THE PHOTOCHEMICAL REACTIONS OF HEPTACHLOR: KINETICS AND MECHANISMS

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ABSTRACT

THE PHOTOCHEMICAL REACTIONS OF HEPTACHLOR:
KINETICS AND MECHANISMS

By

Raymond R. McGuire

The purpose of this investigation was to determine the photochemical reaction mechanisms of a class of pesticides whose general structural characteristics can be represented by heptachlor, 1,4,5,6,7,8,8-heptachloro-3a,4,7,7a-tetrahydro-4,7-methanoindene.

The products formed by the photolysis of heptachlor depend upon the conditions under which the reaction is carried out. The irradiation at wavelengths less than 2600A of heptachlor dissolved in non-triplet sensitizing solvents; e.g., hexane, cyclohexane, etc., yields a mixture of two monodechlorination isomers, 1,4,5,7,8,8-hepachloro-3a,4,7,7a-tetrahydro-4,7-methanoindene and 1,4,6,7,8,8-hexachloro-3a,4,7,7a-tetrahydro-4,7-methanoindene, in equal amounts. These isomers were separated by gas chromatography and characterized by n.m.r. spectrometry. This reaction proceeds with a quantum yield at 2537A of 0.025 and shows zero order kinetics. A simple, nonchain, free radical mechanism involving only the 5,6 double bond of heptachlor is postulated for this photodechlorination reaction.

When the photolysis of heptachlor was carried out at higher wavelength (3000A) in a triplet sensitizing solvent such as acetone, the product was a cage compound, 2,3,4,4,5,-6-10-heptachloro-pentacyclo($5.3.0^{4}.0^{3,9}.0^{5,8}$)decane. The quantum yield of the cage compound under these conditions was 9.35×10^{-5} based on the absorption of light by acetone. The reaction showed "0" order kinetics.

When the reaction was carried out at 3000A in mixtures of cyclohexane and acetone, the major photoproduct was found to be cyclohexyl adduct of heptachlor where a cyclohexyl radical replaced the chlorine on carbon 1. Similar products were found when the photolysis was performed in n-hexane, cyclopentane and ethylacetate rather than cyclohexane. The quantum efficiency of decay of heptachlor was found to increase as the amount of acetone decreased. This phenomenon was shown to be a viscosity effect. A nonchain, sensitized triplet mechanism involving only the 2,3 double bond is postulated for the cage and adduct formation. A kinetic mechanism is derived for the sensitized triplet reaction and the specific rate constants are determined for each of the kinetic steps in this mechanism.

Finally, the formation of the cage compound was found to be a reversible process. Irradiation of a cyclohexane solution of the cage compound at 2000A gave heptachlor as the photoproduct. This reaction showed zero order kinetics and had a quantum yield of 0.195.

THE PHOTOCHEMICAL REACTIONS OF HEPTACHLOR: KINETICS AND MECHANISMS

By

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INTRODUCTION

The use of polychlorinated pesticides has contributed greatly to increases in the efficiency of food production in a major part of the world. These pesticides have the advantages of being broad spectrum; low production costs; storage stability; and low direct toxicity to mammals. However, their field stability has become of increasing concern to agriculturists, conservationists, ecologists, legislators and the general public. The polychlorinated pesticides do not degrade rapidly under normal environmental conditions. They accumulate in ever increasing amounts as they travel along the various food chains until they reach toxic concentrations to some birds and fish. Thus they pose a potential danger to man, himself. This persistence has earned for them the label of "hard pesticides."

A great deal of time, effort, and funds have been expended in determining the mechanisms of bio-degradation of these highly chlorinated compounds. Their metabolisms have been studied in biological systems ranging from bacteria to mammals. However, another, and perhaps more important method of environmental degradation, namely photolysis, was largely unexplored until about 1960. Since then, work in this area

has remained fragmentary and has been undertaken largely from the point of view of toxicology rather than that of the fundamental photochemistry involved. Despite this some important information has been accumulated on the photolysis of these materials.

It has been determined that the "hard pesticides" do, indeed, undergo environmental photolysis. A number of the photolytic products have been isolated, identified and reproduced in the laboratory. The toxicity of these photo-products has been examined and found to be vastly different from those of the parent compounds; some being as much as five times as toxic. These environmental photo reactions fall generally into two categories: cage compound formation where the structure of the parent pesticide permits such structure formation to occur; e.g., heptachlor, dieldrin, aldrin, isodrin etc.; and dechlorination where cage formation is not possible, e.g., DDT.

The present investigation was undertaken to determine the mechanisms by which these types of compounds undergo photolysis, to add to the understanding of the primary photo-chemical processes; and to advance the time when it will be possible to design and synthesize a pesticide which is highly toxic to insects and will environmentally degrade to non-toxic materials in a functional period of time.

Heptachlor was chosen as the model compound because of its close structural relationship to most other "hard

pesticides," DDT and its derivatives excepted, and because the structures of two of its major photoproducts had already been determined by R. D. Flotard, working in these laboratories.

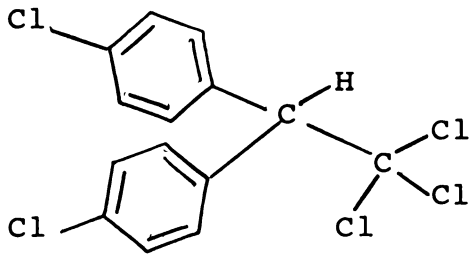
HISTORICAL BACKGROUND

The so-called "hard pesticides" are polychlorinated hydrocarbons which can be divided into two general systems: aromatic and condensed polycyclic systems. The aromatic system is exemplified by DDT, 1,1,1-trichloro-2,2-bis-(p-chlorophenyl)ethane, and its derivatives. The second system, of which heptachlor is a member, is composed of a series of structurally related compounds produced by the Diels-Alder reaction of cyclopentadiene with hexachloro-cyclopentadiene or of cyclopentadiene, ethylene and hexa-chlorocyclopentadiene.

The photochemical reactions of these systems can also be separated into two general categories: Photodechlorina-tion and photocyclization (cage formation). Examples of photodechlorination have been found in both systems while only the condensed polycyclics have been shown to undergo cage formation.

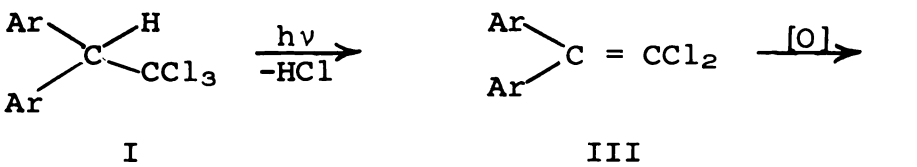
Photodechlorination in the Aromatic System

The prolonged residual action of DDT (I) is due to its low vapor pressure, stability to oxidation and to biodegrada-tion. It was shown by Fleck in 1949 (11) that 4,4'-



I

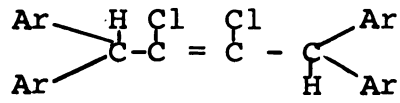
dichlorobenzophenone (II) results from the exposure of DDT to ultraviolet radiation in ethanol solution. This reaction was first thought to proceed by the dehydrochlorination of DDT to yield III, followed by its oxidation to give the chlorinated benzophenone. However, the intermediate



I III II

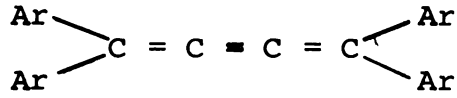
Ar = p-chlorophenyl

dehydrochlorination product (III) could not be isolated even when air was rigorously excluded from the system. The product actually isolated in the absence of air was 2,3-dichloro-1,1,4,4-tetrakis(p-chlorophenyl)butene-2 (IV). It was suggested that (IV) could then lose two molecules of



IV

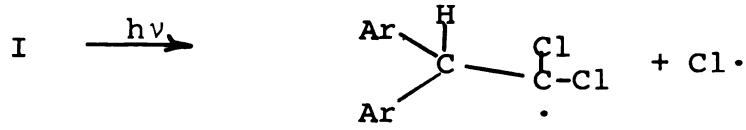
hydrogen chloride to form the butatriene (V) which has been



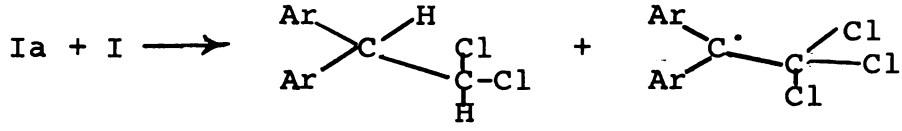
V

shown to yield (II) on oxidation.

Mosier et al. (21) have recently reported on further investigations of the photodegradation of DDT at 2537A both as a solid and in a n-hexane solution and have proposed the following mechanisms for the photochemical reaction.



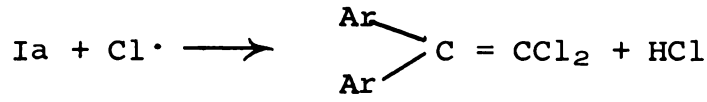
[Ia]



[VI] Ib

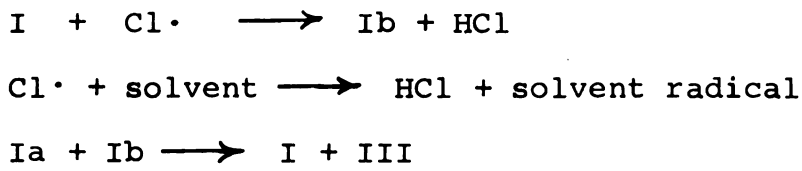
DDT (I) is photodechlorinated by ultraviolet light to give (Ia) and a chlorine radical. (Ia) then reacts with I to give a second radical (Ib) and 1,1,dichloro-2,2-bis-(p-chlorophenyl)ethane (VI) (DDD). (Ia) can also react

with a chlorine radical



III

to give 1,1-dichloro-2,2(p-chlorophenyl)ethylene (III) or (DDE) and hydrogen chloride. DDT can react with a chlorine radical to yield Ib and HCl. The radicals Ia and

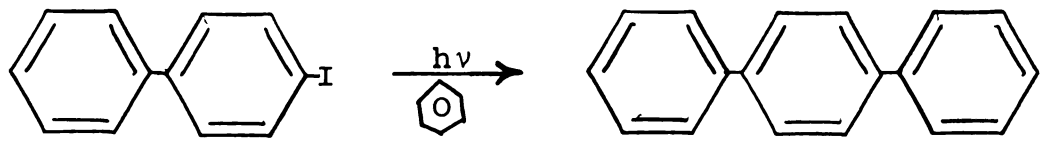


Ib can react to give DDT (I) and DDE (III). A final source of HCl would be the reaction of a chlorine radical with the solvent. III and VI were isolated from their reaction mixtures. These reactions were also run in the presence of the free-radical scavangers iodine and n-butylmercaptan. It was found that the presence of iodine decreased both the rate of disappearance of DDT (I) and the rate of formation of DDD (VI). However, the presence of n-butylmercaptan had no effect on the rate of decomposition of DDT (I) and actually increased the rate of formation of DDD (VI). The authors attribute this to the abstraction of a proton from the mercaptan by the radical (Ia) to form DDD (VI).

Although the conclusion of a nonchain, free radical mechanism is probably correct, the proposed steps cannot be substantiated from the data presented by the authors.

