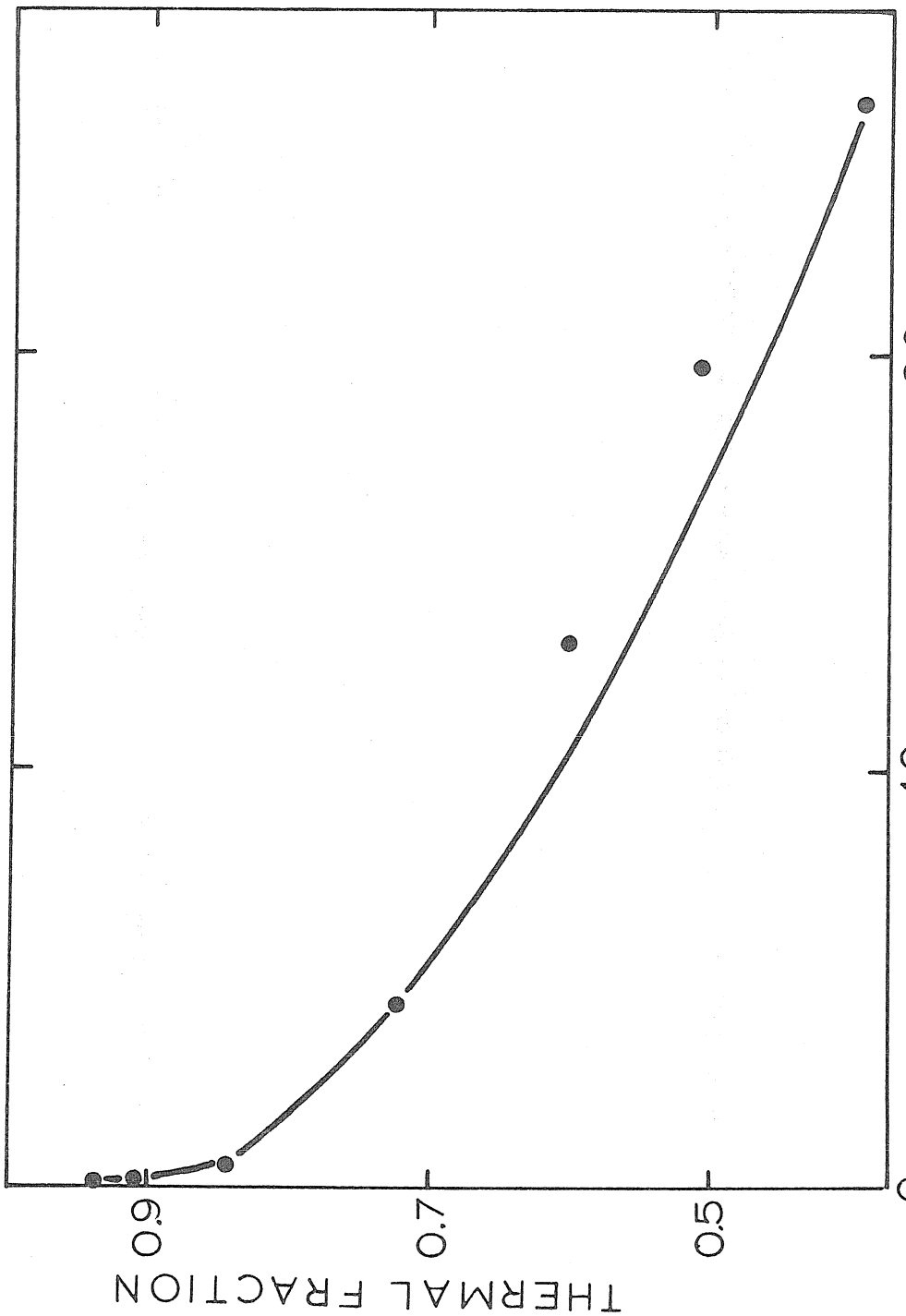


Figure 9. The Variation of the Fraction of Thermal Group Dimers with the Concentration of 1,3-Cyclohexadiene in Benzene Solution.

Table 11. The Variation of the Fraction of Thermal Group Dimers with the Concentration of 1,3-Cyclohexadiene in Benzene Solution. Data for Figure 9.

1,3-Cyclohexadiene, (M)	Fraction Thermal Group
10.40	0.394
7.87	0.510*
5.24	0.603*
1.75	0.724*
0.21	0.840
0.084	0.909
0.021	0.944

* These data are from Whitten (ref. 32).

curve in Figure 9. Sensitization by the benzene solvent occurs at low concentrations since the energy absorbed directly by the diene is too low to effect the dimerization at the level observed. The dimerization resulting from this direct absorption by the diene can be calculated easily from the G values for dimerization in neat diene and the electron fraction of the diene in solution at a given concentration. Subtracting this from overall dimer yields gives the dimerization due to energy absorbed by benzene alone, that is sensitized dimerization values. These are plotted in Figure 10. This correction assumes that the G value for dimerization for energy absorbed by the diene is unaffected by benzene. This is probably not the case. If it were, Figure 10 should not pass through a maximum. Vesley showed that at 1 M 1,3-cyclohexadiene the quantum yield for sensitized dimerization was essentially 1 so that by this concentration $G(\text{photo})_{\text{sens}}$ should have reached a plateau. The decrease in sensitized G values at higher diene concentrations indicates an extra enhancement of dimerization by the benzene at lower concentrations. For example, at intermediate diene concentrations the formation of diene triplets may occur by both triplet energy transfer and charge transfer from benzene, the latter followed by charge neutralization to form diene triplets. Since Figure 9 indicates that the fraction of thermal group dimers decreases monotonically with an increase in 1,3-cyclohexadiene concentration the benzene effect is greater in the case of thermal dimerization than for triplet induced dimer formation. Effects such as a greater electron solvating ability for benzene than for 1,3-

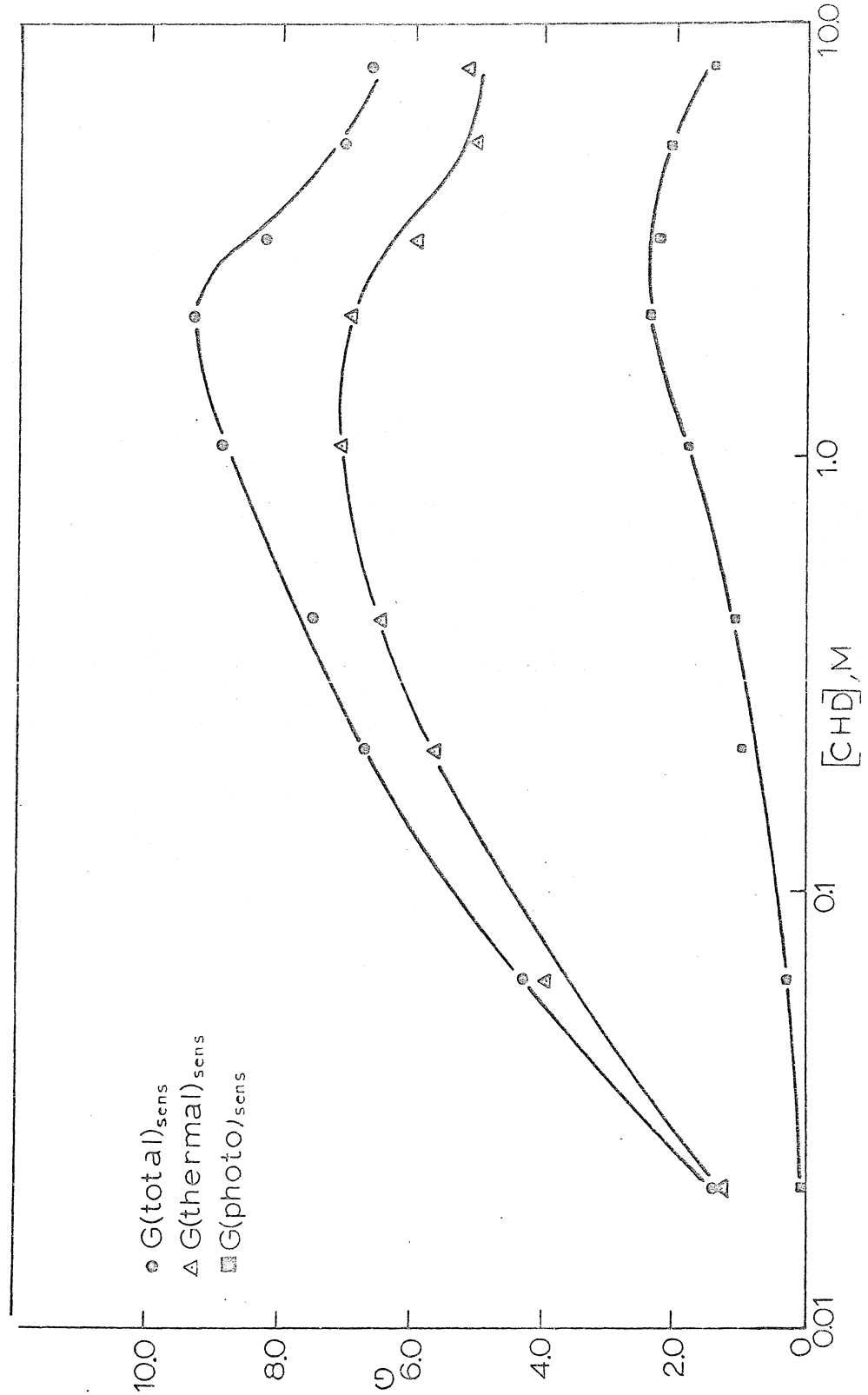


Figure 10. Dimerization G Values Based on Energy Absorbed by Benzene and Corrected for Dimerization Due to Direct Absorption of Energy by 1,3-Cyclohexadiene.

Table 12. The G Values for Dimerization Based on Energy Absorbed by Benzene and Corrected for Dimerization Due to Direct Absorption of Energy by 1,3-Cyclohexadiene. Data for Figure 10.

1,3-Cyclohexadiene	$G(\text{total dimer})_{sens.}$	$G(\text{photo})_{sens.}$	$G(\text{thermal})_{sens}$
7.87	6.67	1.41	5.26
5.24	7.12	2.09	5.03
3.15	8.28	2.31	5.97
2.10	9.35	2.40	6.95
1.05	8.92	1.82	7.10
0.42	7.58	1.09	6.49
0.21	6.70	1.03	5.67
0.063	4.30	0.33	3.97
0.021	1.37	0.07	1.30

cyclohexadiene could be partially responsible for this.

The G values for photo dimer formation in Figure 10 are less than 2.5 at all concentrations. Whitten's cation scavenging results (32) at 0.21 M diene in benzene indicate that diene triplets are derived entirely from benzene triplets with no involvement of CHD^+. The quenching of thermal dimers was almost complete at 0.2 M 2-propanol but there was essentially no quenching of photo dimers. In view of the Cooper-Thomas mechanism for benzene triplet and singlet formation from benzene ions (9), this result also indicates that 2-propanol is ineffective in scavenging benzene cations.

At 0.21 M 1,3-cyclohexadiene in benzene $G(\text{photo})_{\text{sens}}$ is 1.0. Vesley's quantum yield for photo dimerization of 0.21 M diene sensitized by benzophenone, together with a benzene triplet lifetime of 20 nsec (9), give a quantum yield for photodimerization in benzene of 0.72 for 0.21 M diene. Together with $G(\text{photo})_{\text{sens}}$, this results in a G value for benzene triplets of 1.2. This value is far short of the $G \approx 5$ estimated for benzene triplets from stilbene isomerization. There is, however, some disagreement about what this latter number actually represents.* Some workers believe that at the stilbene concentrations necessary for G(isomerization) to reach a plateau, species in addition to triplets and triplet precursors are being scavenged to give isomerization. For example, Fischer et al. (17) estimate that the G value of benzene triplets leading to stilbene

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* A more complete discussion of these results is given in the Introduction to Part III of this thesis.

isomerization is as low as 1.6 - 2. This also agrees more closely with the benzene triplet yield measured by pulse radiolysis, G = 1.8 (9). On this basis the present values are not greatly in error. At higher diene concentrations $G(photo)_{sens}$ is greater than at 0.21 M, but direct diene irradiation and triplet formation from CHD^+ cannot be excluded.

Solvent effects such as those mentioned above can help explain a change in thermal:photo ratios but both Figure 8 and Figure 10 indicate that G(total dimer) passes through a maximum. Therefore, an explanation of the change in dimer yield as a function of concentration in terms of a change in the hospitality of the environment toward the separation versus recombination of ions is not sufficient. With regard to this, a proposal of Schutte and Freeman (21) appears to be pertinent, although as will be shown, there is sufficient disagreement between their results and the present ones to raise some questions.

These workers observed dimers I-IV formed from 1,3-cyclohexadiene in benzene but since they did not separate all the dimers, they were unaware of the thermal and photo groupings these dimers exhibited. They were, however, able to isolate dimers I and IV and as a result could observe the opposing effect CCl_4 had on these dimers and the quenching effect ethanol had on dimer I. This led them to conclude that a cationic and a triplet mechanism were operative and that at least some triplets were formed from ions. The data of these authors indicates that at 0.03 M 1,3-cyclohexadiene G(I) = 11.5. In our terminology this makes

G(thermal) = 14.0. Since the ionization potential of benzene is 9.6 ((59) the energy necessary for this dimerization would be 134 ev per 100 ev energy input if all the dimers originated from radiation-produced CHD^+. These results would require a chain mechanism, which the authors have suggested to be:

$$(CHD)_2^+ \rightarrow D_2^+ \qquad [12]$$

$$D_2^+ + CHD \rightarrow \text{thermal dimer} + CHD^+ \qquad [13]$$

The decrease in G(I) at high diene concentrations is attributed to a reaction such as:

$$(CHD)_2^+ + CHD \rightarrow (CHD)_3^+ \qquad [14]$$

Discrepancy between these results and ours occurs. Above 1 M the two sets of results are fairly similar but below this concentration of 1,3-cyclohexadiene Figure 8 shows the value of G(I) falling. The maximum G value was 8.6 of which 6.6 must have come from ions and 2.0 had triplets as the immediate precursor. The ionization potential and triplet excitation energy (60) of benzene place a minimum of 71 ev required to produce the excitations per 100 ev radiation energy. If the benzene triplets also arise from ions as the results of Cooper and Thomas indicate (9), the energy requirement rises to 83 ev. Although neither case demands a chain reaction, they represent a considerably higher efficiency in utilization of absorbed energy than is generally believed to occur. For example, in the gas phase the G value for the production of ions from electron irradiated benzene is measured at 4.3 (61). Thus a chain mechanism

probably does make some contribution to the thermal dimer yields at least in the region of high G. Our results indicate that both chain dimerization [12]- [13] and reaction [14] are unimportant in neat diene. This conclusion is derived from the constancy of total dimer yield in Figure 2, which requires that reaction [8] is the only significant fate of $(CHD)_2^+$ in pure 1,3-cyclohexadiene. If dimeric ion reacted with diene to form $(CHD)_3^+$ the yield of total dimers should be decreased by electron scavengers. On the other hand if reactions [12] - [13] were to occur, the total yield should be increased since each CHD^+ would lead to more than one dimer. The possibility that both processes occur to about the same extent so that the effect of electron scavengers on both fortuitously cancels out cannot be excluded.