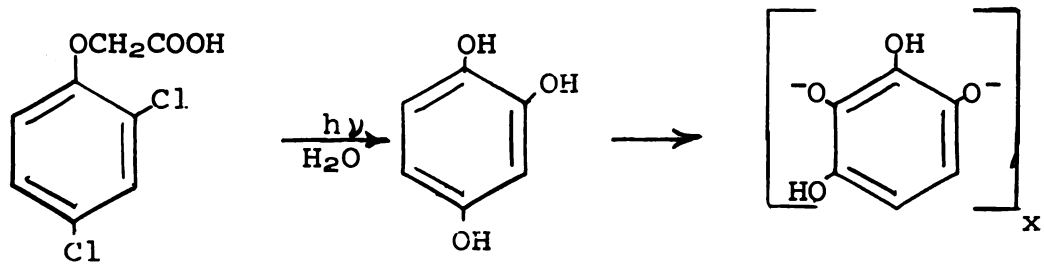
In the first place, the proposed mechanism does not account for the formation of (IV) found by Fleck (11), secondly, most of the photolysis products were not identified, e.g., in one reaction DDT was irradiated in n-hexane for four hours yielding 3% of unreacted DDT, 4% DDD and three unidentified products; thirdly, the fate of the scavangers was not traced and finally, the reported quantum yield (Φ) was improperly calculated.

Although photochemical dehalogenation involving the halogen attached directly to an aromatic ring has been shown to occur quite easily (23,35,36) it has not been noted in the case of DDT. The normal course of these reactions is the abstraction of a proton from the solvent by the radical. However, the aromatic radical can add a solvent radical, i.e., solvent minus proton. Wolf and Kharash (40) have shown that the irradiation of 4-iodophenylbenzene VII in benzene yields 91% p-terphenyl (VIII). In addition,



VII VIII

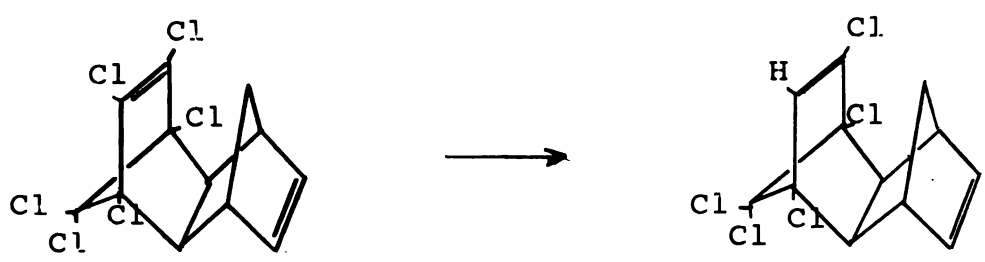
Crosby and Tutass (6), have shown that the irradiation of a water solution of the herbicide 2,4-dichlorophenoxy acetic acid (IX) yields 1,2,4-benztriol (X) and, eventually, polymeric humic acids (XI).



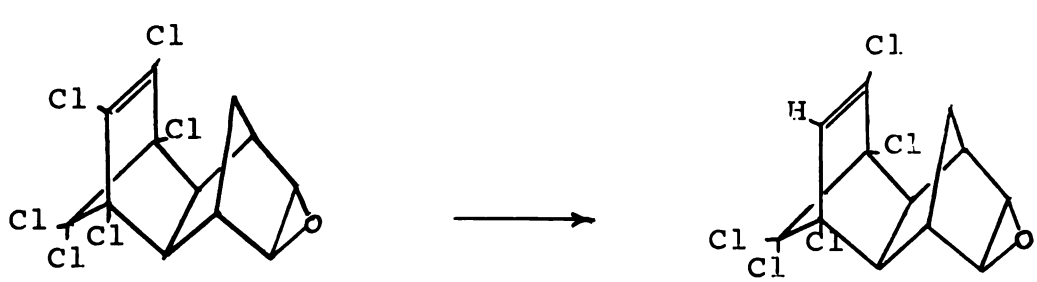
IX (X) (XI)

Photodechlorination in the Condensed Polycyclic System

Photodechlorination in the condensed polycyclic system has only recently been discovered. Henderson and Crosby (15) reported in 1967 that aldrin (XII) and its epoxide dieldrin (XIII) undergo photolysis in hexane solution at 2537Å to give the monodechlorination products XIV and XV respectively. These dechlorination products were

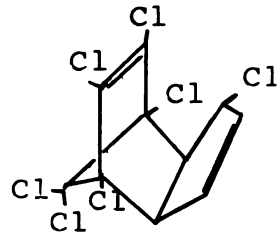


XII XIV



XIII XV

not produced at wavelengths above 2600A. Since solar radiation cuts off at about 2863A (19), it is not surprising that they have not been found under field conditions. Rosen (26) has also reported the photodechlorination of aldrin (XII). Flotard (12) has shown a similar reaction for heptachlor (XVI) while Anderson et al. (1) have investigated the photo-



XVI

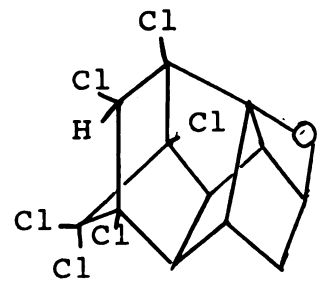
dechlorination of other alicyclic systems.

Cage Compound Formation

The more commonly found products for the photolysis of the condensed polyclic system are cage structures. While cage structures are often formed upon irradiation of the polycyclic systems, even under field conditions, they have not been found as photo-products of the aromatic systems under any conditions.

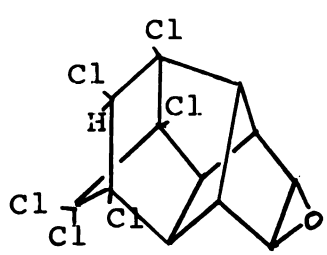
Mitchell (20) in 1961 reported that dieldrin (XIII) and aldrin (XII) were decomposed by 2537A energy radiation and Roburn (25), in 1961, reported finding photoproducts on grass that had been treated with dieldrin and aldrin. Robinson et al. (24) and Rosen et al. (30) isolated these photoproducts

and hypothesized cage structures on the bases of I.R. spectra. Harrison et al. (14) proposed (XVII) as the structure for the cage photoproduct of dieldrin (XIII). This structure is



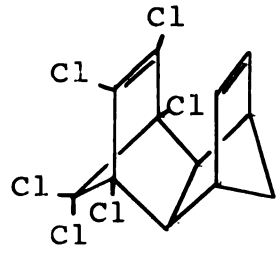
XVII

inconsistent with the nmr spectrum and Parsons and Moore (22) have proposed what is now the accepted structure (XVIII).



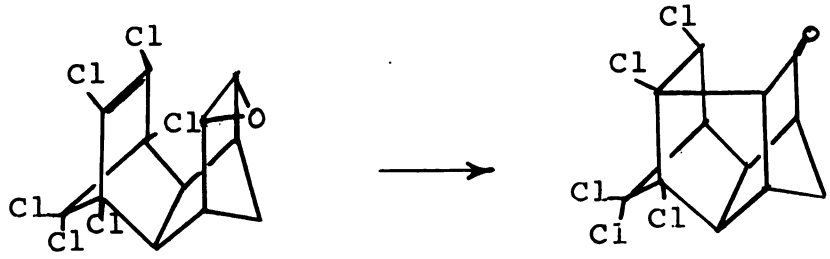
XVIII

Cookson et al. (3,6) had earlier found that isodrin underwent cage formation, as shown by the infrared and ultraviolet spectrum, when irradiated in ethylacetate solution while its isomer aldrin did not. This was taken as proof of the endo-endo structure (XIX) for isodrin and the endo-exo structure



XIX

(XII) for aldrin. Zabik et al. (41) have also shown that the isodrin epoxide endrin (XX) forms a cage compound upon photolysis.

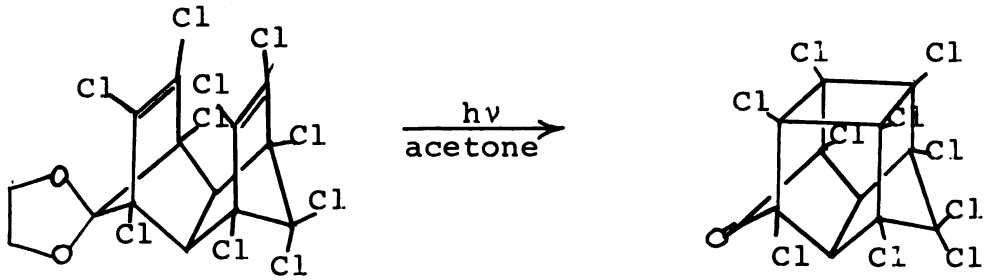


XX XXI

Rosen et al. (27,29) have made the cage photoproducts of aldrin, dieldrin, isodrin and heptachlor and reported them to be sensitized by benzophenone. This is not an established fact, however, since the reactions were carried out in benzene solution and sensitization by benzene cannot be ruled out by the experiments they performed. While it is likely that a reaction sensitized by benzophenone, which has a lowest triplet energy of 69 kcal/mole, would also be sensitized by benzene with a triplet energy of 85 kcal/mole

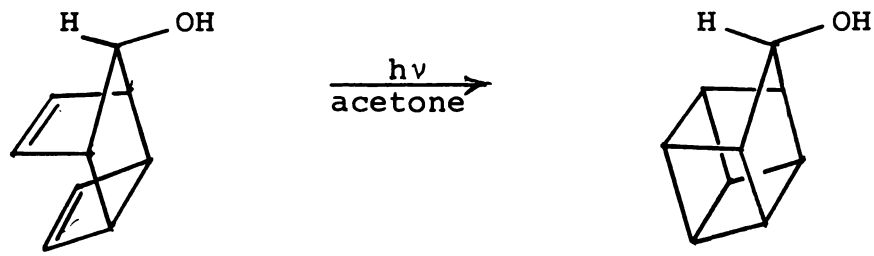
(37) the converse is not necessarily true.

Cage formation, or 4-cycloaddition, has been shown to occur in nonpesticide systems. Stedman and Miller (33) have formed the cage ketone, hexacyclo[5.4.1.$0^{3,6}$.$0^{3,10}$.$0^{8,9}$-$0.^{8,11}$]dodecane-4-one (XXII) by irradiating the diene ketal



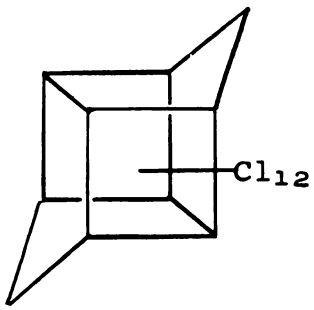
XXIII XXII

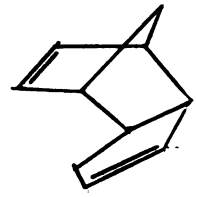
(XXIII) in acetone. It will also occur in the absence of chlorinated double bonds. Barborak and Pettit (2) have obtained homocubanol (XXIV) by irradiating an acetone solution of the diene XXV. The reaction seems to be



XXV XXIV

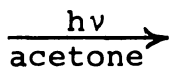
regiospecific. Dilling et al. (10) have obtained the diene (XXVI) by treating the symmetrical chlorinated pentacyclodecane XXVII with lithium metal in tertiary butanol; however,

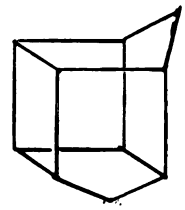




XXVII XXVI

irradiation of the diene XXVI in acetone yields only the unsymmetrical pentacyclodecane XXVIII (31,32).