The origin of the discrepancy in G values is not too clear. The agreement above 1 M 1,3-cyclohexadiene indicates that the effect must be due to minor impurities rather than gross errors in experimental procedure. One possibility might be radiation generated impurities. The present experiments were generally carried out with a total dose of 10^{20} ev/cc whereas Schutte and Freeman used 10^{19} ev/cc. Figure 11 shows the effect of changing the radiation dose on G(total dimer) for 0.21 M diene in benzene. The dose effect in neat diene is included for general information. At 10^{19} ev/cc a G of 8.0 is obtained. That of Schutte is approximately 16. Although our irradiations were carried out at ca. 30°C, while the other workers used 23°C, Whitten's data (32) indicates that there is no appreciable temperature effect on the dimerization yields. If there

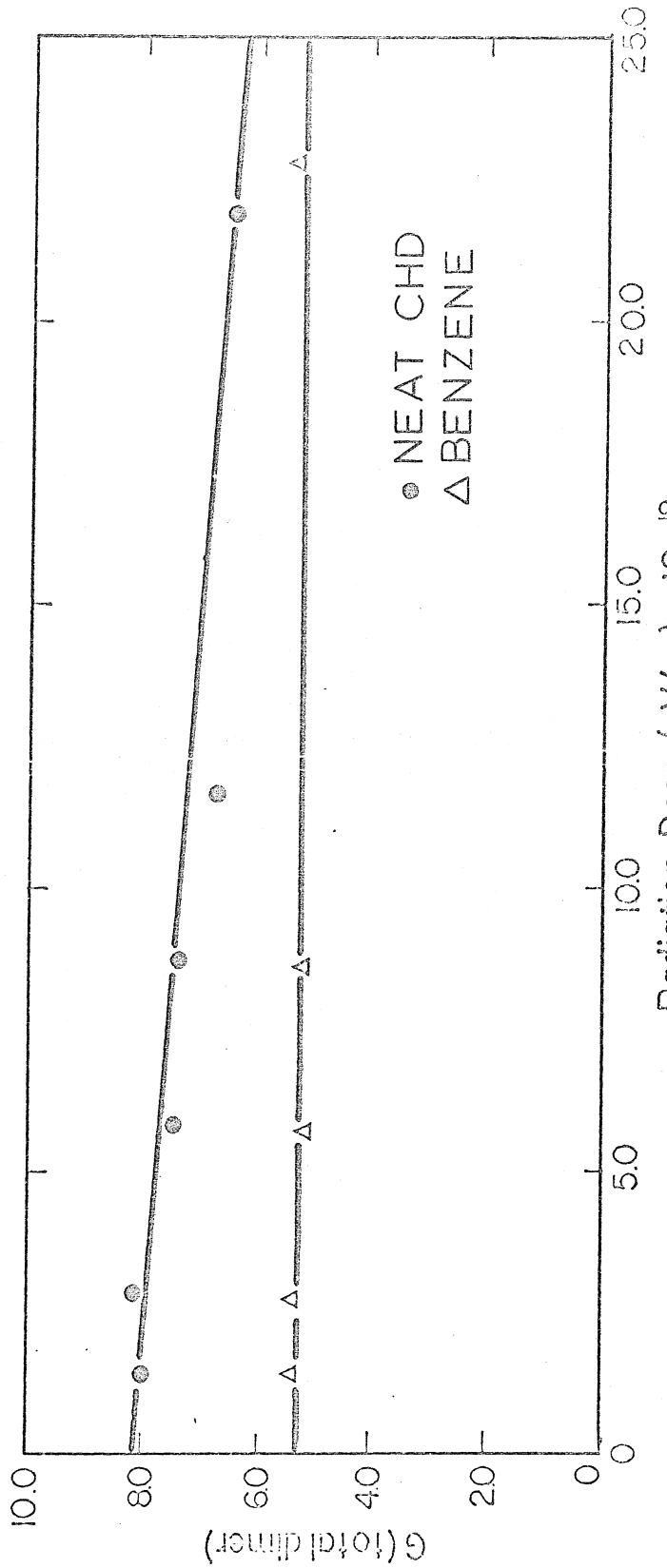

Figure 11. Dose Dependence of G(total dimer) in Neat 1,3-Cyclohexadiene and in 0.21M Diene in Benzene.

Table 13. The Dose Dependence of G(total dimer) in Neat 1,3-Cyclohexadiene and in 0.21 M Diene in Benzene. Data for Figure 11.

Neat Diene		0.21M Diene in Benzene	
Dose(ev/ml)x10^{-19}	G(total dimer)	Dose(ev/ml)x10^{-19}	G(total dimer)
1.42	5.35	1.46	8.02
2.85	5.30	2.90	8.10
5.70	5.16	5.82	7.48
8.56	5.21	8.72	7.42
22.80	5.27	11.63	6.66
		21.80	6.50

is an impurity in our benzene, it is probably a cation scavenger. Water is the most likely candidate. Although our benzene is high purity commercially zone-refined solvent it was not specially dried prior to use. Small amounts of water could be present. In an effort to test this, zone-refined benzene which had been refluxed over sodium was used as solvent in gamma radiation dimerization of 0.21M 1,3-cyclohexadiene. A value of G(total dimer) = 9.8 was obtained. If this value is used and a dose correction of 20% is applied to approximate the G value at 10^{19}ev/cc, a corrected G of 11.8 is obtained for total dimer yield. This effect still leaves the value lower than that of Schutte.

Whitten (32), whose value for G(total dimer) is 6.1 at 0.21 M diene in benzene, observed that when, instead of being zone-refined, the solvent was purified by treatment with sulfuric acid followed by distillation from a drying agent, the G values obtained were about 20% higher. Schutte and Freeman used this purification procedure, and dried the benzene over sodium. Dividing their G by 1.2 gives a value of approximately 13.5. In view of the approximations in these corrections the disagreement between "corrected" G values is not great. Thus, if corrections implying impurities in both types of benzene are applied the discrepancies in the yields of the two groups can be rationalized, at least at 0.21 M diene. The only really significant result of these corrections is that now our results require a chain mechanism rather than only making it probable.

1,3,5-Hexatriene Formation in Benzene. As in neat 1,3-cyclohexadiene, 1,3,5-hexatriene is also produced by γ radiation in

benzene solutions of diene. Investigation of this product in benzene was carried out only at 0.21 M 1,3-cyclohexadiene. The observed G value for cis-1,3,5-hexatriene was 0.38. The presence of the trans isomer could be measured more accurately than in neat diene since the lower diene concentration interferred with analysis less. Its G was 0.09. The effect of quenchers on these yields is given in Table 14. Azulene quenches the trans triene but not the cis indicating that the former is formed from the latter by triplet isomerization. Although the concentration of the cis-triene is so low that it could not compete with 1,3-cyclohexadiene for benzene triplets, it can compete with dimerization for diene triplets. In neat diene this competition is much less favorable. The quantum yield for benzophenone sensitized isomerization of cis-1,3,5-hexatriene was measured to be 1.0. This gives an initial G (cis-triene) of 0.47. This, together with the quantum yield for triene formation from 1,3-cyclohexadiene, gives a G value for diene singlets in 0.21 M solution in benzene of 0.98. This is, of course, subject to the same assumption as in neat diene; that is, that no higher states of the diene are involved. This is probably a good assumption in the present case since it is highly probable that the diene singlets are generated by benzene singlets.

Since the lowest singlet level of 1,3-cyclohexadiene (62) is probably higher in energy than the lowest benzene singlet (60), transfer of energy from the solvent would require a higher benzene energy level. The production of higher excited benzene singlets which do not undergo internal conversion has been suggested on the basis of β radiation scintillation studies (63). The estimated G was

Table 14. The Effect of Scavengers on 1,3,5-Hexatriene Yields from 0.21 M 1,3-Cyclohexadiene in Benzene.

Scavenger	Conc. Scavenger, (M)	G(cis-triene)	G(trans-triene)
—		0.38	0.09
CCl_4	0.090	0.19	0.05
2-Propanol	0.11	0.34	0.09
Azulene	0.0085	0.37	0.02

ca. 1. Energy transfer from such a state to anthracene has been proposed in pulse radiolysis experiments (9).

Charge Scavenger Effects on 1,3,5-Hexatriene Yields in Benzene. In addition to azulene quenching, Table 14 also indicates triene yields in the presence of 2-propanol and carbon tetrachloride. The former has no effect on the yields of the isomers of 1,3,5-hexatriene. This is consistent with the inability of this alcohol to scavenge benzene cations as was discussed in a preceding section and also means that CHD^+ is not involved in diene singlet production. Carbon tetrachloride, however, quenches about half of the triene yield. It may possibly be quenching the higher benzene singlets suggested to be involved in the triene formation. The quenching of diene singlets is ruled out since CCl_4 will not quench cis-triene formation from 1,3-cyclohexadiene at 2537 Å. It is also possible that CCl_4 is involved in the quenching of ionic precursors to benzene singlets. But if this is the case it is difficult to explain why the quenching of photo dimers by CCl_4 in benzene was so small (Figure 6) since these also presumably originate as benzene cations, converted into triplets rather than singlets.

Diene Disappearance Yields. The G values for all products formed from 1,3-cyclohexadiene at 0.21 M in benzene requires a G(-diene) of 13.7. Actual measurement gave a value of 18.4. Thus a G of 4.4 is not accounted for in our analysis. This may be polymer which is observed but cannot be measured quantitatively.

CONCLUSIONS

The gamma radiolysis of 1,3-cyclohexadiene involves cationic and triplet reactions to form dimers and a singlet reaction to produce 1,3,5-hexatriene. The neat solution provides a favorable opportunity to observe the formation of triplet excited states from ions. The same quenching experiments that demonstrate this also indicate that the singlets are not produced in a parallel reaction.

In benzene solution the same products are observed. The results are complicated by solvent effects and chain reactions leading to thermal dimers. At 0.21 M diene energy transfer from benzene — triplet, singlet, and ionic—occurs and little or no formation of excited states from diene ions is involved. The G value for benzene triplets at this concentration of diene agrees moderately well with the value found by pulse radiolysis. At higher diene concentrations reactions such as scavenging of ionic benzene triplet precursors and the formation of diene triplets from diene ions make the results impossible to interpret quantitatively.

The sensitization of the singlet excited state reaction of 1,3-cyclohexadiene by benzene indicates that benzene energy levels higher than the first singlet may be populated by ionizing radiation with a G of 1.

EXPERIMENTAL

Materials.

Benzene was zone-refined (99.99%), obtained from J. Hinton and used as received.

Pyridine was reagent grade and was distilled from sodium hydroxide prior to use.

1,3-Cyclohexadiene was obtained from Aldrich Chemicals. For the experiments involving dimer yields it was purified by distillation from lithium aluminum hydride under a nitrogen atmosphere. The purified diene was degassed and stored at $< 0°C$. The major impurities were cyclohexene (3-4%), benzene (1%) and 1,4-cyclohexadiene (0.3%). Experiments involving yields of C_6 compounds were performed using 1,3-cyclohexadiene which was purified by preparative vpc on a 3/8" x 6' β,β'-oxydipropionitrile column prior to distillation from lithium aluminum hydride. Subsequent to this purification impurity composition was 0.1% cyclohexene, 0.04% benzene and 0.004%-undetectable for 1,4-cyclohexadiene. Since this last compound had the same retention time as cis-1,3,5-hexatriene on the analytical column used, a correction blank was run on each batch of purified 1,3-cyclohexadiene used in triene measurements.

2-Propanol (Matheson, Coleman, and Bell, spectro quality) and carbon tetrachloride (Baker, reagent) were used without purifi-

cation.

m-Dinitrobenzene (Matheson, Coleman, and Bell) was recrystallized from benzene and sublimed.

Benzophenone (Matheson, Coleman, and Bell) was recrystallized from ligroin.

Xanthone (Matheson, Coleman, and Bell) was recrystallized from benzene.

Thermal and photo dimers were prepared as has been previously described (22) and were used for vpc identification and calibration.

1,3,5-Hexatriene, in an isomeric mixture, was prepared by the method of Hwa (64). Isolation of the trans isomer was achieved by treatment of the mixture with a catalytic amount of I_2 which isomerized the cis isomer. This was followed by purification of the trans isomer by preparative vpc on a 3/8" x 6' β,β'-dipropionitrile column. The cis isomer was isolated by treatment of the isomer mixture with maleic anhydride which reacts with the trans-triene. Both isomers were bulb-to-bulb distilled from $LiAlH_4$ under vacuum. They were each >95% pure and exhibited infrared and ultraviolet absorption spectra identical to those in the literature (64).

Irradiations.

The γ irradiations were carried out with a ^{60}Co source. The solutions to be irradiated were degassed by freeze-pump-thaw cycles to a pressure of $<5\times10^{-4}$ mm mercury and sealed in 13 x 100 mm pyrex tubes. The tubes were placed upright around the inside walls of a 400-ml beaker which was lowered into the radiation source.

Dosimetry of the source was carried out by standard Fricke dosimetry (65), using $G(Fe^{+++}) = 15.5$.

The dose rate into solutions other than water is calculated from the electron densities of the solution components. Details of the procedure for calculating these dose rates are given in the Appendix.

Alpha irradiation was carried out with a source consisting of 100 millicuries of ^{210}Po obtained from Nuclear Chicago Corporation. The polonium was electrodeposited onto a steel disk and had a thin mica window sealed over the face. The irradiation cell (Figure 12) was made of pyrex with a 6×10^{-3} mm thick aluminum window cemented over an opening in one side. The window of the α source faced this at a distance of ca. 2mm during the irradiation. Solutions were not degassed in this cell. Nitrogen was bubbled through the 1,3-cyclohexadiene to be irradiated for approximately 30 minutes. The cell was filled with this solution under a nitrogen atmosphere in a glove bag. The dose rate was not measured under these irradiation conditions but was found to be $\sim 10^{19}$ ev hr^{-1} into an aqueous solution of Fe^{++} whose surface was directly exposed to the source at a distance of 2 mm.

Ultraviolet irradiations at 2537Å, 3130Å, and 3660Å were each carried out in a "merry-go-round" apparatus. This, as well as the lamps and wavelength isolation filters used have been described elsewhere (66). Unless otherwise stated triplet sensitizer reactions were carried out with benzophenone using 3660Å light. The main exception was the use of xanthone in investigating the

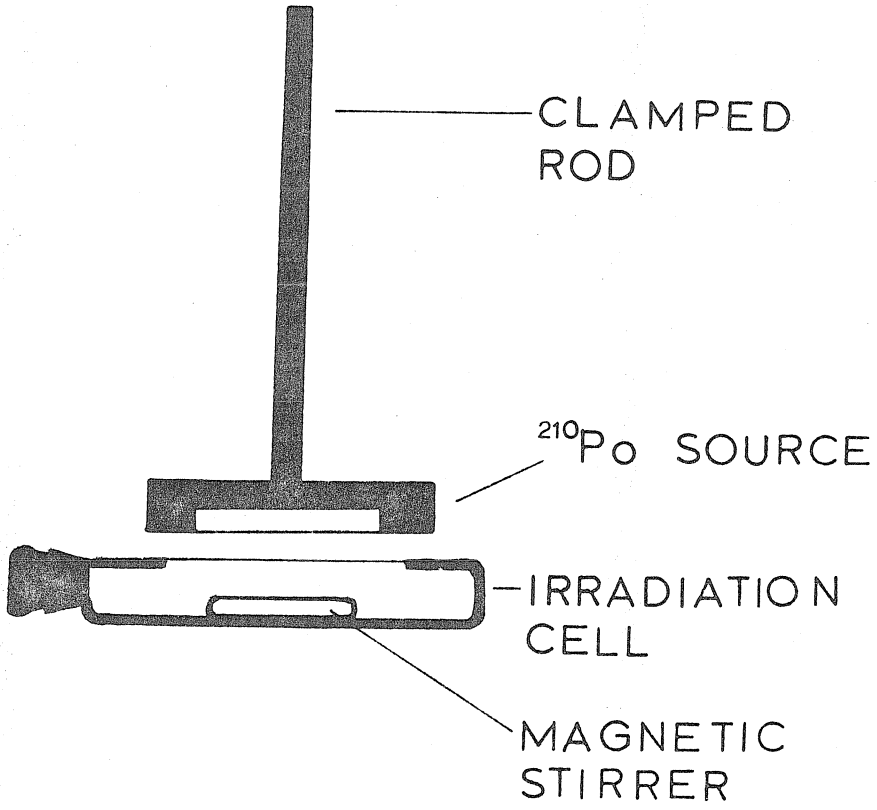

Figure 12. Alpha Irradiation Source and Cell.

quenching of 1,3-cyclohexadiene triplets by m-dinitrobenzene. In this case 3130Å light was used. All sensitized irradiation solutions contained sufficient sensitizer to absorb >99% of the incident light.

Actinometry was carried out using the potassium ferrioxalate procedure standard in this laboratory and which has been described (23).

Analysis.

All product analysis was carried out on a Loenco Model 70 Hiflex vapor phase chromatograph with dual flame ionization detectors. Analysis for total diene dimer yields was performed on a 1/4" x 6' 10% fluorosilicone column using n-hexadecane as an internal standard. Although the dimers were analyzed as a single peak, care was taken to determine that the calibration of the internal standard was independent of the distribution of the dimers among the four isomers present. The individual dimers were separated on a 150-foot capillary column coated with Apiezon-L. This column was also occasionally used to measure absolute dimer yields. In this case n-dodecane was the internal standard. The results obtained were identical to those found with the fluorosilicone column.

Analysis for 1,3,5-hexatriene was performed on a 1/8" x 5' column of 20% dimethylsulfolane. Cyclohexane was used as the internal standard.

In the case of γ irradiated solutions all internal standards were added after irradiation.

The ion cyclotron resonance experiments were run by Professor J. L. Beauchamp of the California Institute of Technology.

The theory and practical aspects of this technique are described in the literature (36).

Product Identification.

The four dimers of 1,3-cyclohexadiene were identified by retention time comparisons with those produced by thermal and triplet photosensitized reactions on capillary, dimethylsulfolane, and β,β'-oxydipropionitrile vpc columns. The latter two columns only gave partial separation.

The isomers of 1,3,5-hexatriene were isolated from samples of 1,3-cyclohexadiene which had been purified by preparative vpc and irradiated with a dose of 10^{21} ev ml^{-1}. Isolation was achieved with a β,β'-oxydipropionitrile preparative column. Sufficient amounts of the trans isomer were isolated to obtain a uv spectrum and a 220 Hz nuclear magnetic resonance (nmr) spectrum. These agreed with the spectra obtained from an authentic sample of the trans-triene. The uv spectrum of the cis-1,3,5-hexatriene also agreed with that of a known sample of this isomer. The amount of this isomer isolated from the γ radiolysis was insufficient to obtain an nmr spectrum. It was, however, possible to observe this compound isomerize to the trans triene under I_2 catalysis. This reaction had previously been reported by Hwa et al. (64). These spectra, the isomerization reaction, and correspondence of vpc retention times on β,β'-oxydipropionitrile and dimethylsulfolane columns provide evidence of the identity of the cis and trans 1,3,5-hexatrienes.

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PART III

THE RADIATION INDUCED ISOMERIZATION OF 1,2-DIPHENYLPROPENE IN CYCLOHEXANE

INTRODUCTION

The isomerization of mono-olefins in organic solutions has been by far the most extensively studied "photochemical" solute reaction induced by γ radiation. One of the earliest of these investigations was carried out by Cundall and Griffiths who, in a series of papers (1-4), reported the cis-trans isomerization of 2-butene in benzene solution. They attributed the reaction to solute triplet states formed by energy transfer from benzene triplets. On the basis of an energy transfer scheme in which reactions [4] and [5] were responsible for the actual isomerization, they concluded that $G_{c,t} + G_{t,c} = G$ (triplet) was 4.2. $G_{c,t}$ and $G_{t,c}$ are the G values for cis → trans and trans → cis isomerization respectively.

$$B \rightsquigarrow B^3 \qquad [1]$$

$$B^3 + c\text{-}S \rightarrow B + S^3 \qquad [2]$$

$$B^3 + t\text{-}S \rightarrow B + S^3 \qquad [3]$$

$$S^3 \rightarrow c\text{-}S \qquad [4]$$

$$S^3 \rightarrow t\text{-}S \qquad [5]$$

B represents solvent, c - S and t - S are the cis and trans isomers of the solute, and B^3 and S^3 refer to solvent and solute triplet states respectively.

The value of G(triplet) was later revised to 4.7 (5), and an estimation was made, based on N_2O electron scavenging, that approxi-

mately 40% of these benzene triplets were formed by ion neutralization. Isomerization reactions involving solute ions were discounted.

A number of other investigations involving such isomerization reactions have also been made. Golub et al. (6) used the solutes cis-2-pentene, cis-2-hexene, cis-2-heptene, cis-2-octene and trans-2-octene and found that they all followed the same curve for G(isomerization) versus olefinconcentration in benzene. The G value for benzene triplets obtained from the 2-octene isomerizations was ~ 5.

Lehman, Stein, and Fischer (7) first reported the use of cis and trans-stilbene (1,2-diphenylethene) as isomerization solutes in γ irradiated benzene. The photochemistry of these solutes has been extensively studied (8-11). Although not all the details of the photochemical isomerization have been completely clarified, initial isomerization quantum yields, steady state isomer ratios, and the character of the triplet isomerization are sufficiently well known to allow the use of the reaction as a solvent triplet counter in high energy irradiations. It is generally agreed among the authors who have investigated this reaction that at concentrations < 0.05 M stilbene, the radiation induced isomerization of both cis and trans isomers is a result of triplet energy transfer from benzene. This conclusion is reached on the basis of the similarity of the cis:trans ratio of the γ radiation stationary state to that of the high energy triplet sensitized stationary state (12,13) or the correlation of $G_{c,t}/G_{t,c}$ with the sensitized quantum yield ratio $\phi_{c,t}/\phi_{t,c}$ (14). Both these equalities hold for a mechanism such as that of reactions [1] - [5] provided that energy transfer from benzene is the same

for both isomers, that is $k_2 = k_3$.

At higher stilbene concentrations discrepancies arise. Because of the short lifetime of benzene triplets (15), >0.1 M stilbene is required to scavenge 90% of these triplets. But the use of concentrations in this range has led to different observations and interpretations. The results of three groups, Fischer, Lehman, and Stein (12), Hammond and co-workers (13), and Burton's group (14) are given in Figure 1. The results of all three for $G_{t,c}$ are fairly close up to 0.05-0.1 M but deviate fairly strongly at higher concentrations. The results for $G_{c,t}$ of the latter two groups also deviate considerably, beginning at quite low concentrations.

Hammond et al. attributed the failure of $G_{c,t}$ to level off and its quite sharp increase beyond ca. 0.6 M to the scavenging of benzene triplet precursors and of triplets which decay within spurs at lower solute concentrations (16). Fischer et al. (12) observed an increase in $G_{t,c}$ at >0.1 M stilbene (not shown in Figure 1) which they believed to be due to the scavenging of ionic and short-lived excited benzene molecules. They have indicated that as little as 30-40% of the trans→cis isomerization observed at high concentration may be due to scavenging of actual benzene triplets (12,17). Burton's results (14) showed $G_{c,t}$ as reaching a plateau at 0.05 M stilbene and only $G_{c,t}$ continuing to increase. Since the cis isomer is thermodynamically less stable than the trans, they proposed that a ground state chain reaction took place in cis → trans isomerization above this concentration. They suggested an anionic chain although they pointed out that a cationic mechanism would also fulfill the requirements.

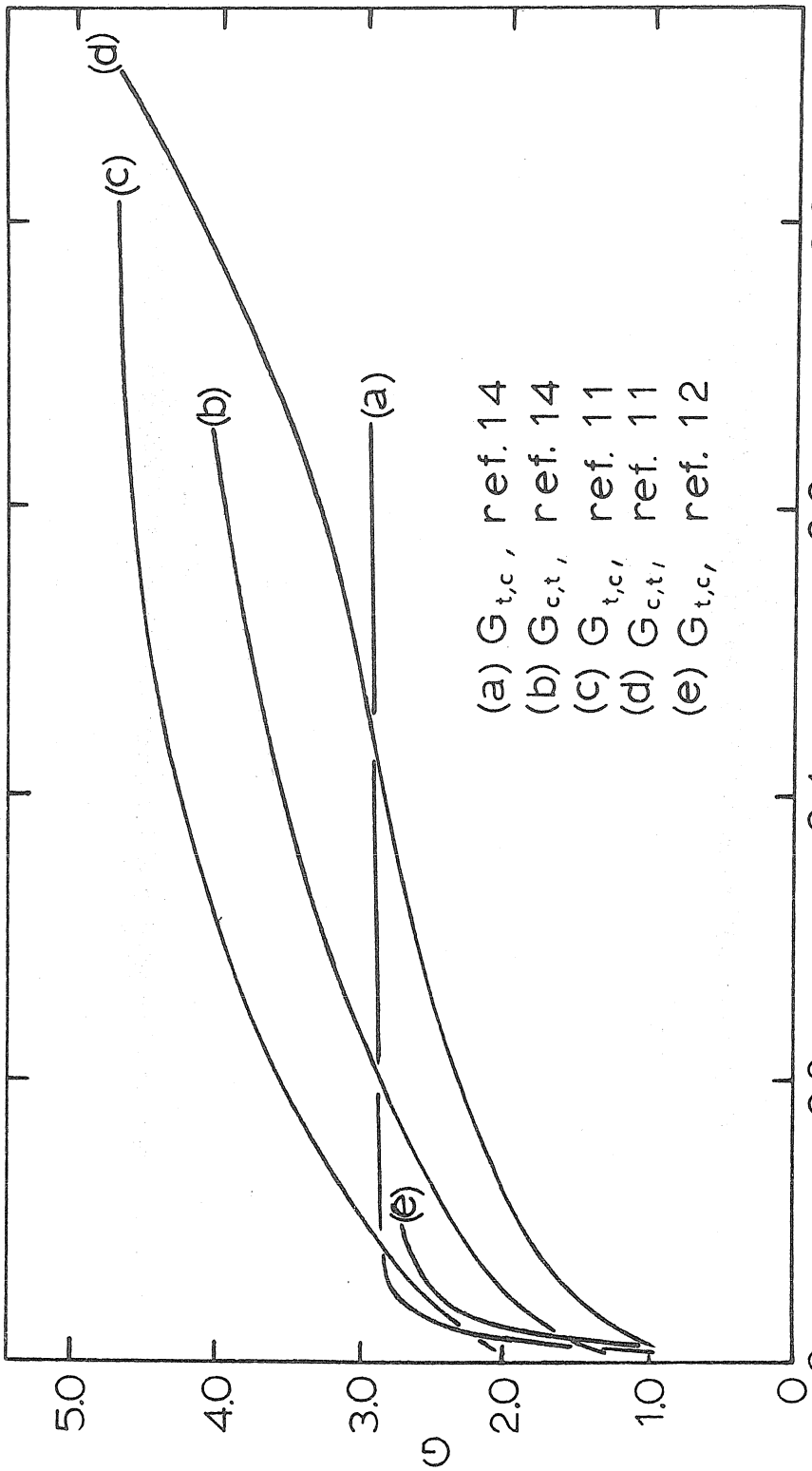

Figure 1. Literature G Values for Stilbene Isomerization by Gamma Radiation.

$$e^- + c\text{-}S \rightarrow t\text{-}S^- \qquad [6]$$

$$c\text{-}S + t\text{-}S^- \rightarrow t\text{-}S^- + t\text{-}S \qquad [7]$$

According to this mechanism reactions [6] and [7] are unimportant below 0.05 M stilbene.

Figure 1 shows that the different quenching mechanisms at high solute concentration are not only the results of different interpretations but are based on different experimental results obtained by the two groups for the same conditions. Burton's introduction of a cis → trans chain was based on $G_{t,c}$ reaching a plateau but a continuing increase in $G_{c,t}$; (e.g., $G_{c,t}/G_{t,c}$ is 0.87 at 0.1 M and 1.11 at 0.3 M). The results of Caldwell, Whitten, and Hammond give a value for $G_{c,t}/G_{t,c}$ which remains between 0.6 and 0.7 from 0.03 to 0.6 M stilbene. The most recent value for $\phi_{c,t}/\phi_{t,c}$ is 0.73-0.76 (11). These authors also investigated the isomerization of 1,2-diphenylpropene by γ radiation in benzene and observed that $G_{c,t}/G_{t,c}$ was essentially equal to $\phi_{c,t}/\phi_{t,c}$ for this compound up to 1 M. These results would argue against any chain isomerization within the concentration ranges for which this equality holds.

The situation is somewhat complicated by the fact that Burton's group has demonstrated that chain isomerization of cis-stilbene does occur, at least under conditions of low dose and high concentration (18). Using 0.5 M cis-stilbene and radiation doses between 2×10^{18} ev ml^{-1} and 7×10^{19} ev ml^{-1} they observed values of $G_{c,t}$ as high as 200 at the lowest doses. The chain reaction is rapidly attenuated with increasing dose but the authors contend that it

probably occurs to a sufficient extent at the radiation doses used in their earlier work (14) to make $G_{c,t}$ anomolously high.

This earlier paper also describes the isomerization of stilbene in cyclohexane. Here they found that $G_{t,c}$ reached a plateau at ~ 0.06 M whereas $G_{c,t}$ did not, continuing to increase with concentration up to the highest stilbene concentration used, 0.2 M. $G_{c,t}/G_{t,c}$ was always greater than 1 and exceeded the value of that ratio at the corresponding concentration in benzene. This was interpreted as an even greater contribution to ionic chain isomerization by cis-stilbene in cyclohexane than in benzene.

The trans → cis isomerization in the aliphatic solvent was attributed to the formation of triplets by neutralization of solute ions. This is probably a reasonable mechanism for the production of solute excited states in solvents which themselves have no stable excited electronic energy levels and is a generally accepted mechanism. The triplets of naphthalene, anthracene (19,20), and biphenyl (21) have been observed in this solvent by pulse radiolysis. The contention that these arise by solute ion recombination was strengthened by the correlation of the decay rate of the biphenyl anion absorption spectrum with the growth of the biphenyl triplet spectrum (21). This mechanism for the production of solute excited states in alkane solutions is supported by scintillation studies. Electron scavengers reduce the yields of scintillator excited states in a manner consistent with the role of ionic precursors to the excited states (22). On the basis of the measured rates of energy transfer to scintillators in cyclohexane (rate constant $> 10^{12}$) it has been concluded (23) that

diffusion controlled energy transfer such as excitation transfer from the solvent is not involved. The alternative of charge transfer, migrating via highly mobile electrons or perhaps positive holes, is not ruled out by these high rate constants.

In view of the somewhat conflicting results which have been obtained in benzene solution it appeared to be of interest to conduct further experiments in cyclohexane solution which could be compared with those of Burton et al. Rather than a direct data comparison using the same compound, stilbene, it was decided to carry out this work using the isomers of 1,2-diphenylpropene. The results obtained with this compound in benzene by Hammond (13) were very similar to those found for stilbene. $G_{c,t} + G_{t,c}$ fell on the same curve and $G_{c,t}/G_{t,c}$ was within experimental error equal to $\phi_{c,t}/\phi_{t,c}$, which for this compound is 0.81. Further it is a cleaner system both photochemically and radiation chemically. It does not undergo side reactions and did not exhibit the concentration dependence of $\phi_{t,c}$ that stilbene appeared to (recently shown not to be real (11)). Thus, making allowances for different quantum yields, 1,2-diphenylpropene can be compared with stilbene.

The possibility of a chain isomerization for cis-1,2-diphenylpropene at low doses was also examined. This included the questions of the species responsible for it and whether such a reaction is still operative at the doses used in the majority of isomerization reactions.

EXPERIMENTAL RESULTS

The values for $G_{c,t}$, $G_{t,c}$, and G(total) = $G_{c,t} + G_{t,c}$ are given in Table 1. Figure 2 also gives $G_{c,t}$ and $G_{t,c}$ derived from Burton's stilbene results. Table 1 also lists $G_{c,t}/G_{t,c}$. All results are the average of duplicate samples.

Figure 3 gives $G_{c,t}$ and $G_{t,c}$ as a function of the radiation dose. The dose dependence of $G_{c,t}$ is given for two independently determined sets of samples. The only difference between them is in the history of the solvent. The determinations which gave the consistently higher yields at low doses (set 1) were made using cyclohexane which, in addition to purification, had been distilled from phosphorous pentoxide immediately prior to use. The other set of results (set 2) was obtained with solvent which had been stored in a flask (opened intermittantly) for several days after distillation from phosphorous pentoxide. In addition to the discrepancy between these sets the duplicate determinations measured in each set exhibited disagreements of about 10%, twice that expected from analytical errors.