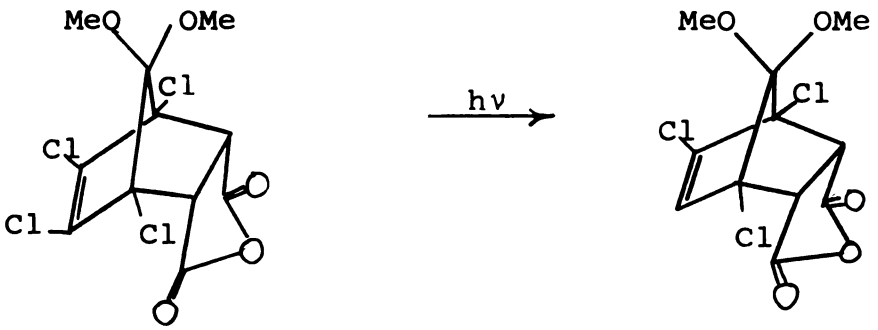
XXVI 



XXVIII

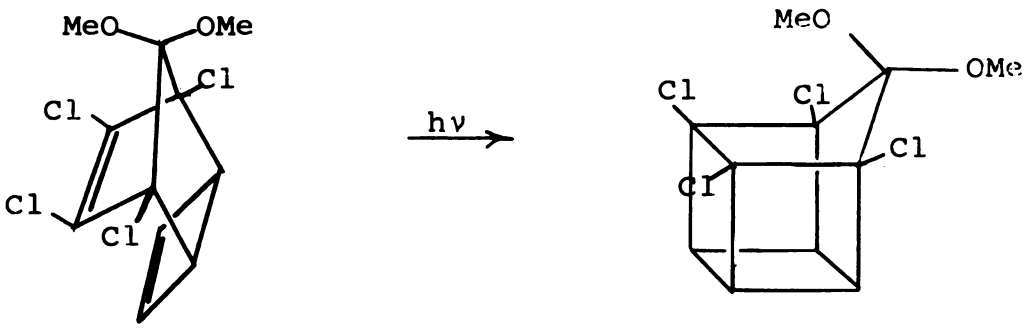
Photodechlorination vs. Cage Formation

In their study of the photodecomposition of dieldrin and aldrin, Henderson and Crosby (15) found that they did not get photodechlorination on irradiating at wavelengths above 2600A. They also found that when they did get photodechlorination they did not get cage formation. Anderson et al. (1) have recently studied the reaction path selectivity in some related alicyclic systems. They have found that the tetrachloro ketal XXIX gave only the trichloro ketal XXX on irradiation at wavelengths above 2100A in ether solution and did not react at all when irradiated above 2900A in



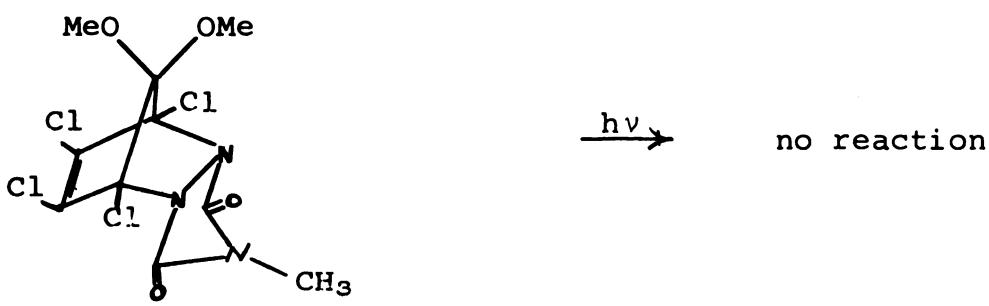
XXIX XXX

the presence of benzophenone. However the ketal XXXI gave the cage compound (XXXII) only when irradiated either in acetone or in carbon tetrachloride with benzophenone added.



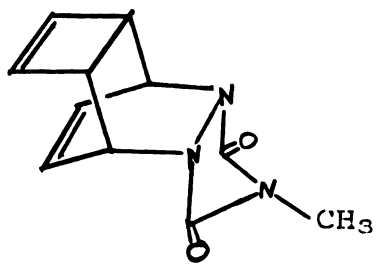
XXXI XXXII

They have also shown that the urazole XXXIII is stable under reaction conditions which normally leads to photodechlorination

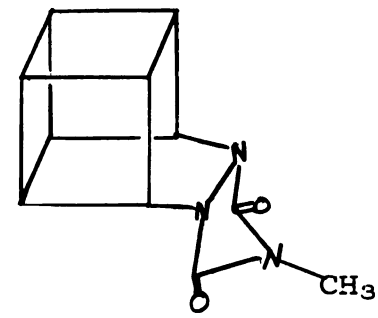


XXXIII

but that the urazole XXXIV yields the cage compound XXXV when



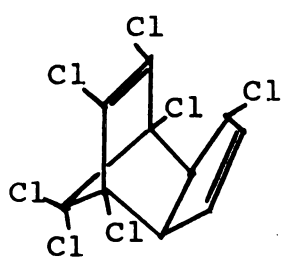
XXXIV



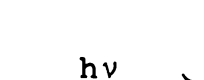
XXXV

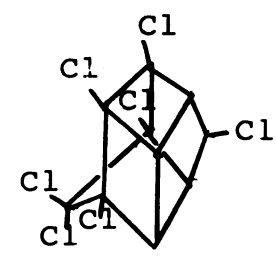
irradiated in acetone solution. They concluded that the photodechlorination takes place by way of a singlet excited state which is quenched by the urazole ring and that cage formation, unquenched by a urazole ring but sensitized by both benzophenone (triplet energy = 69 kcal/mole) and acetone (triplet energy = 76 kcal/mole)(34), goes through an excited triplet.

This conclusion (singlet vs. triplet) has been confirmed by Flotard (12) in his study of the heptachlor system. He has shown that heptachlor XVI gives the cage compound XXXVI



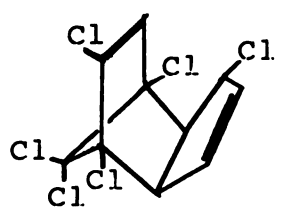
XVI



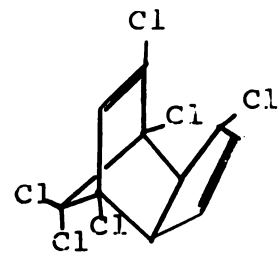


XXXVI

when irradiated in acetone solution but that a mixture of photodechlorination isomers XXXVIIa and XXXVIIb are produced when the reaction is carried out in hexane or cyclohexane.



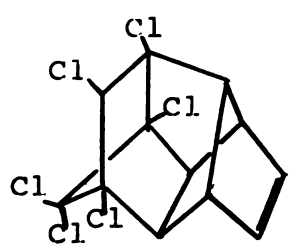
XXXVIIa



XXXVIIb

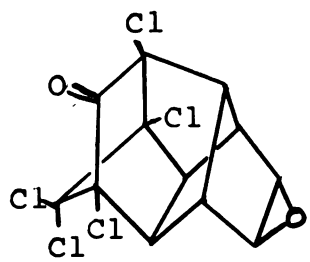
Toxicity of Photoproducts

The increased toxicity of the cage photoproducts is a cause for great concern. Brown et al. (4) and Rosen and Sutherland (28) have reported that the cage photodieldrin (XVIII) is from 2 to 10 times as toxic to several vertebrates as is dieldrin (XIII) itself. The cage compound (XVIII) has also been shown to be more toxic to insects (28,30). The cage photoaldrin (XXXVIII) has been shown to be eleven times more toxic to mosquito larvae than aldrin (XII) itself (34).



XXXVIII

Kahn et al. (16) have attributed this increased toxicity to the formation of XXXIX in the insect metabolism of both cage photoaldrin (XXXVIII) and cage photodieldrin (XVIII). This metabolite is not found in the insect metabolism of either aldrin (XII) or dieldrin (XIII). This metabolite (XXXIX) was first discovered by Klein et al. (18) in the metabolism of dieldrin by male mice and was shown to be significantly more toxic than dieldrin itself. As yet the toxicities of the photodechlorination products have not been reported.



XXXIX

EXPERIMENTAL

Reagents

Heptachlor

The heptachlor used in this study was obtained from R. D. Flotard, of these laboratories, who had prepared it as follows. A commercial sample of heptachlor, 25% by weight, was dissolved in acetone, filtered and the solvent evaporated. The resulting solid was redissolved in n-hexane and chromatographed on an activated alumina column. Fifty milliliter fractions were collected and tested by vapor phase chromatography. Fractions three and four, which contained the heptachlor, were combined and evaporated to dryness. Heptachlor purified in this manner was shown to be identical, when gas chromatographed using an electron capture detector, with a sample purchased from City Chemical Corp., of 99+% purity ("ESA" Pesticide Reference Standard).

Sensitizers and Solvents

The n-hexane, cyclohexane and acetone used in this study were "Distilled in Glass" solvents purchased from Burdick and Jackson Laboratories Inc., and were used as received.

The benzophenone was purified by vacuum sublimation just prior to use.

Instrumentation

Gas Chromatograph

All gas chromatograms were obtained using a Beckman Model GC-4 Gas chromatograph equipped with a fraction collector. Two types of detectors were used: a hydrogen flame ionization detector for concentrated samples such as those used for fraction collecting; and an arc discharge electron capture detector for more dilute solutions such as those used for kinetic studies.

The column packing was prepared by hand shaking approximately 9 grams of 60/80 mesh Gas Chrom Q with approximately 1 gram of DC-11 silicone grease dissolved in 500 ml of ethylacetate. The slurry was then vacuum filtered, air dried and heated in a vacuum oven at 100°C for 24 hrs. The material was then packed into two stainless steel columns, one 1/8" by 6', the other 1/4" by 5' using a vibrator. The packed columns were conditioned on a GC-4 for 5 days at 220°C with periodic injections of cyclohexane and a 1% solution of heptachlor in cyclohexane.

Ultraviolet Spectrophotometer

Ultraviolet spectra were determined in a Beckman Model DB-G Ultraviolet Grating Spectrophotometer.

Infrared Spectrophotometer

All infrared spectra were determined either as potassium bromide pellets (solids), or as smears on potassium bromide pellets (viscous liquids). Spectra were determined on a Perkin-Elmer model 337 Grating Spectrophotometer.

N.M.R. Spectrometer

Nuclear magnetic resonance spectra were determined on a Varian Model 56/60 Spectrometer in deuterated chloroform with tetramethylsilane as an internal standard.

Mass Spectrometer

Mass spectra were determined in a L.K.B. Model 9000 Mass Spectrometer equipped with mass marker, peak matcher and gas chromatographic inlet. Samples were injected as acetone or methylene chloride solutions through the gas chromatograph. The column was 6' by 1/8" packed 2% OV 225 on 120 mesh gas chrom Q.

Irradiation Sources

Four sources of ultraviolet radiation were used in the course of this study. Large scale preparations were run using a 200 watt, medium pressure, wide band mercury discharge immersion lamp manufactured by the Hanovia Lamp Division of Engelhart-Hanovia Inc. For exploratory irradiations and for kinetic determination at 2000A and 3660A a high energy

deuterium source for the Beckman DB-G spectrophotometer (with an effective band width of 55A) was used. This lamp yields about three times the energy of the normal hydrogen source used in this instrument and was found to be adequate for these irradiations. The irradiations at 3000A were carried out in a Rayonet Photochemical Reactor manufactured by the Southern N. E. Ultraviolet Co. This reactor is equipped with filtered medium pressure lamps having a peak output at 3000A. The band width is unknown. The final source was a NFU-300 low pressure mercury discharge lamp manufactured by the Nester-Faust Co. This lamp yields 96% of its total energy as a single line at 2537A as measured with the DB-G. This lamp was further filtered by a K_2CrO_4, K_2CO_3 solution as described by Wagner (38) to give approximately 99% pure 2537A radiation.

Procedure

Determination of Evolved Hydrogen Chloride

A 150 ml volume of a 1.0% solution of heptachlor in cyclohexane was placed in a reaction vessel having a fritted glass bottom and two sidearms for introducing gas through the solution. The solution was irradiated with the 200 watt immersion lamps for periods of 90 to 130 min. Dry nitrogen was continuously passed through the reaction mixture, then through a dry ice cold trap and into 150 ml. of 0.2805 N sodium hydroxide. After completion of the reaction purging

with dry nitrogen was continued for 15 to 20 min. at which time the bottom stopcock of the reaction vessel was opened and the reaction mixture was drained into 50 ml of standard base. The reaction flask was washed out with distilled water and the washings were drained into the base. The aqueous layer was separated, combined with the base removed from the trap and back titrated with 0.2184 N hydrochloric acid to a phenolphthalein endpoint.