Quencher effects on isomerization G values were determined under two different circumstances. In one case a solute concentration of 0.045 M 1,2-diphenylpropene and a radiation dose of 2×10^{20} ev ml^{-1} were used. The effect of carbon tetrachloride, a frequently used electron scavenger (24,25), and methanol which, like other alcohols (26) should be a good cation quencher, on $G_{c,t}$ and $G_{t,c}$ are

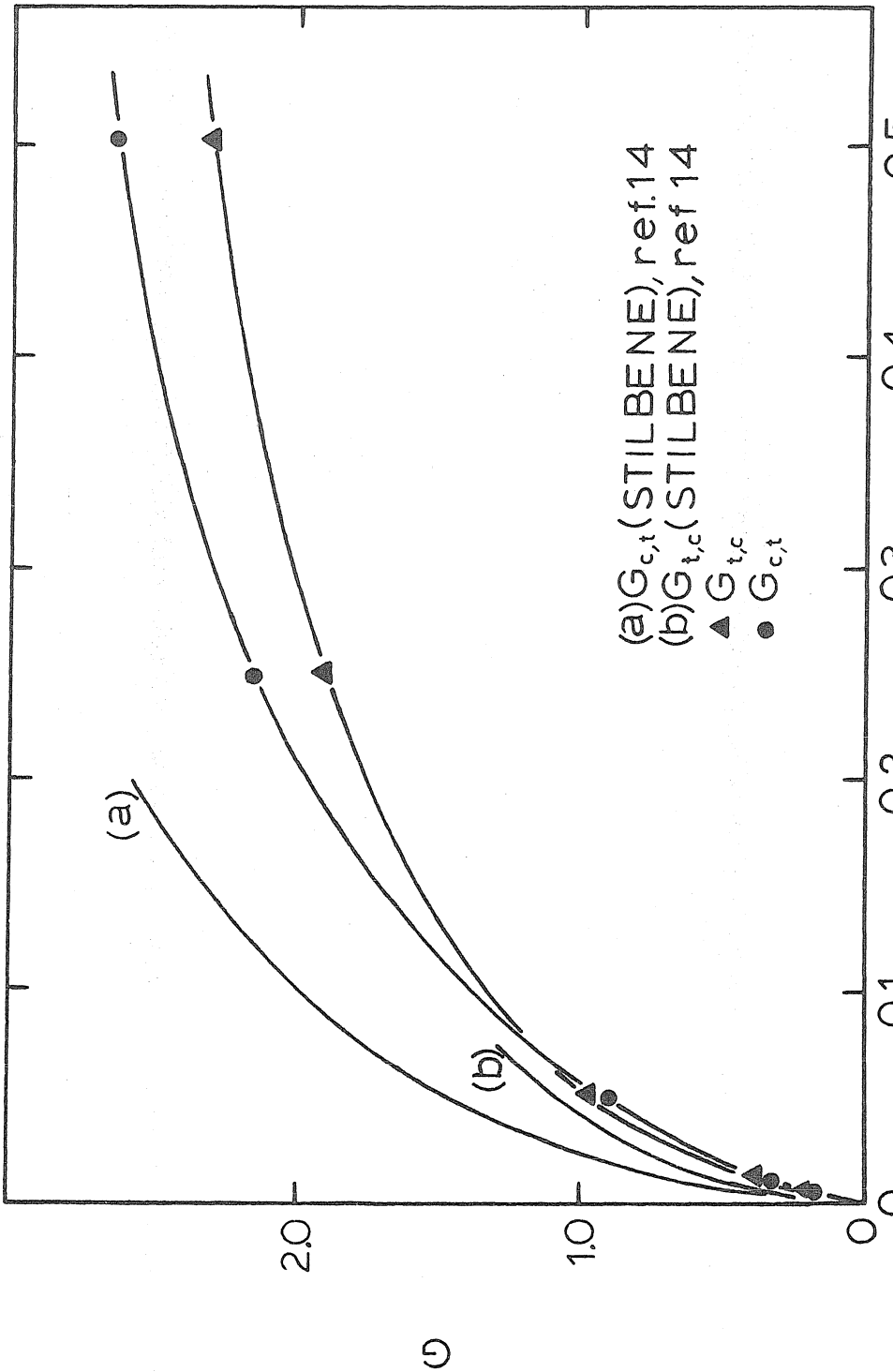

Figure 2. The Variation of $G_{c,t}$ and $G_{t,c}$ with the Concentration of 1,2-Diphenylpropene in Cyclohexane.

Table 1. The Variation of $G_{c,t}$, $G_{t,c}$, and G (total) with the Concentration of 1,2-Diphenylpropene in Cyclohexane. Radiation Dose = 2.5×10^{20} ev ml^{-1}. Data for Figure 2.

Conc. 1,2-Diphenylpropene,(M)	$G_{c,t}$	$G_{t,c}$	G(total)	$G_{c,t}/G_{t,c}$
0.005	0.18	0.22	0.40	0.82
0.010	0.33	0.36	0.69	0.92
0.050	0.90	0.97	1.87	0.93
0.251	2.15	1.92	4.07	1.12
0.502	2.64	2.30	4.94	1.15

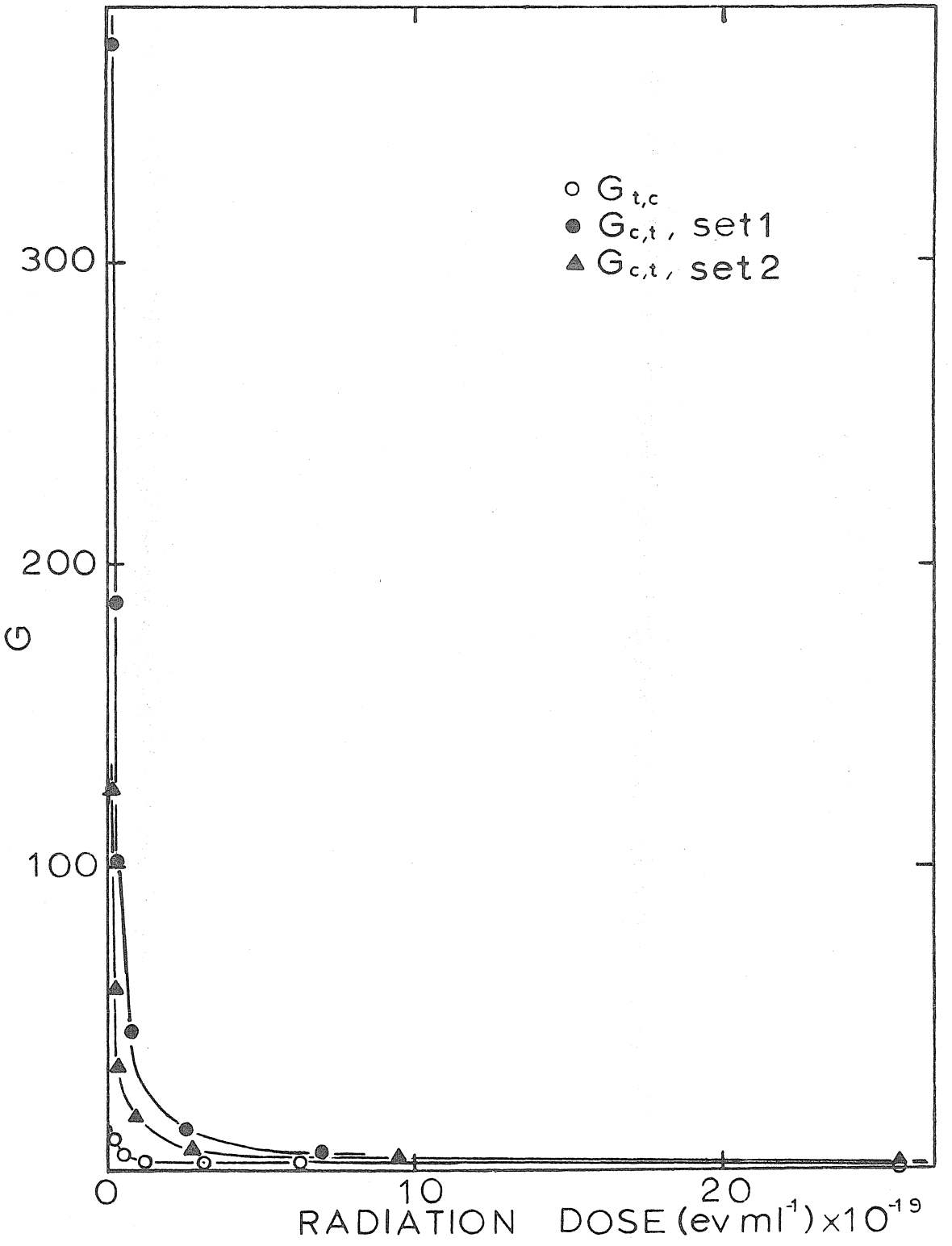

Figure 3. $G_{c,t}$ and $G_{t,c}$ as a Function of Radiation Dose for 0.5M 1,2-Diphenylpropene.

Table 2. $G_{c,t}$ and $G_{t,c}$ as a Function of Radiation Dose for 0.5M 1,2-Diphenylpropene. Data for Figure 3.

Radiation Dose (ev ml^{-1}) x 10^{-19}	$G_{t,c}$	$G_{c,t}$	
		Set 1	Set 2
0.12		372	127
0.23	10.0	188	59
0.35		103	37.2
0.52	5.3		
0.86		45.8	17.1
1.23	3.4		
2.60		13.9	7.8
3.10	2.6		
6.20	2.5		
6.92		6.8	
9.50			3.8
25.68	2.3		2.6

given in Table 3. Table 4 indicates the effect of these additives on $G_{c,t}$ at 0.5 M cis-1,2-diphenylpropene at low radiation dose. Set 1 and Set 2 refer to the two conditions of low dose G measurements mentioned previously where respectively freshly dried and stored cyclohexane were used.

The cis:trans ratio at the stationary state was determined. Since cyclohexane is decomposed by γ radiation more quickly than benzene it was not possible to irradiate pure isomer solutions long enough to have them reach equilibrium. Instead, a series of mixtures of different cis:trans ratios were prepared and after irradiation analyzed for the direction of change in composition to higher or lower percentage cis. Then solutions near the stationary state could be prepared and irradiated until no change was observed. This was done, approaching the final composition from both greater and lower cis:trans values. The final composition obtained was 1.86 for $(\text{cis}/\text{trans})_s$. This was unchanged with doses between 6×10^{20} and 23×10^{20} ev ml^{-1}.

One of the advantages in using 1,2-diphenylpropene rather than stilbene in radiation studies in benzene was that the former did not undergo side reactions. This does not appear to be true in cyclohexane. Both cis and trans isomers have non-isomerization reactions. The G values for disappearance of these isomers were 1.6 for cis at 0.02 M and 1.7 for trans at 0.016 M. $G_{c,t}$ and $G_{t,c}$ are 0.63 and 0.54 at these respective concentrations. No products of significant yield which might correspond to C_{15} compounds were observed in vapor phase chromatography traces. Decomposition

Table 3. The Effect of Quenchers on $G_{c,t}$ and $G_{t,c}$ at 0.045 M 1,2-Diphenylpropene. Radiation Dose = 2×10^{20} ev ml^{-1}.

Quencher	Conc. Quencher, (M)	$G_{c,t}$	$G_{t,c}$
—	—	0.90	0.93
CCl_4	0.10		0.26
CCl_4	0.24	0.48	
CH_3OH	0.12	0.55	0.64

Table 4. The Effect of Quenchers on $G_{c,t}$ at 0.50 M 1,2-Diphenylpropene. Radiation Dose = 3.5×10^{18} ev ml^{-1}.

Quencher	Conc. Quencher, (M)	$G_{c,t}$ Set 1	$G_{c,t}$ Set 2
—	—	103	37
CCl_4	0.16	120	
CCl_4	0.10		55
CH_3OH	0.06		19

products might very well have escaped detection under the conditions used.

DISCUSSION

Isomerization Yields as a Function of Solute Concentration. The G values for trans → cis isomerization of 1,2-diphenylpropene are fairly similar to those found for stilbene by Burton (similarity of $\phi_{t,c}$ for the two compounds makes corrections on that basis minor). This is true up to 0.1 M, the highest concentration of trans-stilbene used by the other group. The values of $G_{c,t}$, however, are quite dissimilar even at low concentrations.

For 1,2-diphenylpropene Table 1 shows that $G_{c,t}/G_{t,c}$ is equal to $\phi_{c,t}/\phi_{t,c}$ (0.81) at the lowest concentration used, but shows increasing deviation at higher concentrations. This is in accord with a mechanism for decay of a common triplet of the alkene to cis and trans isomers in the photochemical ratio with an additional isomerization of the cis at higher concentrations as suggested by Burton (14). The onset and extent of this additional reaction appear less pronounced than was indicated by stilbene but as will be seen conditions such as total radiation dose may account for that. As indicated by $G_{c,t}/G_{t,c}$, the presence of this additional reaction of cis-1,2-diphenylpropene is still quite small up to 0.05M. This is in agreement with the measurement of the stationary state composition of the γ irradiated diphenylpropenes which was carried out out at 0.05 M and doses comparable to those used in Table 1. Since this composition favors the cis isomer, a thermodynamically controlled chain reaction, which as will be seen is the most probable

additional cis → trans isomerization, cannot have a very important contribution under these conditions.

Dose Effect on G Values. The variation of $G_{c,t}$ with the radiation dose provides evidence that the reaction which increases $G_{c,t}/G_{t,c}$ above the value expected from photochemical observations is due to a chain isomerization. $G_{t,c}$ exhibits a small dose effect but $G_{c,t}$ becomes very large at low doses, requiring a chain reaction. The sensitivity of the G values to the time elapsed between final drying of the cyclohexane and its use indicates that water may act as a powerful quencher of this chain isomerization.

As the dose is increased, $G_{c,t}$ is attenuated very rapidly. As a matter of fact, examination of the molecular conversion rather than G values as a function of dose indicates that the chain isomerization is completely quenched at the lowest dose used. Thus in Set 2 the total molecular conversion at 2.4×10^{18}, 3.6×10^{18}, and 9×10^{18} ev ml^{-1} is the same as at 1.2×10^{18} ev ml^{-1}, within an experimental error of about 10%. At longer irradiation times there is an increase in the molecular yield of isomerization. This is presumably due to non-chain isomerization which does not appear at the shorter irradiation times due to its low G values. If the initial low-dose molecular conversion is subtracted from the total conversion at irradiation doses $> 10^{19}$ ev ml^{-1}, where the difference exceeds 10-15% of the initial yield, this difference gives an essentially constant $\Delta G_{c,t}$ of 2.2. Since, as already observed, there is a variation in $G_{c,t}$ at low dose depending on the solvent

treatment it is necessary to use the initial chain conversion within a given set to calculate $\Delta G_{c,t}$ at higher doses in the same set. Thus the $\Delta G_{c,t}$ value in Table 5 for a dose of 2.5×10^{20} ev ml^{-1} was calculated from a set in which the initial chain conversion was 2.89×10^{18} molecules/ml while the other values were obtained from another set of determinations for which the initial chain conversion was 1.45×10^{18} molecules/ml. The values for percent chain reaction were obtained by dividing the initial low-dose isomerization yield by the total conversion at any given dose. In the case of values indicated as ~100% chain isomerization the total conversion did not differ from the initial value by more than ±10-15% and was therefore indistinguishable from it within experimental error.

As can be seen in Table 5, at a radiation dose of 2.6×10^{20} ev ml^{-1}, which is the dose used to obtain the results in Figure 1, approximately 11% of $G_{c,t}$ at 0.5 M is due to early chain isomerization. The value of $\Delta G_{c,t}/G_{t,c}$ is now 0.91, not quite the value of 0.81 expected for triplet isomerization, but not greatly different. The isomerization of cis-1,2-diphenylpropene thus consists of an initial chain reaction which is rapidly quenched by radiation-produced scavengers plus an independent isomerization with a relatively low yield (G = 2.2) so that it does not become evident until a considerable dose has been absorbed. At lower solute concentrations the contribution of the chain isomerization would be less important.

Scavenger Effects at High Dose. Under conditions of high radiation dose (2×10^{20} ev ml^{-1}) and low solute concentration (0.045 M) where the chain isomerization discussed above will be minimal, both cation

Table 5. Residual Non-chain $\Delta G_{c,t}$ Values and the Percent Chain Isomerization of 0.5 M cis-1,2-Diphenylpropene as a Function of Radiation Dose.

Radiation Dose (ev ml^{-1})x 10^{19}	Isomerization (molecules/mlx10^{18})	$\Delta G_{c,t}$	Percent Chain
0.12	1.45	-	~100
0.23	1.35	-	~100
0.35	1.24	-	~100
0.86	1.47	-	~100
2.6	2.01	2.2[a]	73
9.5	3.58	2.2[a]	41
25.4	6.80	2.1[b]	11

a. Calculated using 1.45×10^{18} molecules/ml as the initial chain isomerization yield.

b. Calculated using 2.89×10^{18} molecules/ml as the initial chain isomerization yield.

and electron scavengers decrease $G_{c,t}$ and $G_{t,c}$. This is consistent with the participation of both positively and negatively charged species in the isomerization of 1,2-diphenylpropene. These results agree with the current concept of the formation of solute excited states in saturated aliphatic solvents as discussed in the Introduction. Burton (14) also observed a quenching effect on $G_{t,c}$ induced by CCl_4 in stilbene solutions.

Scavenger Effects at Low Doses. At a concentration of 0.5 M cis-1,2-diphenylpropene and a radiation dose of 3.5×10^{18} ev ml^{-1} the effect of methanol is still to quench isomerization; but now CCl_4 enhances it. Under these conditions the chain isomerization makes the major contribution to $G_{c,t}$ so that it appears that cations are involved in the chain propagation but electrons or anions are not. Rather these negatively charged species appear to be involved in chain termination.

A Possible Isomerization Mechanism. The preceding results can be incorporated into a mechanism which included solute triplet production by the process discussed in the Introduction, an isomerization process consistent with the $G_{c,t}/G_{t,c}$, and scavenger effects observed. B represents the solvent, cyclohexane.

$$B \rightsquigarrow B^+ + e^- \qquad [8]$$

$$B^+ + e^- + t\text{-}S \rightarrow B + S^3 \qquad [9]$$

$$B^+ + e^- \rightarrow B \qquad [10]$$

$$S^3 \rightarrow c\text{-}S \qquad [11]$$

$$S^3 \rightarrow t\text{-}S \qquad [12]$$

Reaction [9] included processes such as:

$$B^+ + t\text{-}S \rightarrow B + t\text{-}S^+ \qquad [9a]$$

$$t\text{-}S^+ + e^- \rightarrow S^3 \qquad [9b]$$

$$t\text{-}S + e^- \rightarrow t\text{-}S^- \qquad [9c]$$

$$B^+ + t\text{-}S^- \rightarrow B + S^3 \qquad [9d]$$

$$t\text{-}S^+ + t\text{-}S^- \rightarrow t\text{-}S + t\text{-}S^3 \qquad [9e]$$

Reaction 10, charge neutralization without solute triplet formation, could involve some or all of the same reactions as [9a]-[9e], only with the production of ground state solute molecules.

It is difficult to estimate the relative importance of the reactions [9a]-[9e]. There must be an appreciable contribution from [9b] relative to [9e] since electron scavenging occurs primarily as a result of decreased negative charge mobility (27). Thus, if the negative charge involved mainly $t\text{-}S^-$ little change in this mobility would occur as a result of negative charge transfer to CCl_4.

The analogous reactions could occur for cis-1,2-diphenylpropene although, except for reactions [11] and [12], the rate constants need not be the same. In addition, at high concentration and low dose the cis-1,2-diphenylpropene can undergo a cationic chain reaction such as the following:

$$c\text{-}S^+ \rightarrow t\text{-}S^+ \qquad [13]$$

$$t\text{-}S^+ + c\text{-}S \rightarrow t\text{-}S + c\text{-}S^+ \qquad [14]$$

Under the conditions of little or no chain isomerization, the mechanism [8]-[12] accounts for the observed equality of $G_{c,t}/G_{t,c}$

and $\phi_{c,t}/\phi_{t,c}\left(= k_{12}/k_{11}\right)$ if k_9/k_{10} is the same for both isomers. This can be seen from the expression for the G values:

$$\frac{1}{G_{c,t}} = \frac{1}{G_+\phi_{c,t}} \left(1 + \frac{k_{10}\,t}{k_{9t}\,[t - S]}\right) \qquad [15]$$

$$\frac{1}{G_{t,c}} = \frac{1}{G_+\phi_{t,c}} \left(1 + \frac{k_{10c}}{k_{9c}\,[c - S]}\right) \qquad [16]$$

The numerical subscripts of the constants refer to the reaction number. The letter subscripts c and t refer to cis and trans isomers. For $[c - S] = [t - S] \equiv [S]$,

$$\frac{G_{c,t}}{G_{t,c}} = \frac{\phi_{c,t}}{\phi_{t,c}} \qquad \frac{\left(1 + \dfrac{k_{10t}}{k_{9t}\,[S]}\right)}{\left(1 + \dfrac{k_{10c}}{k_{9c}\,[S]}\right)} \qquad [17]$$

which requires $\dfrac{k_{10t}}{k_{9t}} = \dfrac{k_{10c}}{k_{9c}}$ to give $G_{c,t}/G_{t,c} = \phi_{c,t}/\phi_{t,c}$

Equations [15] and [16] predict a Stern-Volmer plot for the concentration dependence of isomerization G values. $G_{t,c}$ obeys a moderately good straight line for $1/G_{t,c}$ versus $1/[t\text{-}S]$ (Figure 4), with $k_{10t}/k_{9t} = 0.021$. The value of $G_+ = 4.4$ so that at the highest yield of 1,2-diphenylpropene triplets in cyclohexane is also 4.4. This agrees with pulse radiolysis results which have shown at least as high a yield of solute triplets in cyclohexane as in benzene (19). Although a Stern-Volmer plot is not possible for $G_{c,t}$, an estimation for G_+ may still be gained if it is assumed that $k_{10c}/k_{9c} = 0.021$. Then at 0.5 M cis-1,2-diphenylpropene $\dfrac{k_{10c}}{k_{9c}\,[c\text{-}S]} \ll 1$ and using

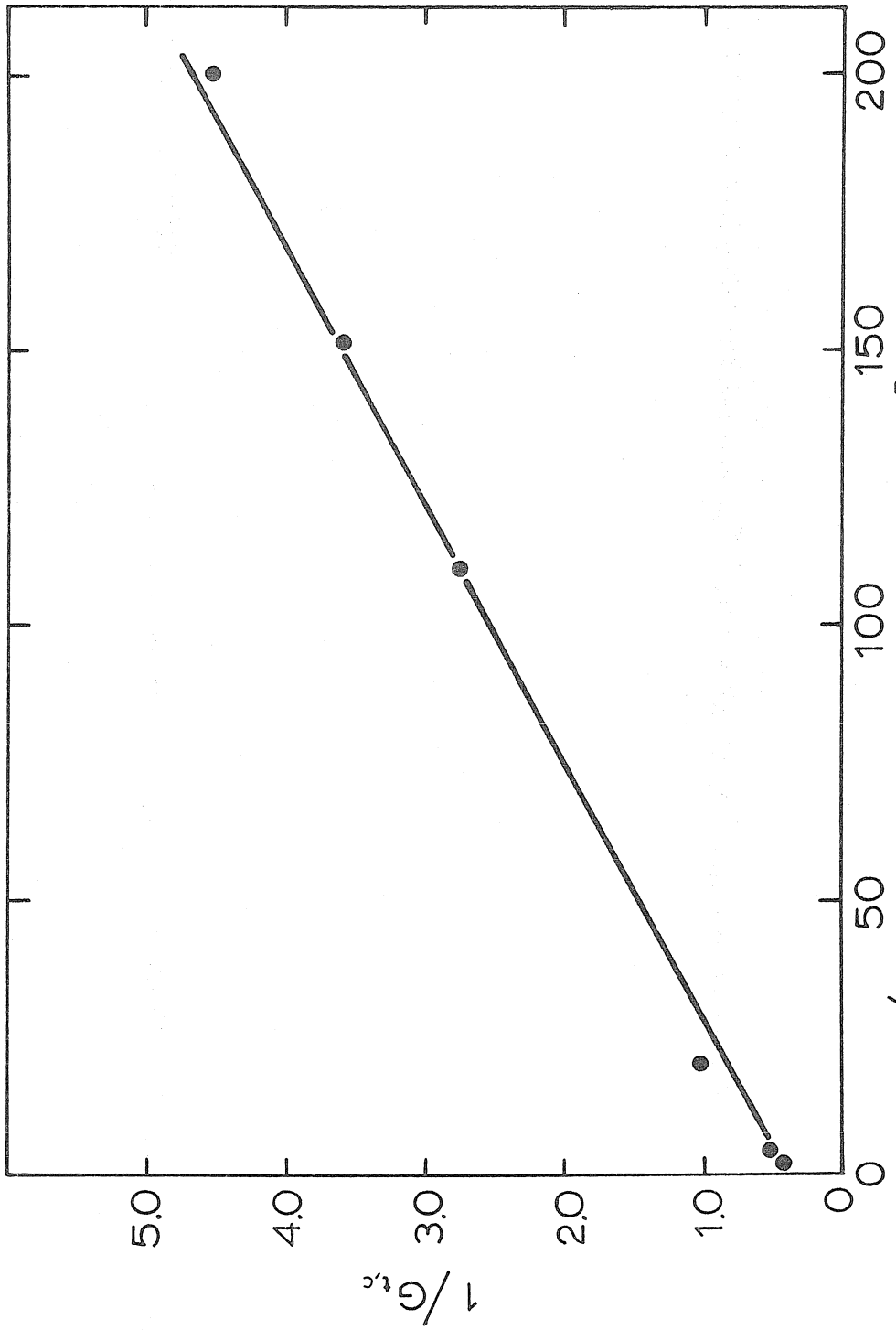

Figure 4. $1/G_{t,c}$ versus 1/Concentration for 1,2-Diphenylpropene in Cyclohexane.

$\Delta G_{c,t}$ as the non-chain isomerization, equation [15] gives $G_+ = 5.0$. The chain isomerization of cis-1,2-diphenylpropene makes a comparison of k_{10c}/k_{9c} with k_{10t}/k_{9t} impossible.

The non-chain mechanism gives an expression for the stationary state composition of:

$$\left(\frac{\text{cis}}{\text{trans}}\right)_s = \frac{k_{11}k_{9t}}{k_{12}k_{9c}} = \frac{\phi_{t,c}\, k_{9t}}{\phi_{c,t}\, k_{9c}} \qquad [18]$$

Since $\phi_{t,c}/\phi_{c,t} = 1.2$ and $(\underline{\text{cis}}/\underline{\text{trans}})_s = 1.8$, $k_{9t}/k_{9c} = 1.5$.

The mechanism can thus accomodate the observations provided suitable assumptions are made concerning the rate constants of the reactions. Of course, this does not prove the mechanism or provide insight into the details of reactions [9] and [10].

CONCLUSIONS

The isomerization of trans-1,2-diphenylpropene in cyclohexane and that of cis-1,2-diphenylpropene under conditions of low concentration and high radiation dose can adequately be described as proceeding through triplets generated by solute ion neutralization. The maximum G for these triplets is 4.4(5.0 based on the less reliable results of $\Delta G_{c,t}$). At low dose and high concentration cis-1,2-diphenylpropene undergoes a cationic chain isomerization which is rapidly quenched by radiation impurities.

The general mechanistic conclusions are similar to those of Burton et al. although the charge on the ion undergoing chain isomerization has been shown to be different. This chain reaction observed using 1,2-diphenylpropene is considerably less extensive than observed by these workers in stilbene. Thus $G_{c,t}/G_{t,c} = 1.1$ at 0.25M 1,2-diphenylpropene and 1.8 for 0.1 M stilbene. However, these authors did not report the dose they used so that they may have had a larger chain contribution because of a lower dose.

EXPERIMENTAL

Materials

Cyclohexane (Matheson, Coleman and Bell) was stirred for two months over batches of sulfuric acid which were frequently changed. The cyclohexane was washed with sodium carbonate solution, then with water, dried over magnesium sulfate, and distilled from phosphorous pentoxide through a one foot Vigreux column under a dry nitrogen atmosphere.

Methanol was Baker Reagent, used as received.

Carbon tetrachloride (Matheson, Coleman, and Bell) was used as received.

cis-1,2-Diphenylpropene was prepared from benzoin by a synthetic procedure described by Cram and co-workers (28,29). Purification was by preparative vapor phase chromatography on a 3/8" x 5' XE-60 cyanosilicone column, followed by sublimation. The trans impurity was $< 0.01\%$ but, in view of some of the low conversions used, correction based on quantitative analysis was applied.

trans-1,2-Diphenylpropene was synthesized and recrystallized by L. Altman. The cis impurity was $< 0.05\%$ and correction was applied to radiolysis conversion.

Analysis was carried out on a Loenco Model 70 Hiflex gas chromatograph with dual flame ionization detectors. The analytical columns used were 1/4" x 5' XE-60 cyanosilicone, which gave complete isomeric separation. Analysis was carried out at 190°C

at which temperature no thermal isomerization of cis-1,2-diphenylpropene was observed. The internal standard used for quantitative analysis was phenanthrene. It was added after irradiation.

γ Irradiations were carried out with a ^{60}Co gamma radiation source. Samples of 1-3ml were prepared, degassed to a pressure $< 5 \times 10^{-4}$ mm mercury, and sealed in 13mm diameter pyrex tubes. The radiation source dose rate was determined by standard Fricke dosimetry as described in the Appendix. The radiation dose into a given sample was determined from the electron densities of the components of the solution relative to that of water (see Appendix). This correction requires the densities of the isomers of 1,2-diphenylpropene in cyclohexane solution to be known. These were determined at a concentration of 0.5 M and the approximation was made that these densities do not change with concentration.

The sample tubes lowered into the radiation source were arranged upright around the inside edge of a 400-ml beaker.

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PART IV

APPENDIX

APPENDIX

The ^{60}Co Source Intensity and the Calculation of Dose Rates into Solutions.

Dosimetry on the ^{60}Co radiation source located at the Jet Propulsion Laboratory was carried out using the oxidation of Fe^{++} in aerated aqueous solution as a calibrated reaction (Fricke Dosimetry, $G(Fe^{+++}) = 15.5$). The procedure used is that given by Spinks and Woods (1). The dosimetry was carried out on October 23, 1968 when the dose rate into water was 6.87×10^{19} ev $ml^{-1}hr^{-1}$ and again on April 22, 1969 after the source intensity had been reduced by removal of cobalt rods. At this later time the dose rate was 4.35×10^{19} ev $ml^{-1}hr^{-1}$. For any other time the dose rate was calculated from these two measured values using the equation for the decay of natural radioactivity with time:

$$D_t = D_o e^{-\lambda t} \qquad [1]$$

D_t is the dose rate at time t, D_o is the dose rate at the time of measurement, t is the time elapsed since measurement of source intensity, and $\lambda = 0.693/\text{half life}$. The half life of ^{60}Co is 5.27 years. Prior to April 22, 1969, 6.87×10^{19} ev $ml^{-1}hr^{-1}$ was used for D_o; after that date 4.35×10^{19} ev $ml^{-1}hr^{-1}$ was used. In the former case t could be positive or negative depending on whether D_t was obtained after or before October 23, 1968.

The Fricke dosimetry, corrected for source decay, gives the dose rate into water. For the dose rate into other materials use

is made of the fact that the absorption of electromagnetic energy by Compton interaction is directly proportional to the electron density of the material. For a given compound A the electron density in electrons/cc is:

$$\text{Electron Density} = \frac{\rho_A}{M_A} \sum Z_A \qquad [2]$$

$\sum Z_A$ is the number of electrons in a molecule of A, M_A is the molecular weight, and ρ_A is the density of A in gm/cc. Then to convert the dose rate absorbed by water into that absorbed by A, the former is multiplied by the ratio of the electron density of A to the electron density of water:

$$D_A = \frac{\rho_A \; M_{H_2O} \sum Z_A}{\rho_{H_2O} \; M_A \sum Z_{H_2O}} \; D_{H_2O} \qquad [3]$$

If a solution has more than one component the concentration and density in solution of each component are used to calculate its volume. The dose absorbed by each compound is then the product of its volume, the dose rate for that component, and the time of irradiation. The total radiation dose is then the sum of the doses of all the solution components.