Determination of Light Intensity and Quantum Yield

The intensities of each of the sources, with the exception of the wide band prep source, were measured actinometrically using a potassium trisoxalatoferrate III actinometer according to the method described by Calvert and Pitts (5). The quantum yields (ϕ) were calculated from the formula, $\phi = n/I_o^a Z$, where n is the number of molecules of product produced per minute or the number of molecules of reactant disappearing per minute, I_o^a is the intensity of light at the inside face of the reaction vessel as measured by the actinometer and expressed in quanta/minute, and Z is the fraction of this light which is absorbed by the reactant. This equation can be expressed as $\phi = k^o A\ V/I_o^a\ X$ where k^o is the zero order rate constant (in moles/liter minute), A is Avagadro's number and V is the volume of the reaction vessel in liters.

Kinetic Measurements

Kinetic measurements were determined using the gas

chromatograph. The 6' by 1/8" column described above was used in conjunction with the electron capture detector. The flow of prepurified helium and the temperature were adjusted to give adequate peak separation for accurate measurements without excessive broadening or tailing. Under the conditions normally employed, 130°C and 40 ml/min. helium flow, the photodechlorination isomers eluted in two minutes; heptachlor, 3 minutes; cage compound, 4.2 minutes and the cyclohexyl adduct in 5.5 minutes from the solvent peak. The general procedure used in these rate measurements is as follows.

A sample of heptachlor, 1.0×10^{-4} molar, dissolved in the solvent to be studied was pipetted into the reaction vessel. For irradiations at 3000A, spectronic '20' sample tubes containing 6.0 ml each were used as reaction vessels. All other irradiations were carried out in silica DB cells containing 3.7 ml of sample. The vessels were stoppered, specially designed septum stoppers were used for the DB cells, and placed in the reactors. A carrosel was used with the 2537A source to insure even irradiation of all samples. (The irradiation sources were all operated for an hour prior to exposure of the reaction mixture to allow them to stabilize.) A 0.5 microliter sample of the starting material was injected into the gas chromatograph and the supression voltage adjusted so as to give a peak height of 60 to 80% of the full scale. At various times, depending on

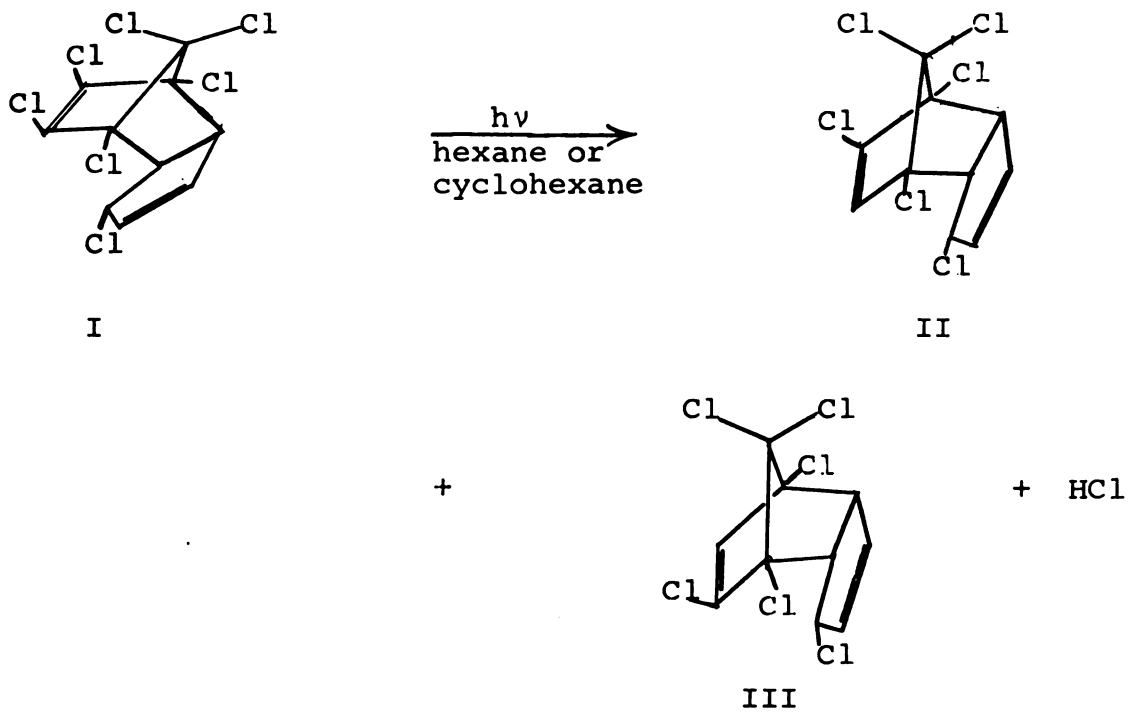
the rate at which the reaction was progressing, 0.5 microliter samples were removed from the reaction flasks and injected into the gas chromatograph. The areas of the peaks were measured with a planimeter, normalized and expressed as a percentage of the total peak area. This procedure was deemed to be valid since the reactions were allowed to proceed only to the point of initiating competing reactions.

Separation and Identification of Products

The photodechlorination isomers and the cage compound had been identified and characterized by Flotard (12). Other products were obtained by collecting fractions from the gas chromatograph using the 5' by 1/4" column described above. These samples were identified either by spectroscopic methods or by comparison of their chromatographic behavior with authentic samples.

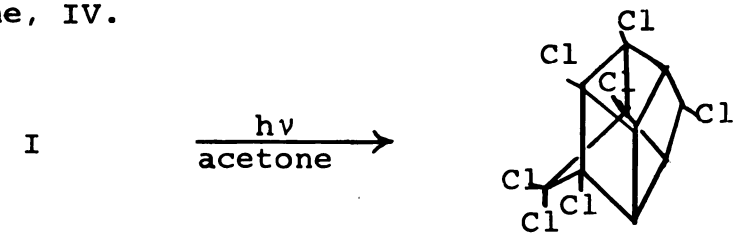
RESULTS AND DISCUSSION

Flotard (12) reported that the products of the photolysis of heptachlor (1,4,5,6,7,8,8-heptachloro-3a,4,7,7a-tetrahydro-4,7-methanoindene)(I) were dependent upon the reaction conditions. When the photolysis was carried out with a high pressure, broad spectrum lamp in either hexane or cyclohexane the predominant products were a pair of monodechlorination isomers, 1,4,5,7,8,8-hexachloro-3a,4,7,7a-tetrahydro-4,7-methanoindene (II) and 1,4,6,7,8,8-hexachloro-3a,4,7,7a-tetrahydro-4,7-methanoindene (III). Hydrogen chloride was also evolved in the course of this reaction.



I II III

When the reaction was carried out in acetone, a triplet sensitizing solvent, the photolysis product was the "cage" compound 2,3,4,4,5,6,10-heptachloro-pentacyclo(5,3.$0^{2,6}$.$0^{3,9}$-.$0^{5,8}$)decane, IV.



IV

Rosen et al. (29) have obtained the same product (IV) from the photolysis of I in the presence of benzophenone in benzene as a reaction solvent. Flotard (12) suggested that, by analogy to the findings of Anderson et al. (1), that the photodechlorination of heptachlor (I) proceeds through a singlet transition state, while the 4-cyclo addition ("cage" formation) proceeds by way of a triplet state. This study was undertaken to gain a more complete understanding of the mechanism or mechanisms of these reactions.

Photodechlorination

Stoichiometry

An initial experiment was performed in an attempt to establish a 1:1 relationship between the number of moles of hydrogen chloride produced and the number of moles of heptachlor reacting. It quickly became apparent that the results had little significance since the hydrogen chloride to heptachlor ratios obtained were usually high and depended upon the

length and intensity of irradiation. On only one occasion was the expected 1:1 relationship found. This indicates that the secondary reactions, under these conditions, evolve hydrogen chloride much faster than does the primary, monodechlorination reaction. Further experimentation along these lines was abandoned at this point.

Wavelength Dependence

Henderson and Crosby (15) in their investigation of the photodechlorination of dieldrin and aldrin (see Historical Section) found that the reaction did not occur at wavelengths above 2600A. The analogous situation was found in the photodechlorination of heptachlor. Irradiations of heptachlor solutions were carried out at wavelengths ranging from 3000A to 2000A with the principal work carried out at 2537A. Even though the extinction coefficient of heptachlor is essentially zero at wavelengths above 2800A and is low at 2537A ($\epsilon_o \approx 75$), the reaction proceeds smoothly at the latter wavelength. Solutions irradiated at 3000A remained unchanged after three hours. Thus, the results for the heptachlor system are in agreement with those found by Henderson and Crosby for related systems.

Kinetics of the Reaction

The photolysis of a 10^{-4} M solution of heptachlor in cyclohexane proceeds smoothly at 2537A. For irradiation times of up to three hours ($\approx$10% reaction) the only products detected were the pair of monodechlorination isomers reported by Flotard (12). No attempt was made to separate these

isomers and they were treated, kinetically, as one product. Hydrogen chloride and bicyclohexyl were also identified in the reaction mixture. The reaction was carried out in both open and closed vessels. As the rates were essentially the same, showing no effect by the evolved hydrogen chloride, the data was combined. A plot of concentration versus time gives a straight line showing the reaction to be "0" order as expected (Figure 1). The rate, determined from the slope of the least squares line, is 6.25×10^{-8} moles/liter·minute. Based on an effective intensity of 5.66×10^{15} quanta/minute (only 2% of the incident radiation is absorbed), this gives a "0" order rate constant $k^{o} = 1.11 \times 10^{-23}$ moles/liter·quanta or a quantum yield $\phi = 0.025$. Flotard's findings (12) showing that this reaction is not sensitized by acetone were corroborated in this study.