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PART V

PROPOSITIONS

PROPOSITION I

Abstract A flash photolysis apparatus capable of resolution on the picosecond time scale is described and proposed as a technique for the attempted study of the rate of internal conversion from higher singlet states to the first excited singlet (S_1) in aromatic hydrocarbons.

Subsequent to the introduction of Q-switched lasers with pulse rates on the order of nanoseconds, flash photolysis apparatuses have been constructed capable of time resolution down to 25 nsec (1-3). These have allowed the observation of processes of interest to photochemists such as $S_1 \rightarrow S_n$ absorption, $S_1 \rightarrow T_1$ intersystem crossing, and the fluorescence decay of short-lived singlets. Measurement of such processes is of immense value since phenomena and parameters previously available only indirectly or not at all can be studied directly.

Relatively recently (4) it has been observed that under certain conditions lasers can be mode-locked, a process which fixes the relative phases of the oscillating frequencies of the light in a laser pulse within the cavity. Interference occurs, resulting in a series of narrow pulses within the original pulse width. These are spaced 2L/c seconds apart, where L is the cavity length and c is the speed of light. This mode-locking condition is automatically achieved by including a dye cell in the laser cavity of the same type

used in Q-switching, provided that the dye has a relaxation time of less than 2L/c. Such a laser is simultaneously Q-switched and mode-locked (5). The result is a pulsed laser with pulses as narrow as 1 picosecond (1 psec = 10^{-12} seconds), pulse separation of afew nanoseconds, and power which can be > 10 billion watts per pulse.

The excitation light is thus available for flash photolysis on a picosecond time scale. There are considerable difficulties associated with time response on this order and no apparatus of this type has been constructed, although the potential of mode-locked lasers in this regard has been mentioned (6). It appears that such a device is possible and the existing methods and apparatus are sufficient to construct and use it within certain limitations.

Figure 1 indicates the general design of the apparatus. Existing ruby lasers with the proper Q-switch dye can give pulses of 5 psec at a wavelength of 6942 Å. A KDP doubling crystal is able to convert about 5% of this light into the harmonic at 3471 Å. With a large laser the individual pulses at the basic frequency can contain as much as 0.1 J energy (7). Only a fraction of the energy possessed by the 6942 Å analyzing beam is required so that a beam splitter (not shown) can be used to divert the majority away from the aligned path. The difference in the path length of the two beams determines the time delay between excitation and analysis. This time delay can be varied by adjusting the

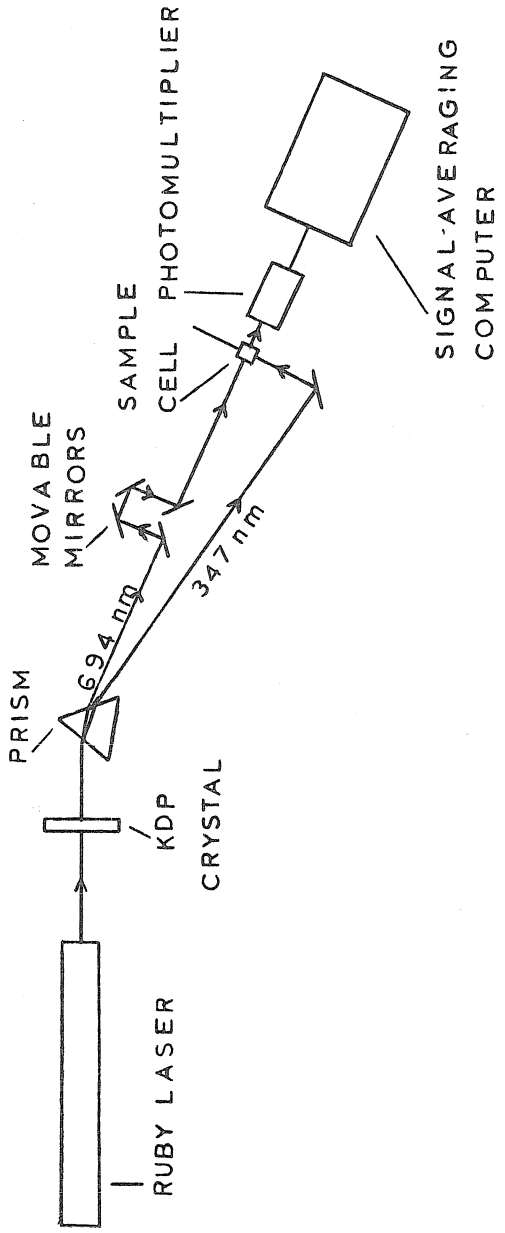
RUBY LASER
KDP CRYSTAL
PRISM
694 nm
347 nm
MOVABLE MIRRORS
SAMPLE CELL
PHOTOMULTIPLIER
SIGNAL-AVERAGING COMPUTER

FIGURE 1

position of the two 90° reflection mirrors fixed on a movable carriage. Small changes in path length are critical since light only travels 3 mm in 10 psec. Thus the delay system must be calibrated accurately. This can be accomplished by measurement of the interference pattern formed by split beams from a laser directed along the light paths.

The sample cell has 2 mm path lengths in both excitation and analysis directions and the excitation light is focused to this dimension. By making the analysis delay at least 10 psec, passage of the total excitation pulse through the solution prior to analysis is assured. Thus a lower limit of 10 psec is imposed on the resolution time.

The major limiting factor in the apparatus is the monochromatic analyzing light. Since the exciting and analyzing pulses must be so closely synchronized, a source of analyzing light independent of the excitation appears to be impractical. Novak and Windsor (1) used a laser pulse-induced gas spark which provided a spectral continuum. But this spark had a lifetime of 30 nsec, too long for use in the present case. Thus at present, the analyzing wavelength is limited to the laser frequency. The pulse delay set-up is essentially that used by Hunt (8) for pulse radiolysis at picosecond times. A series of up to 100 excitation and analysis pulses are passed through the solution successively. The photomultiplier response is not crucial since the total number of photons determines the signal

accumulated and stored by the electronics. For the experiments envisioned at present the decay of the intensity with time rather than the actual intensity is important. In order to obtain this decay the signal accumulated over a period of about a microsecond is measured. This is repeated for a series of analyzing path lengths, using the same time period for signal accumulation.

The proposed investigation to be carried out with this apparatus is the attempted measurement of the internal conversion rate from S_2 to S_1 in aromatic hydrocarbons. Since this rate is not known within an order of magnitude, it is uncertain whether 10 psec resolution is sufficient to observe the transition. Under favorable conditions, however, there is a fairly high probability that it is. It is stated (9) that the rate of internal conversion from higher states to S_1 must have a rate constant of the order of 10^{11} to 10^{13} since this process dominates fluorescence from upper electronic levels. This rate probably varies considerably with the compound involved, depending on the energy separation of the electronic states. Azulene is the only known compound for which fluorescence from S_2 predominates over radiationless decay to S_1 and this is generally attributed to the large $S_2 - S_1$ energy gap of 40 kcal/mole. Approximate calculations by Hunt *et al.* (10) indicate that the rate of radiationless internal conversion is in fact strongly dependent on the energy difference between the levels. They state that since

most aromatic hydrocarbon compounds with three or more rings have fairly close upper energy levels, internal conversion will always be quite fast, with a rate constant $>10^{10}$. Just how much greater is difficult to say.

Compounds to be observed for internal conversion must be chosen rather carefully in view of the limitations of the instrument. One substance that appears to be a favorable choice from the point of view of known properties is 1,2-benzanthracene. The onset wavelengths of S_1, S_2, and S_3 are respectively 385, 359, and 290 nm (11) so that the 347 nm laser light can cause excitation to S_1 and S_2 but not to S_3. Singlet-singlet absorption from S_1 of this compound has been observed by nanosecond flash photolysis (3, 6). Absorption with a maximum at 560 nm and an estimated molar extinction coefficient (ϵ) of 9700 was observed (3). This spectrum shows a second maximum at 590 nm with an ϵ of $0.8\epsilon_{560}$. This is a broad absorption for which the optical density has only decreased by about 15% at 600 nm, the longest wavelength investigated. These absorptions are in all likelihood $S_1 \rightarrow S_4$ transitions since the $S_1 - S_4$ energy difference is correct for the wavelengths observed (11, 12).

The energy difference between S_1 and S_2 is such that the absorption at 600 nm for $S_1 \rightarrow S_4$ would lie at 680 nm for $S_2 \rightarrow S_4$ (11). Since the absorption is broad, the laser light at 694 nm should probably still see a considerable ϵ,

provided that the transition is still allowed (both S_1 and S_2 are L states and S_4 is a C state in Platt classification (12)).

Using the figure 0.1 J per 5 psec pulse, a 5% efficiency of frequency doubling, and a solution concentration such that 1/3 of the pulse light is absorbed, the concentration of excited species is 10^{-4} M. Thus an ϵ as low as 1000 would still provide an absorbance of 0.05, which has proved sufficient for laser flash photolysis in the past (3).

The main drawback of the 1,2-benzanthracene system is the small S_1 - S_2 separation (5 kcal). This probably means that the internal conversion rate to S_1 is quite fast. On this basis 1,2-benzanthracene may be an unfavorable compound to study, although the previous nanosecond flash spectroscopy study and the energy level distribution would make it ideal from the point of view of the instrument.

An alternative compound, whose excited singlet absorption has not been studied but which might provide a better chance to see $S_2 \rightarrow S_1$ decay is pentacene. The onset wavelengths for the first three excited singlets are at 588, 417, and 310 nm respectively (12). The extinction coefficint at 347 nm is about 10^3 (13). Thus S_2 will receive essentially all the laser light. Unfortunately the position of S_4 is not really known for this compound since the $S_0 \rightarrow S_4$ transition is forbidden. The position of S_4 in tetracene has been indicated at about 230 nm (12). All the energy

levels move to lower energy upon increasing the linear ring systems, although to different extents. It would be possible for S_4 to be located near 260 nm in pentacene where the wavelength for $S_2 \rightarrow S_4$ would be 690 nm but there is no way of knowing. Information concerning the singlet-singlet absorption based on nanosecond flash photolysis would provide valuable information on this point. In view of the relatively large $S_1 - S_2$ splitting (20 kcal/mole) it is possible that the intermal conversion rate in this case will be sufficiently slow to be observed even if it is not in the case of 1,2-benzanthracene.

Addendum to Proposition I: Subsequent to the formulation of the preceding proposition a paper has been published (14) describing the operation of a Q-switched mode-locked Nd-glass laser in a measurement of excited state relaxation on a picosecond time scale. The apparatus is similar to that described in the present proposal. The authors vary the time delay by the insertion of quartz blocks of various thicknesses into the analyzing beam. The laser has a wavelength of 1.06μ. The experiment described is the measurement of the relaxation time of a Q-switch dye which absorbs strongly at the laser wavelength. The analyzing beam measures the extent of bleaching of the dye by the excitation pulse on the basis of the transmitted intensity of the analyzing light as a function of time after the pulse. For this purpose, the use of excitation and analyzing light of the same wavelength is appropriate.

The apparatus suggested for the flash photolysis in the present proposition was formulated prior to the appearance of this paper (September 19, 1969) and was based essentially on the nanosecond flash photolysis apparatus of Novak and Windsor (6) and the stroboscopic analysis system of Hunt (8). The Nd-glass laser has a wavelength which does not appear to be suitable to the study of most systems of photochemical interest, even when doubled (530 nm). The use of the analyzing beam as a measure of decreased ground state population resulting in increased transparency

is also not a very flexible process. It measures a ground state depopulation, requiring a large excited state population and is capable only of measuring total relaxation time to the ground state. The use of quartz blocks to increase the path length of the analyzing beam is however preferable to the movable mirror technique which this proposition suggests.

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PROPOSITION II

Abstract: It is proposed to study the production of carbonium ions generated from alkyl halides by high energy radiolysis.

It is generally accepted that ionic species are formed in the gamma radiolysis of organic compounds. In recent years the production and reactions of ions in such systems have become subjects of considerable interest and research. Cationic and anionic species have been observed in low temperature glasses containing alkyl halides (1-3). Electron and cation scavenging experiments demonstrate the involvement of ions in liquid phase reactions as well (4-7). Pulse radiolysis spectra also support this, indicating that ionic lifetimes are sufficient to allow charge transfer in suitable cases (8,9). Such studies, which have included correlations with theoretical models (5, 7, 10, 11) have generally been concerned with parent ion reactions. Cation fragmentation in liquids has, with afew exceptions, been ignored even under conditions where it might be expected to make a contribution.

Although radiation chemistry is frequently classified as a branch of physical chemistry, this may be of historical rather than contemporary accuracy. Much of current radiation chemical research involves reactions of the sort that have concerned organic chemists. This is especially true of free

radical and excited state reactions. That ionic reactions have not involved such a correlation is due largely to the above observation that fragmentation ions have usually not been dealt with in radiolysis studies, although they constitute the majority of ionic organic chemistry reactions (e.g. carbonium ions). Thus a study of such processes is of interest since it helps to extend the incorporation of radiation chemical reactions into existing chemistry and may even be of use in initiating organic reactions under conditions where conventional methods are unfavorable — for example carbonium ion reactions under non-polar conditions.

The likelihood of fragmentation of radiation produced parent ions (Reaction (I)) has been investigated on an

$$RY^+ \longrightarrow R^+ + Y \qquad (I)$$

energetic basis by Williams (12). It was concluded that if fragmentation is endothermic for ground state RY^+, it can not compete with ion neutralization, but that if it is exothermic it can. As a result, fragmentation of n-alkane ions is considered unlikely, but branched chain alkanes are able to undergo reaction (I) if a stable carbonium ion R^+ results. The dissociation of neopentane and neohexane was studied from this viewpoint. Isobutene is formed on radiolysis of neopentane and this has been taken as a measure of the formation of tert-butyl carbonium ion (13). It should be pointed out that tert-butyl free radicals can

also form isobutene, by disproportionation termination (isobutane is also a product of neopentane radiolysis). It has been pointed out (12) that the successive reactions:

$$(CH_3)_3CCH_3^+ \longrightarrow (CH_3)_3C^+ + \cdot CH_3 \qquad (II)$$

$$(CH_3)_3C^+ + e^- \longrightarrow (CH_3)_2C{=}CH_2 + H\cdot \qquad (III)$$

followed by combination of $H\cdot$ and $\cdot CH_3$ cannot be distinguished from the intermediates produced by:

$$(CH_3)_4C \rightsquigarrow [(CH_3)_4C^+ + e^-] \longrightarrow [(CH_3)_3C\cdot + \cdot CH_3] \qquad (IV)$$

followed by disproportionation. Thus it is not clear that tert-butyl carbonium ion is actually formed or if so to what extent it is the source of isobutene.

Another approach to this problem has been taken by Hamill (14). In this experiment carbonium ions produced in a reaction such as (I) by gamma rays were scavenged by alcohols. Measurement of the yield of the ether resulting from the conventional carbonium ion reaction indicated the formation of significant amounts of R^+. The quantitative estimation of carbonium ion yields is, however, rather uncertain. This is in part due to the high concentrations of alcohols needed to ensure complete carbonium ion scavenging. This leads to other reactions such as those suggested by Hamill which may form the same products:

$$R'OH \longrightarrow R'O\cdot + H\cdot \qquad (V)$$

$$RH \longrightarrow R\cdot + H\cdot \qquad (VI)$$

$$R'O\cdot + R\cdot \longrightarrow R'OR \qquad (VII)$$

In addition, no attempt was made to measure alkene yields which might arise from the carbonium ions. The uncertainty in the interpretation of the origin of alkene products has already been discussed. Thus these results do not constitute a quantitative measure of carbonium ion yields either, although the presence of some ether products at low alcohol concentrations does indicate the formation of at least some of this intermediate.

The question of the importance of reaction (I) is therefore still an open one. A system in which the carbonium ion reactions could be differentiated from the other processes would be of considerable value. The neopentyl halides appear to provide such a system.

Both free radicals (15-17) and ions are produced in liquid alkyl halides irradiated by gamma rays of high energy electrons. The latter have been observed in the pulse radiolysis of alkyl iodides (18), and of alkyl chlorides containing aromatic solutes (19). The free radicals are generally believed to be formed by electron attachment.

There is no direct evidence for the formation of carbonium ions in irradiated halogenated alkanes, but both the energetics and mass spectral data (20) indicate that it is

probable, at least in bromides and iodides. Reaction (I) is exothermic for all halides except F so that Williams' criterion is satisfied. The important reactions in alkyl halides, especially iodides, are then:

$$RI \longrightarrow RI^+ + e^- \qquad \text{(VIII)}$$

$$RI^+ \longrightarrow R^+ + I \qquad \text{(IX)}$$

$$RI + e^- \longrightarrow R\cdot + I^- \qquad \text{(X)}$$

These reactions probably enhance one another with electrons released by (VIII) captured in (X). This would tend to hinder neutralization of RI^+ and would make fragmentation more probable.

The mass spectrum of neopentane (21) indicates that very little $C_5H_{12}^+$ is formed but rather that $C_4H_9^+$ predominates. However, this is not likely to be the case in neopentyl iodide. Although I have been unable to find the mass spectrum of neopentyl iodide, those of isobutane and isobutyl iodide give a good indication of what can be expected. Similar to neopentane, isobutane shows $butyl^+/propyl^+ = 0.03$. But for isobutyl iodide $butyl^+/propyl^+ = 16$. It is highly probable that $C_5H_{11}^+$ from neopentyl iodide is also greatly enhanced over that from neopentane.

The neopentyl carbonium ion is a classical example of an ion that undergoes essentially complete rearrangement prior to reaction (22, 23). Some evidence indicates that

under special conditions a maximum of 10% product may form from the unrearranged ion (24). But on the whole, the product is that derived from the tertiary cation. In contrast to this, no 1,2-methyl shift has ever been observed in an alkyl radical (25).

Then, neglecting processes not relevant to the carbonium ion studies, the reactions in the radiolysis of neopentyl iodide in the presence of an alcohol are:

$$(CH_3)_3CCH_2I \longrightarrow [(CH_3)_3CCH_2I]^+ + e^- \qquad \text{(XI)}$$

$$(CH_3)_3CCH_2I + e^- \longrightarrow (CH_3)_3CCH_2\cdot + I^- \qquad \text{(XII)}$$

$$[(CH_3)_3CCH_2I]^+ \longrightarrow (CH_3)_3CCH_2^+ + I \qquad \text{(XIII)}$$

$$(CH_3)_3CCH_2^+ \longrightarrow (CH_3)_2\overset{+}{C}CH_2CH_3 \qquad \text{(XIV)}$$

$$(CH_3)_2\overset{+}{C}CH_2CH_3 \begin{cases} \xrightarrow{e^-} (CH_3)_2C{=}CHCH_3 + CH_3CH_2(CH_3)C{=}CH_2 + H\cdot \\ \xrightarrow{R'OH + e^-} CH_3CH_2(CH_3)_2COR' + H\cdot \end{cases} \qquad \text{(XV)}$$

$$R'OH \longrightarrow R'O\cdot + H\cdot \qquad \text{(XVI)}$$

$$(CH_3)_3CCH_2\cdot + R'O\cdot \longrightarrow (CH_3)_3CCH_2OR' \qquad \text{(XVII)}$$

The yield of neopentyl carbonium ion can then be found by measuring the products from reaction (XV). In order to prevent the olefins from reacting further, conversions must be kept low.

It is likely that some tert-butyl ions and radicals will also be formed. It would not be possible to distinguish between these two intermediates. However, the products from the neopentyl carbonium ion, the neopentyl radical, and the butyl intermediates combined can all be distinguished.

In addition to providing a measure of the yield of neopenyl carbonium ion, analysis of the products should allow the extend of reaction (XVII) to be measured. This would be of use in determining the concentrations of alcohol that could safely be used in ion scavenging in studies such as that previously mentioned where radical and ion products cannot be distinguished.

By using a radical scavenger (Br_2, I_2) instead of an alcohol the radical yield from reaction (XII) can be measured, providing a comparison of the importance of reactions (XII) and (XIII).

In addition to neat alkyl halide, the study can be carried out in various solvents, allowing effects such as charge transfer and solvent polarity to be investigated. Neopentyl compounds other than the iodide can also be used. A correlation of carbonium ion yields with C-Y bond strength could be investigated. The unambiguity of the source of rearranged product makes the use of this reaction quite advantageous in the study of the effect of conditions on reaction (I).

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PROPOSITION III

Abstract: It is proposed to examine the effect of changing the nature of ionizing radiation on a number of charge scavenging reactions in an effort to observe whether the implications of charge scavenging models are experimentally valid.

Within the past three or four years a number of theoretical or semi-empirical calculations have appeared in the radiation chemical literature attempting to describe ion neutralization processes and ion-molecule reactions induced in organic liquids by radiation. One approach (1-4) has been to assume or extrapolate from data an approximate distribution of initial ion-pair separation distances and from this calculate a lifetime distribution for ions. The kinetics of ion scavenging can be incorporated into the model since it provides the concentration of ions remaining after a given time. This aspect has been tested (1) with assumed values for certain parameters which depend on the molecules present. The yields of the reactions:

$$C_6H_{12}^+ + ND_3 \longrightarrow C_6H_{11}\cdot + ND_3H^+$$

$$C_6H_{12}^+ + C_2H_5OD \longrightarrow C_6H_{11}\cdot + C_2H_5ODH^+$$

$$e^- + N_2O \longrightarrow N_2 + O^-$$

which have been characterized (5-7), were used to provide a favorable test of the solute concentration-yield profile.

This model used isolated ion pairs in the recombination rate calculation, as do all the others proposed up to the present. The reasonably good fit obtained with experimental results suggests that this may be physically true rather that merely a simplifying assumption and that so-called spur effects are not important. A spur is defined as a grouping of reactive intermediates that are close enough together that there is a significant probability that the intermediates in it will react with each other (1). The concept arises in radiation chemistry as a result of the spacially inhomogeneous distribution of energy in the medium, giving rise to localized high concentrations of intermediates. The agreement of the isolated ion-pair neutralization model with experimental quenching data indicates that aggregates of more than one ion pair, which would affect ion recombination rates and therefore the concentration dependence of scavenging, are not required to describe the results. The suggested reason for this is that all ion pairs in a spur, but the last, are neutralized very quickly under the influence of the total coulombic field before ion molecule reactions can occur (8, 9). These reactions then compete with the recombination of single ion pairs.

In an alternative, more empirical approach, Hamill (10, 11) derived an expression for the initial distribution of ion pair separations from luminescence decay data in

cyclohexane and an expression for the rate of recombination of ion pairs. Using free ion yield data in cyclohexane to obtain parameter values, an expression for charge scavenging product yields as a function of scavenger concentration was derived:

$$G/G^{o} = \sum_{K}^{\infty} \{1 - \exp[-2.5kc(R-K)]\} \Delta \left(\frac{R}{K}\right)^{-2.7}$$

where c is the scavenger concentrations, k is an adjustable parameter and K is defined by:

$$G_{fi}/G^{o} = \left(\frac{e^2}{kT}/K\right)^{-2.7}$$

G_{fi} is the yield of ions which escape recombination in the absence of a scavenger. G^{o} is the maximum yield of scavengable ions. (G is defined as the molecules, ions, etc. formed per 100ev energy absorbed).

This expression was used to test experimental results. It gave a good fit to data in cyclohexane and was also found to apply to ionic radiation chemical reactions in ethanol, methyltetrahydrofuran, and water, although it had been derived only for the first solvent. Hamill pointed out the implication in the fit of the data to an isolated ion-pair model--that spur effects are unnecessary to explain ion scavenging data. The fit of several solvent systems to the same general equation also supports this since spur conditions would be expected to be considerably different in these solvents.

It would be of considerable interest in terms of the mechanism of charge scavenging if this conclusion could be tested. One possible method for such a test would be to carry out the same charge scavenging irradiations using positive ion radiation such as protons or helions rather than gamma radiation. Under these irradiation conditions, the initial energy deposition instead of being primarily in the form of isolated blobs or spurs containing 1 - 3 ion pairs occurs in the form of cylindrical tracks which are essentially overlapping spurs. This greater undimensional concentration of intermediates formed by the initial energy deposition, including ions, results from the greater interaction of the heavy ions with the liquid than is exhibited by electrons. It is characterized by the linear energy transfer (LET), $-\frac{dE}{dx}$. This LET effect is thus a pronounced spur effect. If the applicability of the models discussed is due to a situation in which only single ion-pair neutralization versus scavenging is actually involved, no appreciable effect on the <u>form</u> of the ion scavenging concentration dependence should be observed. Ion recombination under conditions of a number of ion pairs in close proximety should probably be faster under higher LET conditions of irradiation leaving single ion pairs at least as rapidly as gamma radiation. The results should therefore follow the same model as in the case of gamma radiation. On the other hand, the apparent ability of the ion-pair

models, especially Hamill's, to account for scavenging-concentration dependence under diverse solvent conditions where spur effects should already be influential, may be due to factors other than a true reflection of the physical situation. If this is the case, and spur conditions are actually important, this should be reflected in an LET effect. A deviation from the predicted curve and from the results in gamma irradiated systems should result. To test that this is a true LET effect, the energy of the particle beam could be varied between, say, 5 and 1 Mev which will cause LET to increase in an approximately known manner. A systematic change in the deviation of scavenging G values should then be observed.

The following reactions, which are among those used in the testing of Hamill's model, could be used in the proposed study. The term CH represents cyclohexane. All reactions are in cyclohexane solution.

$$e^- + N_2O \longrightarrow N_2 + O^- \qquad \text{(I)}$$

$$e^- + RX \longrightarrow R\cdot + X^- \qquad \text{(II)}$$

$$R\cdot + {}^{131}I_2 \longrightarrow R^{131}I + I\cdot$$

$$CH^+ + ND^3 \longrightarrow C\cdot + ND_3H^+ \qquad \text{(III)}$$

$$ND_3H^+ \xrightarrow{e^-} 3/4ND_2H + 3/4D + \tfrac{1}{4}ND_3 + \tfrac{1}{4}H$$

$$D\cdot + CH \longrightarrow C\cdot + HD$$

$$CH^+ + C_2H_5OD \longrightarrow C\cdot + C_2H_5ODH^+ \qquad \text{(IV)}$$

$$C_2H_5ODH^+ \xrightarrow{e^-} \tfrac{1}{2}C_2H_5OH + \tfrac{1}{2}D + \tfrac{1}{2}C_2H_5OD + \tfrac{1}{2}H$$

$$D + CH \longrightarrow C\cdot + HD$$

$$2CH^+ + 2c\text{-}\overset{*}{C}_3H_6 \longrightarrow {}^*C_3H_8 + C_6H_{11} - {}^*C_3H_7 + C_{12}H_{10}^+ \qquad \text{(V)}$$

These reactions are from references 7, 12, 5, 6, and 13 respectively. Low concentration extrapolations of reactions (III) and (V) have given values for G_{fi} the free ion. G^o, the upper limit of scavengable ions is also required. This information can be derived from reaction (II). It should be noted that it is G/G^o that is used in the comparison with the gamma radiation results which Hamill has fit to his semiempirical curve. It is expected that G^o itself will be smaller for high LET even if there is no LET effect on the form of the scavenging curve. This is so since as mentioned the recombination of ions under multiple ion conditions will be more extensive for high LET leaving fewer ion-pairs for the scavenging versus neutralization stage.

In the event that there is an LET effect, some information can still be obtained from the results. Hummel has shown (14) that if the effective concentration of scavengable ions is left as an indeterminate function of time, n(t), this function can be determined if the scavenging yield G can be found as an explicit function of concentration. This was determined to be possible for reactions (II) and (V) (12, 13). The same is presumably also possible using high LET radiation rather than gamma rays. Thus n(t) under different LET conditions can be compared. No assumptions about the details of the model are required. Such a comparison would be of value.

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PROPOSITION IV

Abstract. It is proposed to investigate the possibility of electronic effects due to β secondary hydrogen isotopic substitution through the study of an alkyl free radical by electron spin resonance spectroscopy.

Changes in the rates or equilibria of organic reactions upon substitution of deuterium for a hydrogen atom not directly involved in bond breaking or formation have been known for some time (1-4). These are termed secondary isotope effects.

Of special interest are the β secondary isotope effects, those in which isotopic substitution takes place on an atom α to the one directly involved in the reaction. This is so because there is no general agreement on how the isotopic substitution causes the observed effect. It is generally accepted (5) that the effects are ultimately vibrational in origin. The problem is the manner in which these vibrational effects manifest themselves.

The earliest explanation and the one that has received the most support is based on the proposal that hyperconjugation is important in transition states that have cation or free radical character (5-7). The mechanism whereby this hyperconjugation affects reaction rates is still the subject of debate.

One interpretation (2, 6, 8) is that in transition states (or in the case of equilibria, intermediates) resembling carbonium ions (I) or free radicals (II) hyperconjugation causes a decrease in the force constants of certain C-H stretching or bending vibrations.

$$\underset{\text{I}}{\text{H-C-C}^{+} \longleftrightarrow \text{H}^{+}\ \text{C=C}}$$

$$\underset{\text{II}}{\text{H-C-C}\cdot \longleftrightarrow \cdot\text{H}\ \text{C=C}}$$

As a result these vibrational frequencies and therefore the zero-point energy will be lower in the transition state than in the initial state. This decrease will be greater for hydrogen than for deuterium so that the activation energy for the latter will be greater. Reactions for which the force constants increase exhibit an inverse isotope effect.

Alternatively, it has been proposed that it is a difference in the abilities of H and D to participate in hyperconjugation that gives rise to β secondary isotope effects (9, 10). As a result of anharmonicity in vibrations, the C-D distance is considered to be less than the C-H distance. The C-D bonding electrons are held more tightly and are less able to participate in hyperconjugation. Hyperconjugative stabilization of the transition state is therefore reduced upon deuterium substitution. This is a vibrationally induced electronic effect and is analogous to

saying that the force constants discussed above are changed to different extents for H and D on formation of the transition state.

Other proposed explanations of the β isotope effect also rely on a decrease in bond length on deuterium substitution. Such a difference in bond lengths implies that the electron density near the carbon atom is greater for C-D than for C-H. Thus deuterium is more electron releasing than H and should have a different inductive effect (11, 12).

Secondary β isotope effects have also been attributed to non-bonded interaction on the basis of a shorter C-D bond length than C-H (13, 14). However, more recent experiments on molecules in which steric effects are highly improbable (15) or alternatively, where they are expected to be important (16) concluded that non-bonded interactions could cause only a small part of the observed β secondary isotope effect.

Support for the idea that isotopic substitution can cause electronic effects comes from experiments in which deuterium substitution for hydrogen caused a change in the dipole moment of a number of compounds (17) in a direction indicating greater electron release from CD_3 than from CH_3. It has also been shown that compounds of the type $CHDR_1R_2$ can be optically active (18). Therefore an explanation of β secondary isotope effects based on electronic differences between D and H substituted compounds is not implausible.

Although β secondary isotope effects are not as large for free radical reactions as they are for carbonium ion processes, magnitudes of k_H/k_D, the relative rates of reaction for hydrogenated and deuterated compounds, have been measured to be as large as 1.23 (7).

It would be of interest to perform an experiment in which electronic effects due to β secondary hydrogen isotopic substitution could be studied directly. An electron spin resonance (esr) measurement of the ^{13}C hyperfine splitting of t-butyl and t-butyl-d_9 free radicals in which the central carbon atom is ^{13}C should allow an indication of such an effect to be made. The ^{13}C hyperfine splitting, a_C, will reflect the unpaired electron density on the central carbon atom and this in turn will be different for the two radicals only if deuterium substitution has an electronic effect. The ^{13}C splitting is quite sensitive to the spin population in the unbonded pπ orbital. Within the limitations of current esr theory for converting hyperfine splitting constants to unpaired electron densities, a quantitative estimation of the effect can be obtained.

A semiempirical calculation for relating a_C to unpaired electron density on the ^{13}C atom has been derived for alkyl radicals (19). For t-butyl radical the expression is:

$$a_C = -12.7 + 48.9\rho$$

where ρ is the unpaired spin density on the central ^{13}C atom. Then $\Delta\rho$ the change in this value upon deuterium substitution would be:

$$\Delta\rho = \frac{1}{48.9}\left[a_C(D) - a_C(H)\right]$$

where $a_C(H)$ and $a_C(D)$ are the ^{13}C coupling constants for $(CH_3)_3{}^{13}C\cdot$ and $(CD_3)_3{}^{13}C\cdot$ radicals respectively. If no difference between $a_C(H)$ and $a_C(D)$ can be observed the experimental results will at least allow an estimation of an upper limit to any electronic effect.