Identification of the Photoisomers

Flotard (12), in his study of the photodechlorination of heptachlor, referred to the monodechlorination isomers by their order of elution from the gas chromatograph (peak 1 and peak 2) without attempting to assign definite structures to them. However, a close inspection of the nmr spectra of the isomers (Table I) makes it possible to assign structures to these isomers. Examination of the molecular model of heptachlor (I) shows that the allyl hydrogen (H_c in Table I) should be shielded by the electronic clouds of both the chlorinated double bond and the chlorine attached to carbon 6. Replacement of the

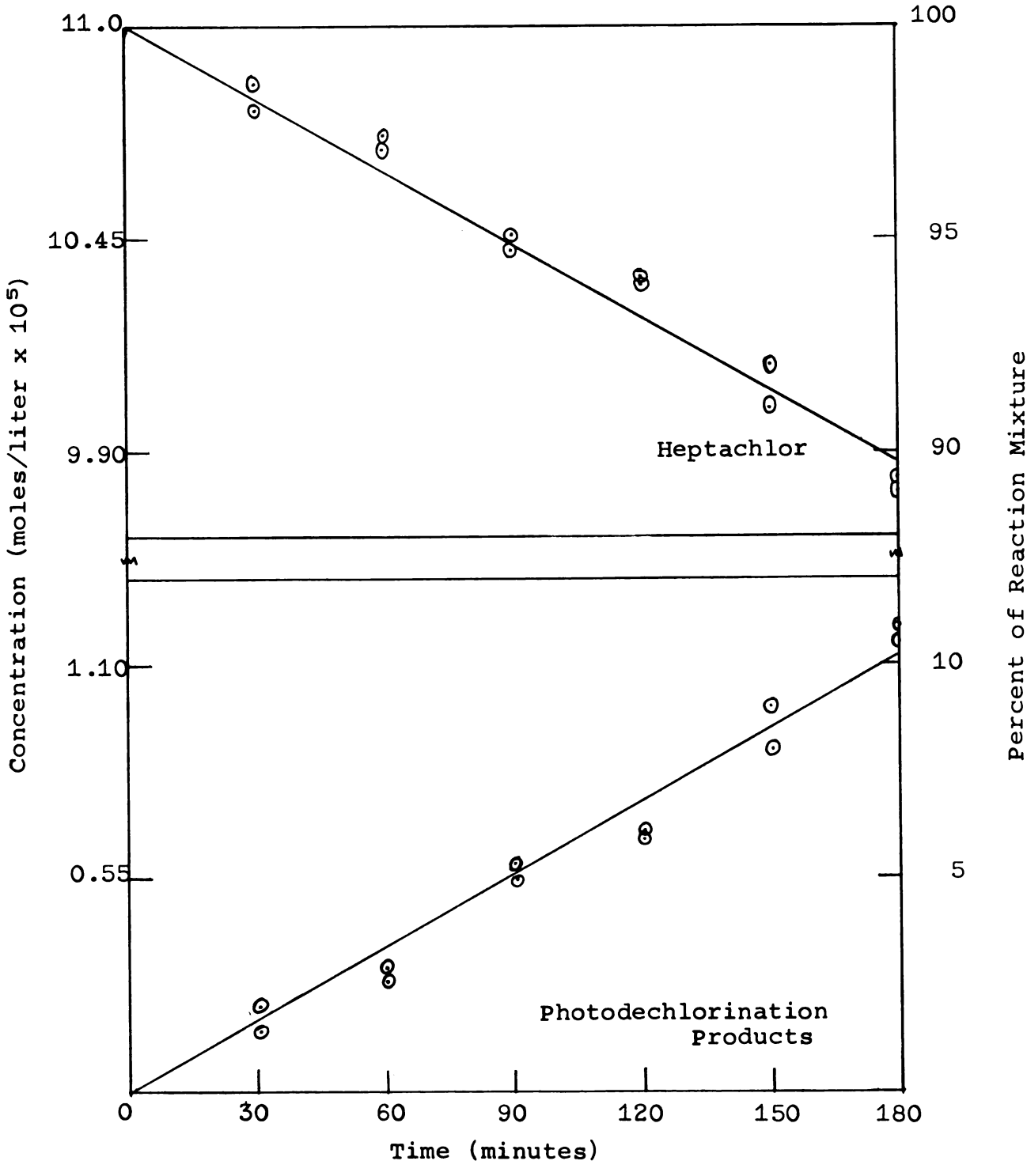
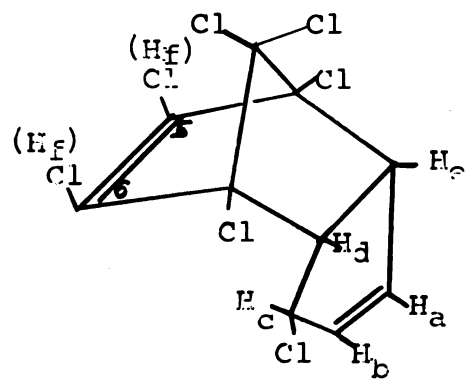


Figure 1. Rate of photodechlorination of heptachlor at 2537A.

TABLE I

The NMR Chemical Shifts of Heptachlor and Its Monodechlorination Isomers



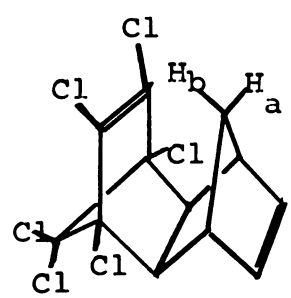
(I)

Proton	Chemical Shifts (tau)		
	Heptachlor	Peak 1	Peak 2
H_a } H_b	4.1 (s)	4.25 (s)	4.30 (s)
H_c	5.2 (m)	5.42 (m)	5.5 (m)
H_d	6.5 (m)	6.5 (m)	6.5 (m)
H_e	5.9 (m)	6.07 (m)	6.09 (m)
H_f	---	4.20 (s)	4.20 (s)

(s) = singlet; (m) = multiplet

electronegative chlorine atom from either carbon 5 or carbon 6 by a hydrogen (H_f) should cause an increase in size of the electronic cloud associated with the 5,6 double bond and, consequently, increase the shielding of H_c causing an upfield shift of its nmr absorption (an increase in the tau value of the chemical shift). Table I shows that this upfield shift of H_c does, indeed, occur in the nmr spectra of both peak 1 and peak 2. However, the replacement of the chlorine on carbon 6, while it increases the shielding due to the double bond, eliminates the shielding due to the replaced chlorine. Consequently, the replacement of the chlorine on carbon 6 would have less of an overall shielding effect on H_c than replacement of the chlorine on carbon 5. On this basis structure II is assigned to peak 1 and structure III to peak 2.

Rosen (26) has recently noted the same phenomenon (change in the chemical shift of a nearby proton upon dechlorination) in his study of the photolysis of aldrin (V). Replacement of one of the vinyl chlorines (they are equivalent due to the



V

symmetry of aldrin) caused a shift in the tau value for H_b.

The shift was, however, in the opposite direction from that found on dechlorination of heptachlor (τH_b = 8.40 in aldrin, τH_b = 7.34 in the photoproduct). Examination of the molecular model of aldrin shows that H_b lies in the deshielding field of the double bond rather than being shielded by it. Further deshielding by replacement of one of the vinyl chlorines by hydrogen is, therefore, to be expected.

The Sensitized Triplet Reaction, Cage Formation

Anderson et al. (1) have shown that cage formation occurs through an excited triplet state and is susceptible to sensitization. Flotard (12) and Rosen et al. (29) have confirmed this finding for the heptachlor system. Rosen claims that the cage formation of heptachlor is sensitized by benzophenone (E_T = 69 kcal/mole) (37). Our investigations have failed to substantiate this claim. A 10^{-4} M cyclohexane solution of heptachlor, 10^{-2} M in benzophenone, remained unchanged after a two hour irradiation at 3660A (n-π^* transition for benzophenone). However it should be noted that Rosen carried out his irradiations in benzene solutions. Benzene is, itself, a triplet sensitizer (E_T = 85 kcal/mole) (37) although a poor one. It is possible, then, that what Rosen observed was, actually, sensitization by benzene.

Photolysis of Heptachlor in Pure Acetone

The irradiation of 3000A of a 10^{-4} M solution of heptachlor in acetone proceeds smoothly yielding the cage compound

IV as the sole product during irradiation periods of up to 60 minutes ($\approx$10% raction). A plot of cage compound concentration versus time gives a straight line, showing "0" order kinetics (Figure 2). The reaction rate was determined to be 1.21×10^{-7} moles/liter·minute giving a "0" order rate constant (k^o) and quantum yield (ϕ) of 2.57×10^{-26} moles/liter·quanta and 9.35×10^{-5} respectively. These values are based on the absorption of the light, measured at 4.72×10^{18} quanta/minute, by the acetone. (The dependency of the rate on the concentration of sensitizer will be discussed in the section on mixed solvents.) It should be noted here that the low value of the quantum efficiency is not a true measure of the facility of this reaction. This term, in a sensitized reaction, must include a term for the quantum efficiency of intersystem crossing of the sensitizer. This is a very inefficient process in acetone ($\approx 10^{-3}$). Thus, the quantum yield of a sensitized reaction is, primarily, a measure of the efficiency of the sensitizer in converting the incident energy to a usable form.

Henderson and Crosby (15) and Anderson et al. (1), in their investigations of the potolytic reactions of systems similar to heptachlor, have found that the two processes, cage formation and photodechlorination, do not occur under the same reaction conditions. Under reaction conditions where photodechlorination occurs, lower wavelengths and no sensitizer, no cage compound formation is detected and when cage formation does occur, higher wavelengths in the presence of

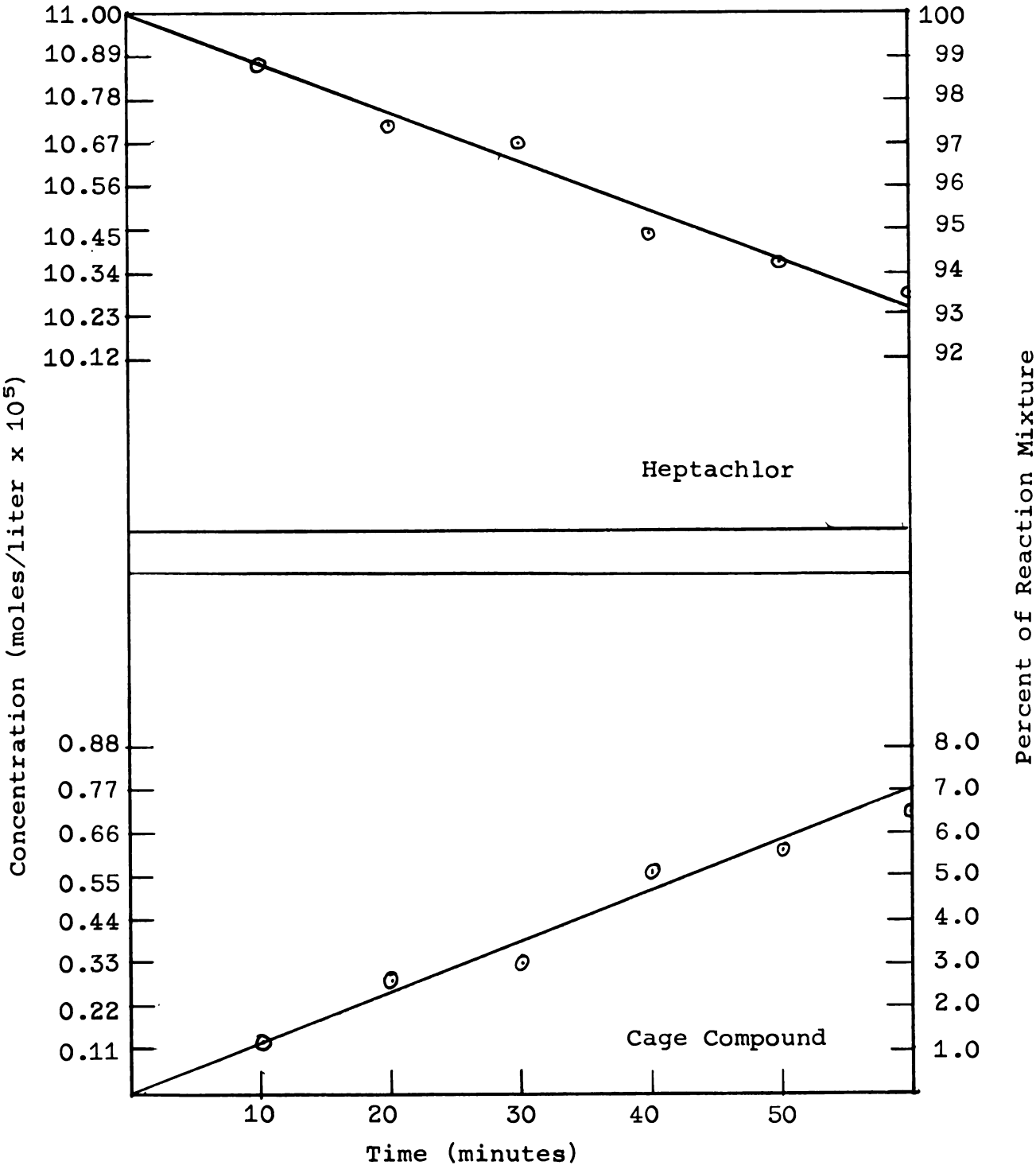


Figure 2. Rate of formation of cage compound in acetone and 3000A.

a triplet sensitizer, there is no photodechlorination. This is in contrast to Flotard's finding that when heptachlor was photolyzed in hexane solution (photodechlorination) cage compound was also obtained in $\approx$ 5% yield. Our investigation has shown that the irradiation of undegassed solutions of heptachlor in cyclohexane at 2200A yielded a small amount of cage formation. This is probably due to sensitization by oxygen. Since Flotard's reactions were carried out with undegassed solutions using a high pressure lamp (continuum of wavelengths to about 1850A) it is understandable that a small amount of cage formation was obtained in nonsensitizing solvents.

Photolysis of Heptachlor in Mixed Solvents

Based on the above discussion it is possible to conclude that either the photodechlorination and cage formation proceed through different and distinct mechanisms or that the efficiency of intersystem crossing (S' $\longrightarrow$ T') is very low. Based on the study of the photolysis of heptachlor in mixed solvents it is possible to determine which of these possibilities is correct.

The photodecomposition of heptachlor proceeds rapidly in mixed cyclohexane/acetane solutions (10% to 50% acetone by volume) at 3000A. Unexpectedly, the rate of decay of heptachlor is much greater in the mixed solvents (2.49×10^{-6} moles/liter·minute for 10% acetone) than in pure acetone (1.21×10^{-7} moles/liter·minute), and the major reaction

product is not the cage compound (IV) but a solvent adduct (VI) where a cyclohexyl group replaces the allyl chlorine attached to carbon 1. (The identification and structure determination of this compound is discussed in a separate section below.) The rates of formation of cage compound (IV) and cyclohexyl adduct (VI) and the rate of decay of heptachlor (I) are shown in Figures 3 through 7 and summarized in Table II. Inspection of Table II shows that the values of the "0" order rate constants for the reaction in pure acetone are out of line with the other values.

It is usually assumed in photochemical reactions that quenching or sensitization reactions are diffusion controlled and that the rate constant, kq, varies as a function of $1/\eta$. Wagner and Kochever (39) have shown that for solutions of low viscosity $Kq < k$ diffusions. If the sensitization step is rate controlling or of the same order of magnitude as the rate controlling step (this is not unlikely in this case where the sensitization if such an inefficient process), the rates of reaction should be related to the amount of sensitizer (X) and the speed with which the reactant (heptachlor) comes in contact with the sensitizer (acetone) which is in turn related to the viscosity (η^n). Thus, if log of the rate constant or quantum efficiency divided by the mole fraction of sensitizer is plotted against the log of the viscosity a straight line should result of slope en. That this is indeed the case can be seen in Figures 8 through 10. These figures show that the

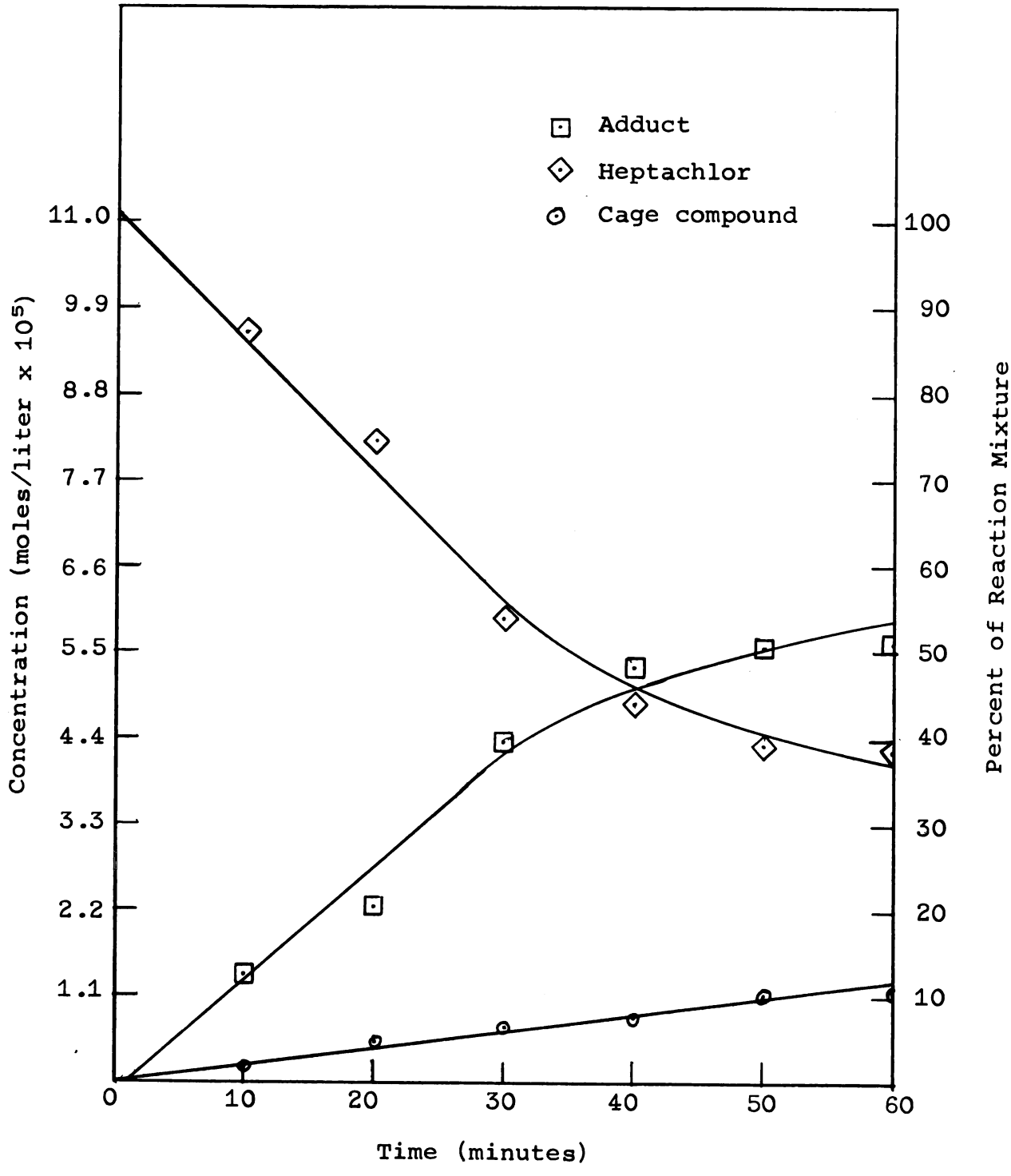


Figure 3. Reaction of heptachlor in 50% acetone, 50% cyclohexane.

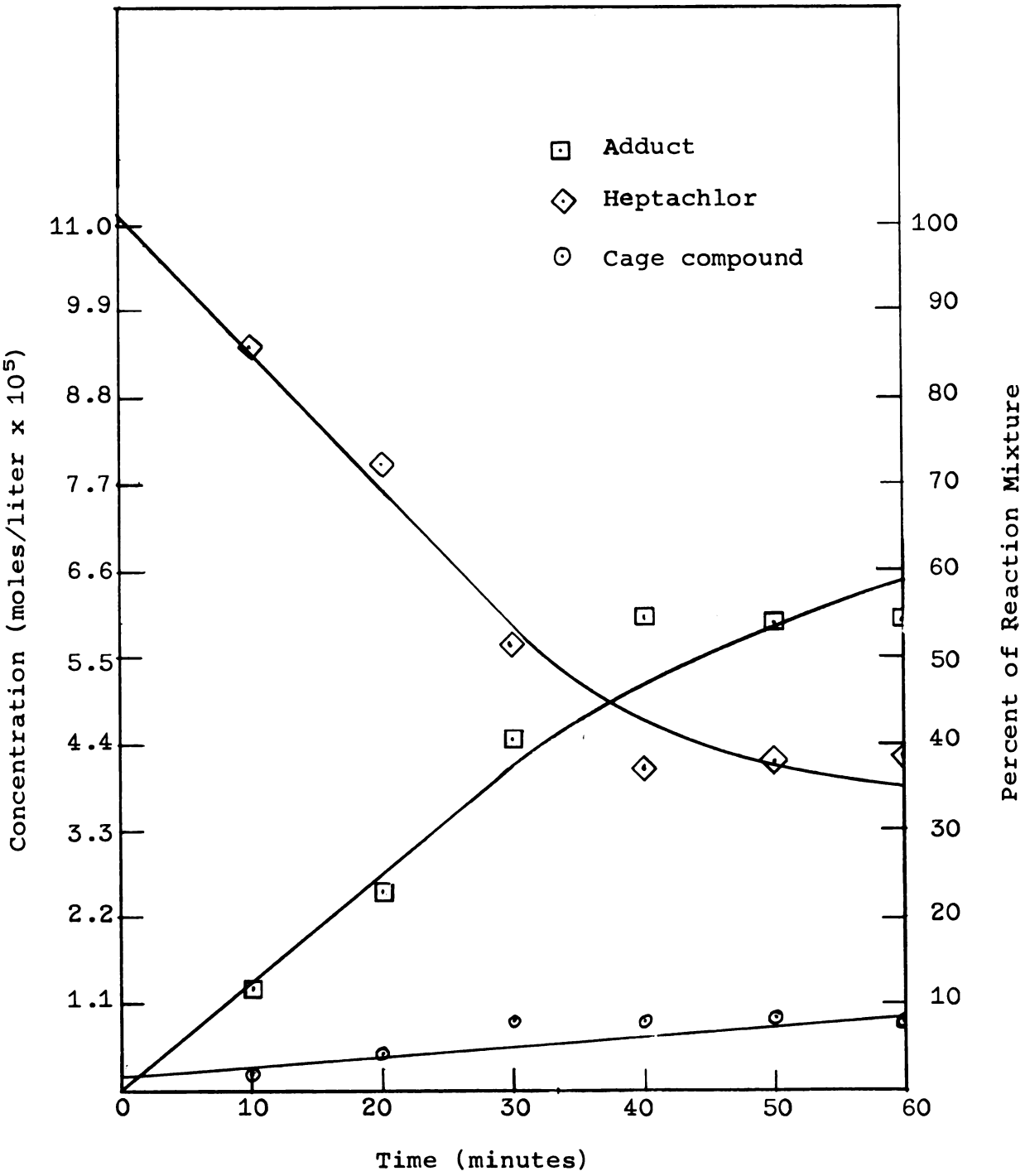


Figure 4. Reaction of heptachlor at 3000A in 40% acetone, 60% cyclohexane.