It is proposed to generate the t-butyl radical by the method recently devised by Krusic and Kochi (19). Di-t-butyl peroxide is photolyzed in the cavity in the degassed esr sample tube, using light between 3400 and 2200 Å. The resulting t-butoxy radical can abstract hydrogen from alkanes. By using 10% peroxide and 50% alkane in a non-extractable solvent (e.g. cyclopropane at -130°C) only the most easily extracted hydrogen in the alkane is removed:

$$(CH_3)_3COOC(CH_3)_3 \xrightarrow{h\nu} 2(CH_3)_3CO\cdot$$

$$(CH_3)_3CO\cdot + (CH_3)_3CH \longrightarrow (CH_3)_3COH + (CH_3)_3C\cdot$$

Narrow lines ($G < 0.08$) can be obtained. Approximately 0.5 gm of alkane is required.

The preparation of the isotopically substituted starting materials is proposed as follows. $^{13}CO_2$ is available

commercially at 90% purity. CD_3I is available at virtually 100% purity.

$$CD_3I + Mg \longrightarrow CD_3MgI$$

$$^{13}CO_2(solid) + CD_3MgI \longrightarrow CD_3{}^{13}CO_2MgI$$

$$CD_3{}^{13}CO_2MgI \xrightarrow{H_3O^+} CD_3{}^{13}COOH$$

$$CD_3{}^{13}COOH + CH_3OH \xrightarrow{H^+} CD_3{}^{13}COOCH_3$$

$$CD_3{}^{13}COOCH_3 + 2CD_3MgI \longrightarrow (CD_3)_3{}^{13}COMgI$$

$$(CD_3)_3{}^{13}COMgI \xrightarrow{H_3O^+} (CD_3)_3{}^{13}COH$$

$$(CD_3)_3{}^{13}COH + SOCl_2 \longrightarrow (CD_3)_3{}^{13}CCl + HCl + SO_2$$

$$(CD_3)_3{}^{13}CCl + Mg \xrightarrow{ether} (CD_3)_3{}^{13}CMgCl$$

$$(CD_3)_3{}^{13}CMgCl \xrightarrow{H_2O} (CD_3)_3{}^{13}CH$$

$(CH_3)_3{}^{13}CH$ can be prepared in an analogous manner.

An indication of the approximate esr spectra can be obtained from the following considerations. The H hyperfine coupling constant of t-butyl radical is 22.7g (20) which, neglecting any isotope effect would make the D coupling constant 3.5g. The ^{13}C hyperfine splitting will be of the order of 20-25g using the central carbon unpaired spin density estimated from the H splitting in t-butyl radical by Fessenden and Schuler (20). The spectra will then have approximately the appearance indicated in the figure (20g was used for both $a_C(H)$ and $a_C(D)$). It is anticipated that the coupling constants can be obtained with at least 0.5% accuracy.

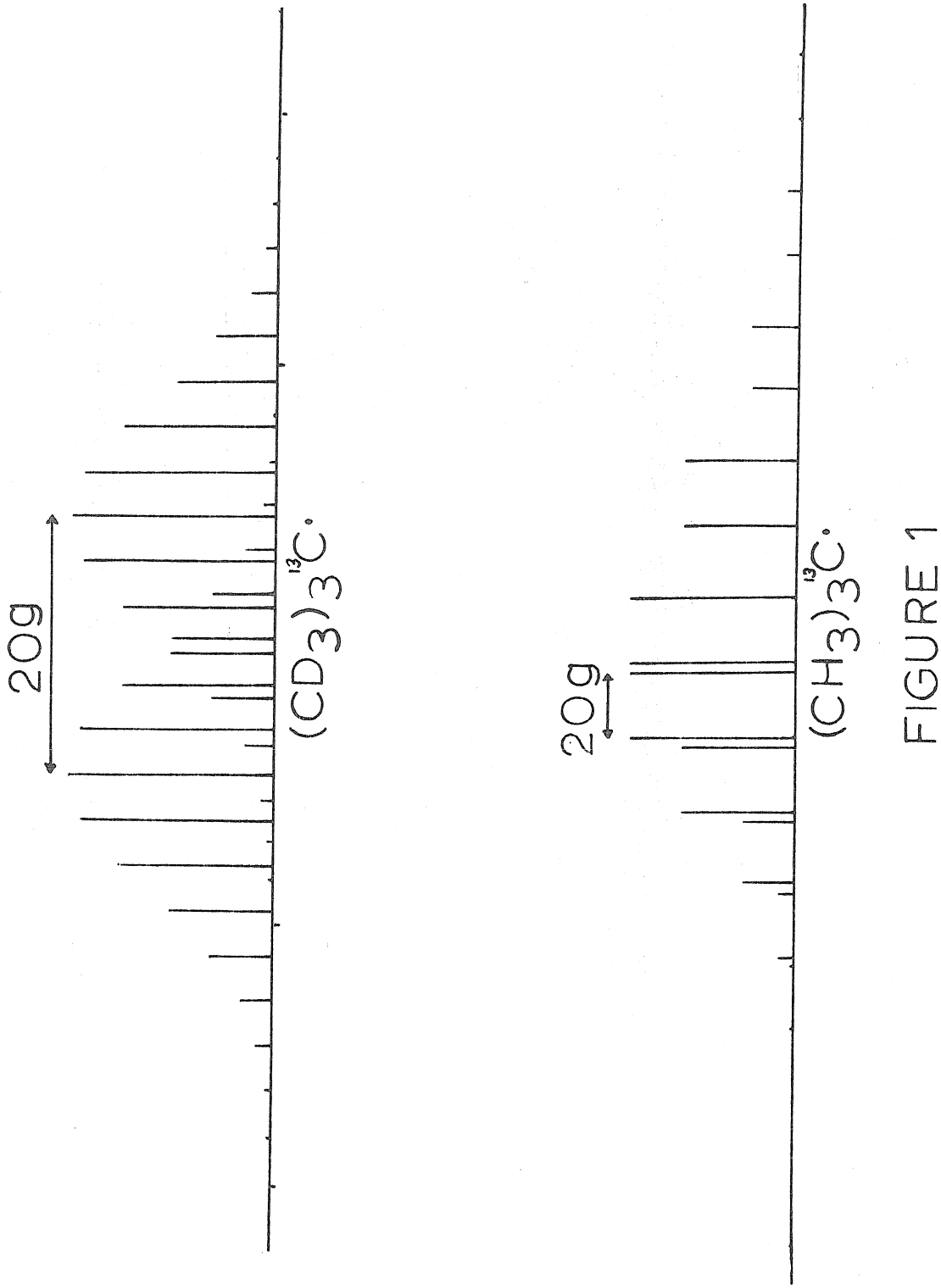

FIGURE 1

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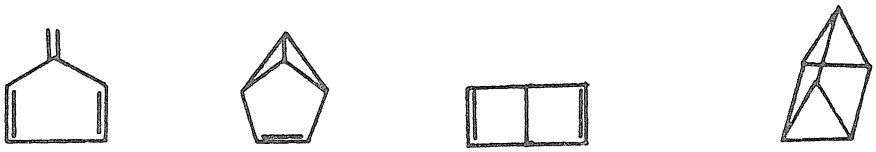
PROPOSITION V

Abstract: It is proposed to study the possibility that radical intermediates are formed in the 2537Å irradiation of benzene by an electron spin resonance trapping technique.

The photochemical reactions of benzene and substituted benzenes have been the subject of considerable research activity (1). The area has been of interest because a large percentage of the absorbed light is dissipated in a non-radiative fashion and also because some of the products which are formed are of structural and reactivity interest. The photochemistry has been studied at a number of wavelengths down to the vacuum ultraviolet both in liquid and in vapor phases. This proposed investigation will be restricted to the liquid phase and to wavelengths of excitation into the first benzene singlet (specifically 2537Å). Most of the observed processes are similar under other conditions although both pressure and wavelength effects on yields are observed. Decomposition processes are also greater at shorter wavelengths.

Early reports on liquid benzene irradiation indicated that a compound, identified as fulvene (I) was formed (2, 3).

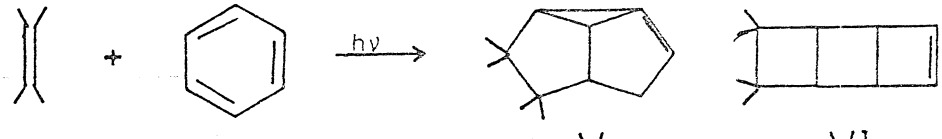


I II III IV

More recently benzvalene (II) has been observed (4) and it has been suggested that fulvene arises from rearrangement of II via triplet benzene sensitization (5). Although neither Dewar benzene (III) or prismane (IV) have been reported in the liquid phase 2537Å irradiation of benzene, the former has been reported at 2000Å (6) and the analogous products derived from 1,3,5-tri-t-butylbenzene (7) and perfluorobenzene (8) have been observed. The formation of these isomers appears to be an internal process since mixtures of C_6H_6 and C_6D_6 resulted in no isotope mixing (6). The benzene carbon atoms undergo a 1,2 shift on photo-irradiation and this is believed to proceed through benz-valene (9). At 2000Å, the quantum yields of I, II, and III are respectively 0.012, 0.03, and 0.006. (Some or all of I may be derived from II).

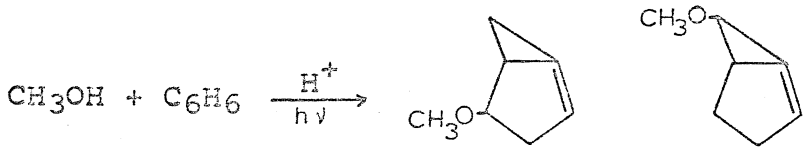
In addition to these internal rearrangements, the irradiation of benzene vapor in a flow system, followed by freeze trapping, yields an esr signal which has been assigned to either C_6H_5 or C_6H_7 (10).

The inclusion of additives in the irradiated benzene can result in the formation of adducts. Both 1,3 adducts to give V (11) and 1,2 adducts to give VI (12) have been observed on the addition of alkenes. At the same time

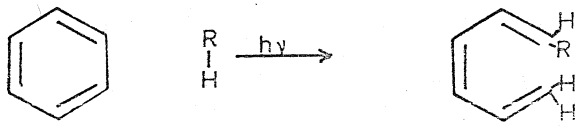


V VI

time fulvene and benzvalene formation are quenched. Methanol also forms adducts (13), quenching isomerization.

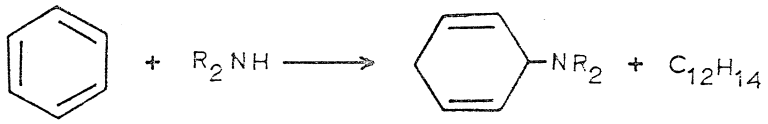


In very viscous solvents or hydrocarbon glasses at low temperature hydrocarbons add to benzene under 2537Å irradiation (14, 15). Hydrogen is also evolved and has been shown to arise independently of the substituted hexatriene.



Evidence has been presented indicating that this latter product is derived from a triplet benzene precursor (16). The mode of hexatriene formation is not known.

The presence of hydrogen doner substances also leads to addition products (17):

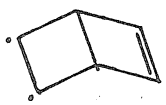


In a similar manner it was observed that when perfluorobenzene was irradiated at 2537Å in diethylether, in addition to the benzvalene, prismane, and Dewar benzene, hydrogen abstraction from the solvent occurred which could be a tricyclohexane or a 1,4-dihydrobenzene.

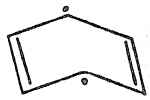
The precursor(s) to these reactions including the valence isomerizations and fulvene formation are not known. Possible intermediates have been suggested by Bryce-Smith (18, 19). He has proposed the diradical VII arising from the first excited singlet of benzene. This is the suggested

VII

precursor to benzvalene, fulvene, the methanol adduct, and 1,3 alkene addition. The further suggestion was made that triplet benzene can lead to a diradical of the form of VIII.



VIII



IX

This can give rise to Dewar benzene or can interconvert to IX. The latter is the diradical which is postulated to be responsible for the formation of cyclohexadiene adducts in the presence of hydrogen doners (presumably H abstraction by IX, followed by radical coupling).

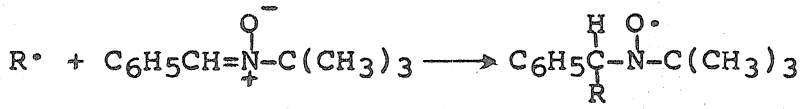
Objections to the intermediate VII have been raised because the methanol adduct is formed in yields comparable to the benzvalene in the absence of the alcohol, but the alkene adduct V has a yield ten times as great. Presumably if both additives were trapping the same specie, their yields should be comparable (9).

The possibility of a diradical or free radical intermediate derived from triplet benzene has received support in a very recent report (20). Using fast spectroscopic resolution techniques a transient specie has been observed in benzene-cyclohexane mixtures irradiated by an electron pulse, which has a benzene concentration dependence identical to that of triplet benzene. Its growth and decay times preclude benzene excited states as does the lack of quenching by naphthalene, piperylene, biacetyl and other excited state quenchers. These compounds did reduce the intensity of the transient absorption indicating quenching of a precursor. Oxygen quenched the absorption. A free radical or diradical formed from triplet excimer or reaction of B and B^3 was proposed.

Thus the evidence, including addition products, hydrogen abstraction from solvent or additives, and spectroscopy, is consistent with the formation of a biradical or free radical formed from benzene triplets.

It is proposed to attempt to detect and identify such an intermediate by the method of spin trapping. Although this method has been used in the past for free radical rather than diradical trapping, the evidence described above indicates that if a benzene diradical is formed, it abstracts hydrogen from added doners to form a cyclohexadienyl free radical and a free radical of the doner. The method should therefore be applicable under these circumstances.

Spin trapping relies on the addition reaction of a free radical with another compound (the spin trap) with a functional group such as nitro, nitroso, or nitrone, to form a stable free radical (21, 22). The compound which has been most studied in this application is phenyl-t-butylnitrone (PBN) (22, 23, 23). The reaction with a free radical is given by:



The resulting nitroxide is a stable free radical so that its concentration builds up as more R· is formed and trapped. Identification of R· can be accomplished by observing the N and β H coupling constants and comparing them to the values obtained with known radicals. A given radical R· has always provided the same coupling constants, independent of the manner of generation (24). The method does not require a flow system.

The experiment envisioned would consist of 2537Å irradiation of degassed benzene with added PBN (0.05M) in the esr cavity and observation of any long-lived signal after the light has been turned off. Solutions of benzene in ether or with an added amine (e.g. n-butylamine) could be used. Formation of additional radicals would be expected from these additives. But these should be distinguishable from the cyclohexadienyl -PBN adduct spectrum. Since

identification is by comparison of coupling constants with known radical adducts it will be necessary to generate cyclohexadienyl radicals. Tri-n-butyltinhydride could be mixed with 3-bromo-1,4-cyclohexadiene in the presence of PBN. The coupling constants of the hydrogen donor radicals should also be determined. The expected additional radical in ether would be $C_2H_5OC_2H_4\cdot$. This could be prepared by photolysis of benzophenone in ether in the presence of PBN. The expected radical from n-butylamine, C_4H_9NH can be generated by photolysis (25) (along with H which will give a much different spectrum (24)).

Of course since the diradical IX is only hypothetical there is no guarantee that a cyclohexadienyl radical or, for that matter, any other radical will be formed during the photolysis. If there is, but it isn't cyclohexadienyl, a rather difficult task of identification would be presented. The possibility of phenyl could be tested easily as the N and β H coupling constants are known in this case (24). Other than that only a rather tedious preparation and measurement of "reasonable" radical-PBN adducts would be possible. However, the benzene adduct evidence argues that if radicals are in fact involved, the cyclohexadienyl structure is the strongest possibility. Its identification would add considerable weight to Bryce-Smith's proposed intermediates.

References

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