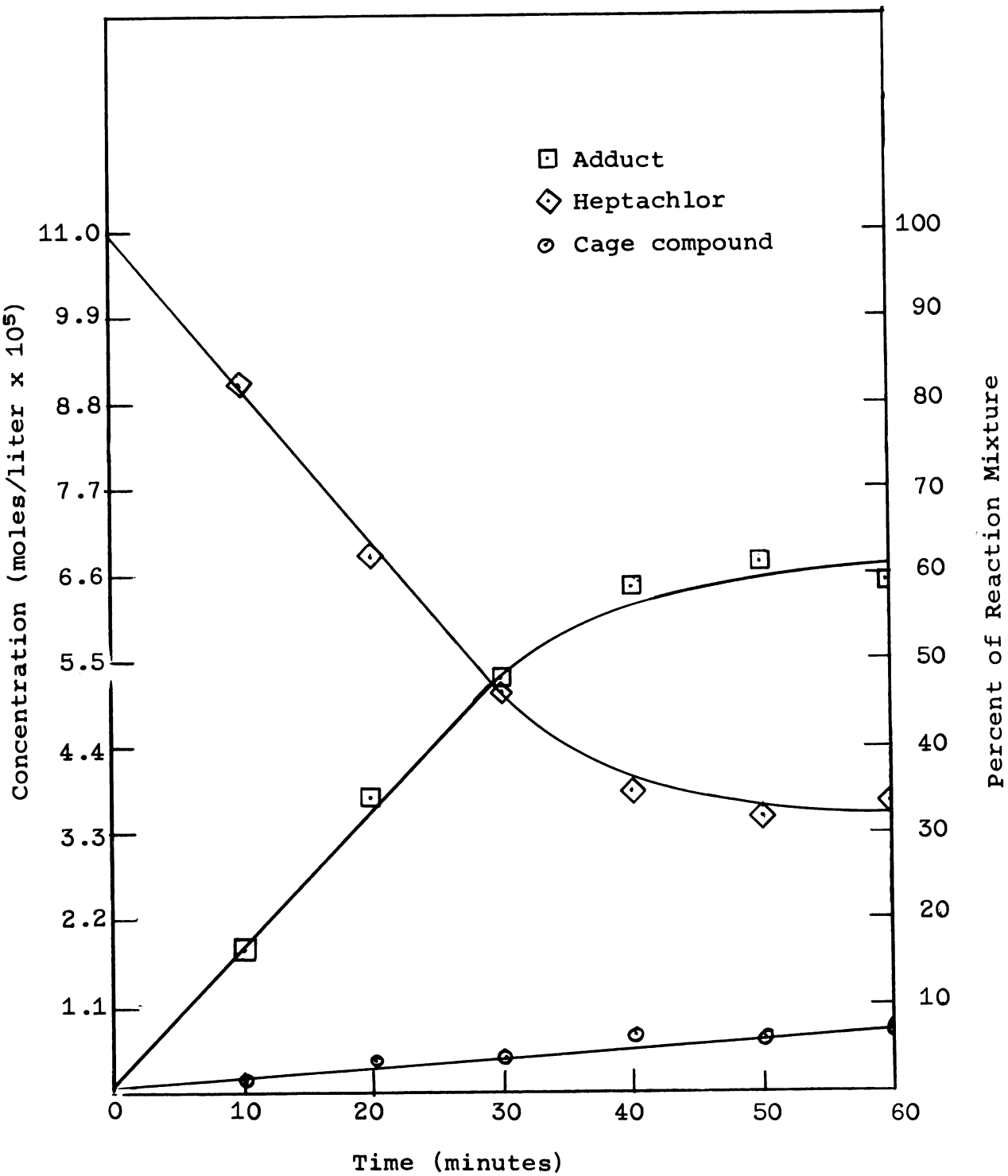


Figure 5. Reaction of heptachlor at 3000A in 30% acetone, 70% cyclohexane.

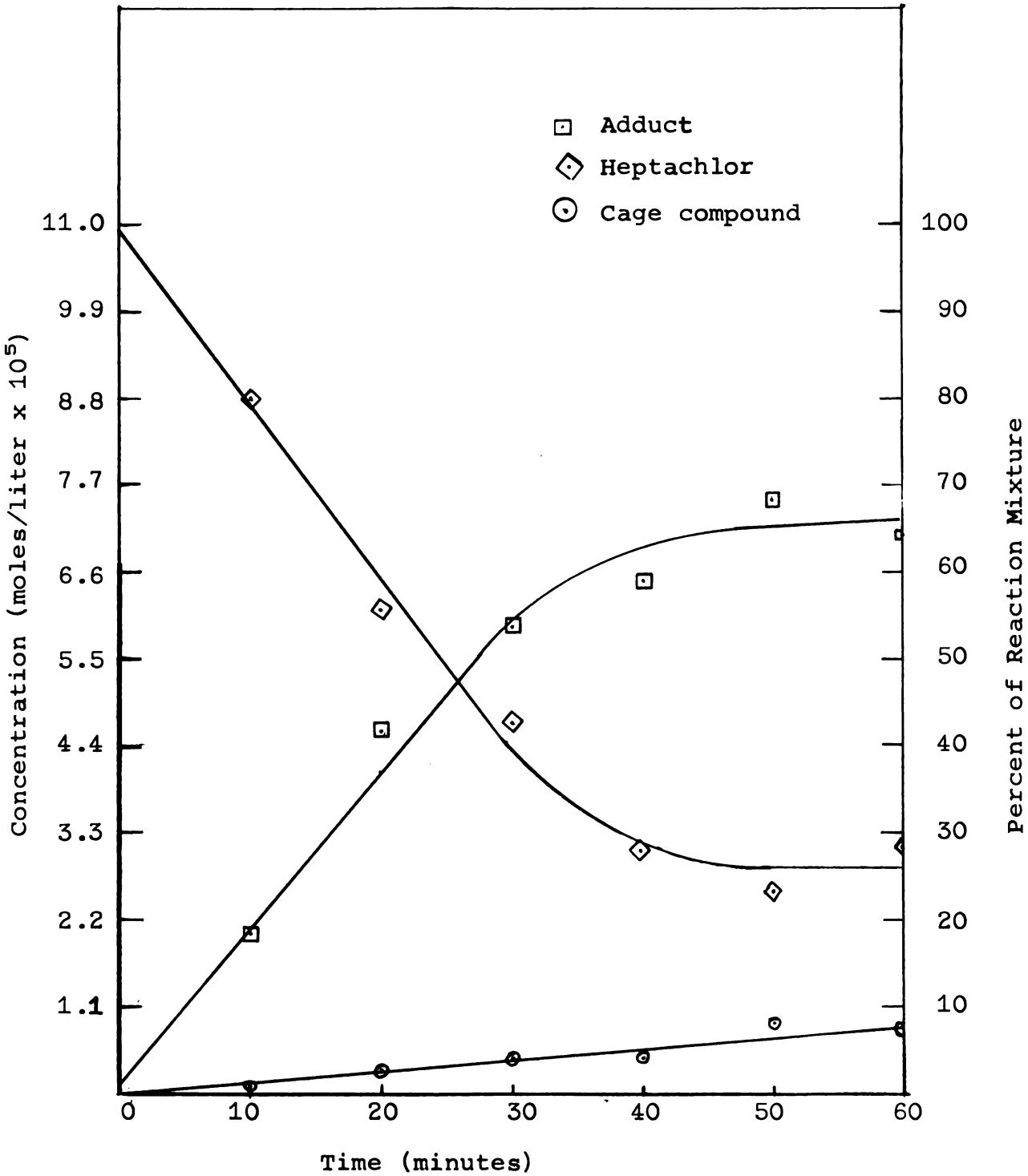


Figure 6. Reaction of heptachlor at 3000A in 20% acetone, 80% cyclohexane.

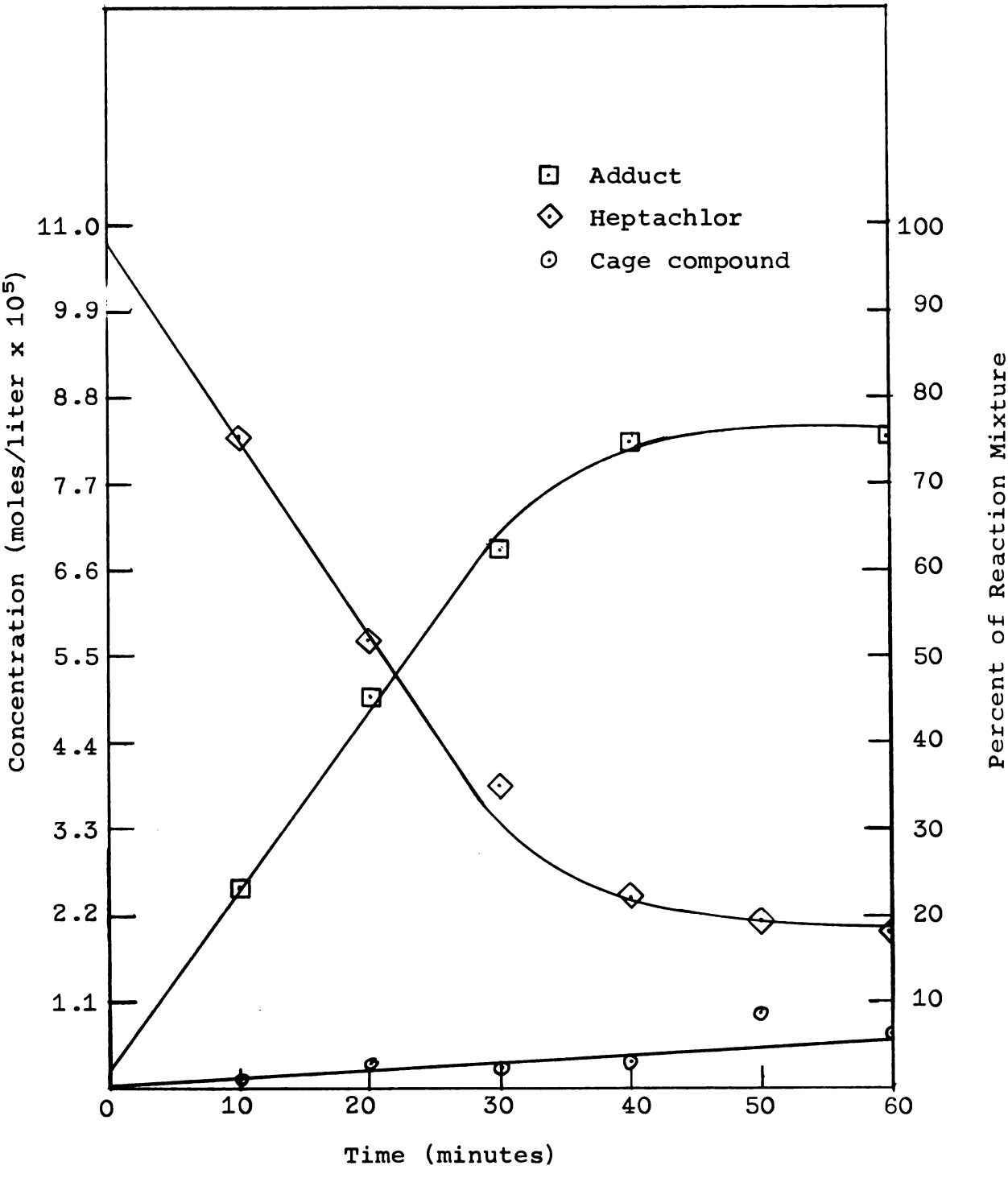


Figure 7. Reaction of heptachlor at 3000A in 10% acetone, 90% cyclohexane.

TABLE II

Effect of Viscosity on the Rate of Photodecomposition of Heptachlor

Mole Fraction Acetone X	Viscosity η	*"0" Order Rate Constant k^o x 10^{26} moles/liter·quanta		
		Cage Formation	Adduct Formation	Heptachlor Decay
0.141	0.756	2.27	50.1	52.8
0.269	0.673	2.86	42.4	45.7
0.387	0.595	2.77	37.7	41.2
0.495	0.536	3.26	29.1	36.9
0.594	0.482	4.57	29.9	35.0
1.000	0.303	2.72	----	2.72

*Based on an effective intensity of 4.72 x 10^{18} quanta/minute.

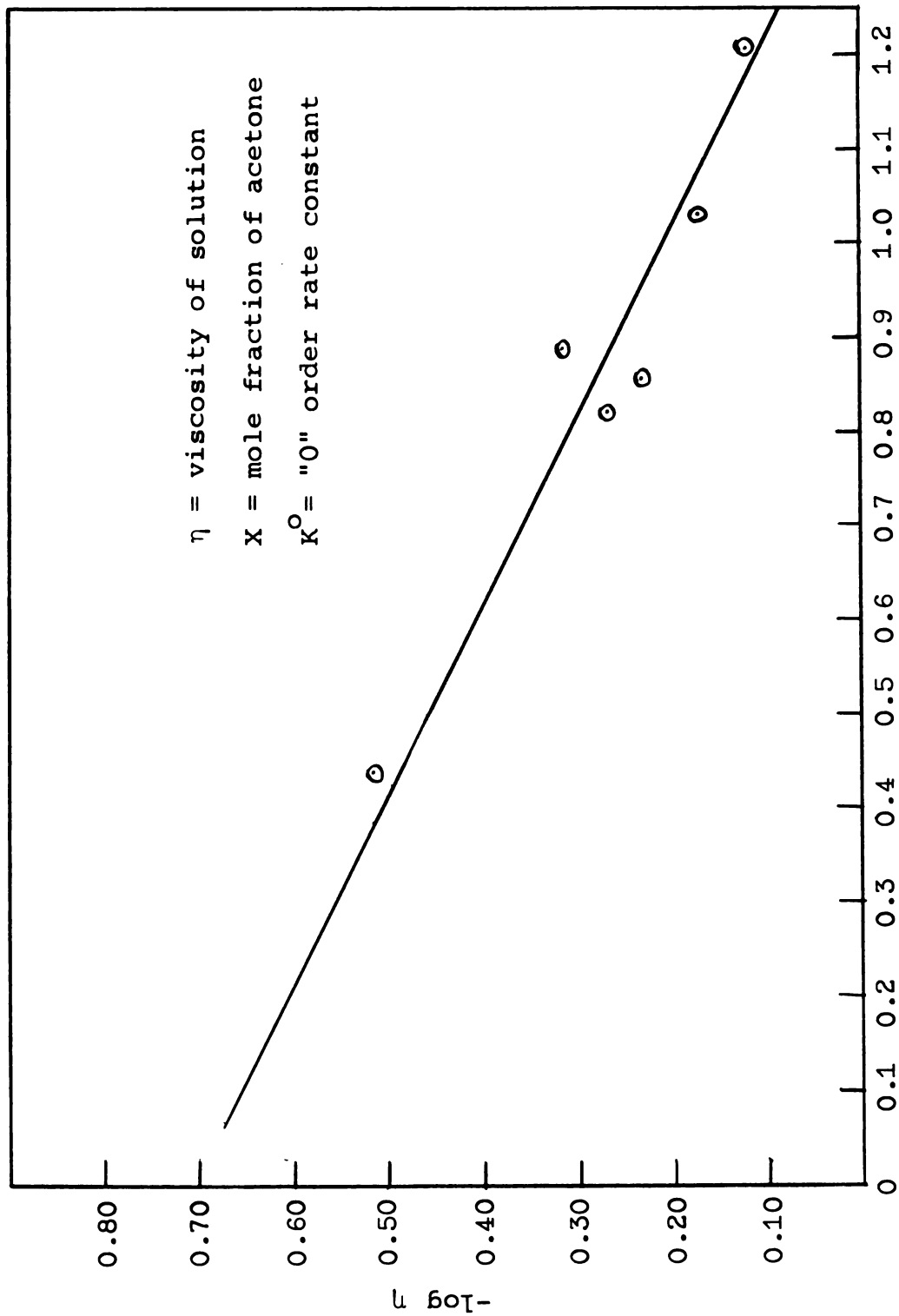


Figure 8. Effect of viscosity on the rate of formation of cage compound.

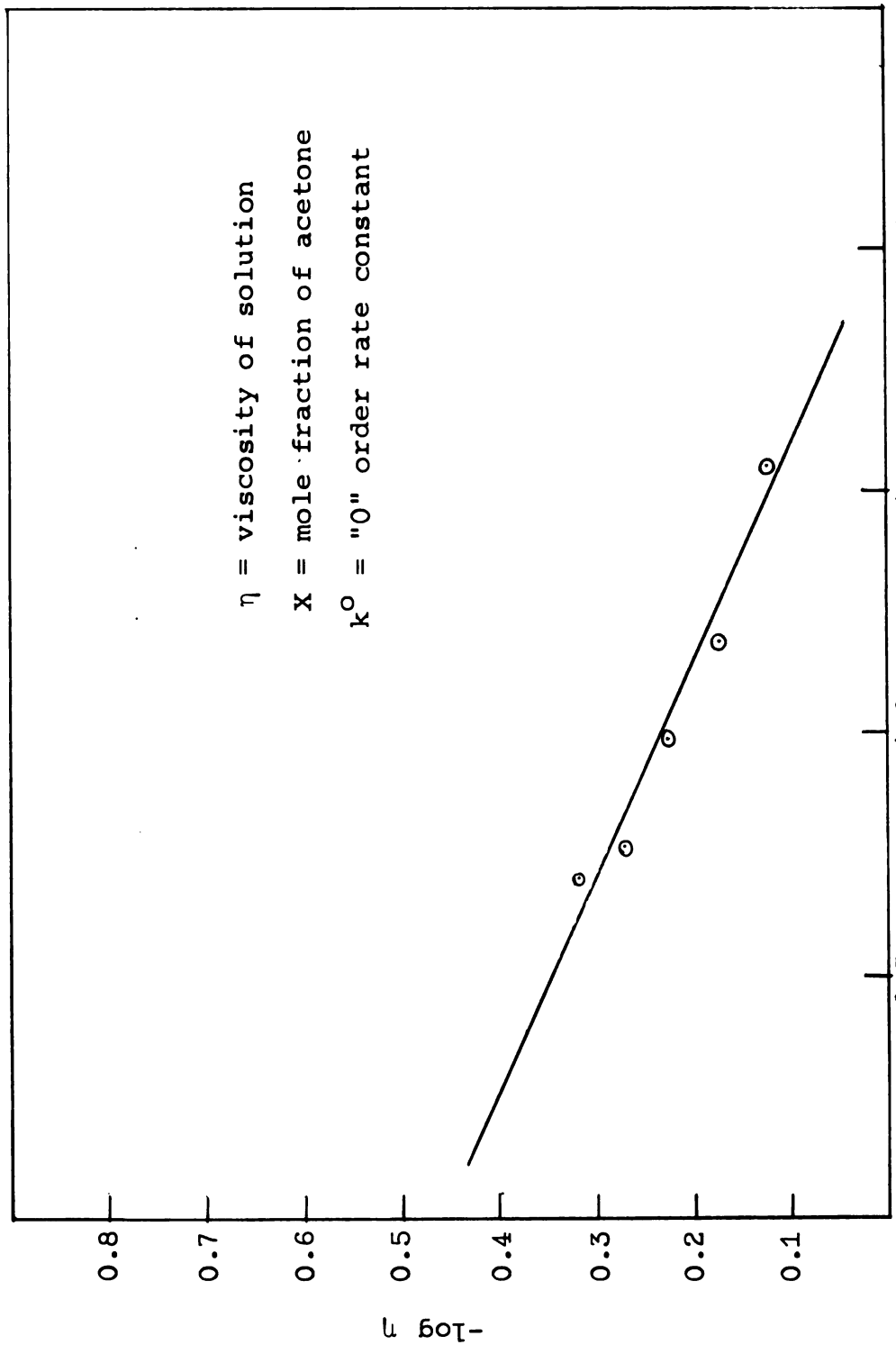


Figure 9. Effect of viscosity on the rate of adduct formation.

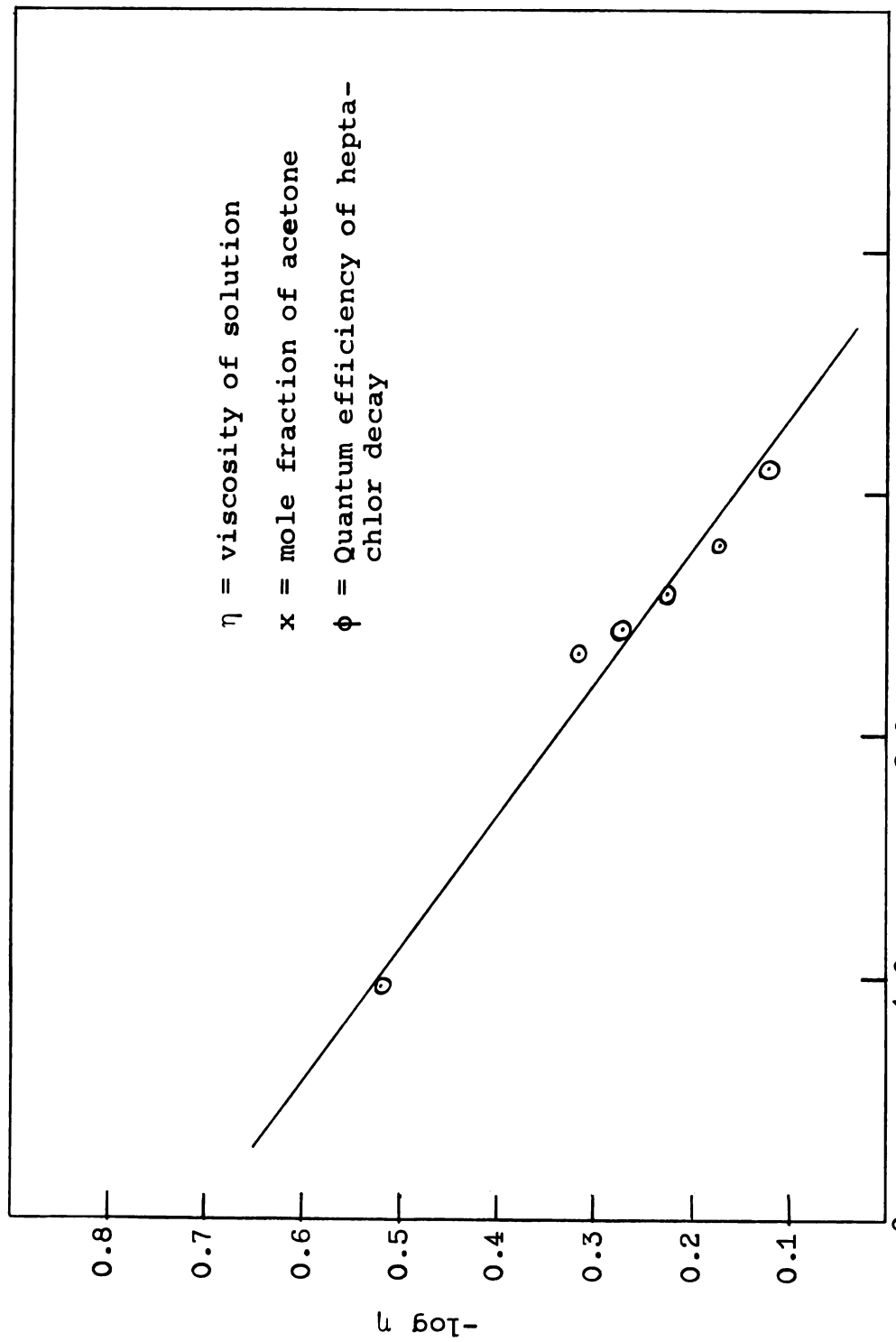
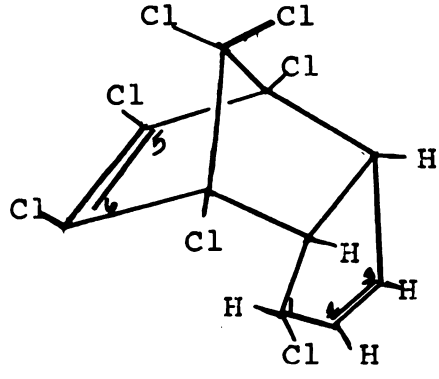


Figure 10. Effect of viscosity on the quantum efficiency of heptachlor decay.

rate of cage formation depends upon X $\eta^{\frac{1}{2}}$ while the rate of formation of the cyclohexyl adduct and the rate of decay of heptachlor depend on, approximately, X $\eta^{\frac{1}{5}}$ (n = 0.182 for heptachlor and 0.225 for the adduct). Values for the viscosities for the binary mixtures were calculated by the method of Kendall and Monroe (17).

That the adduct formation is a general reaction is shown by the formation of similar products from the photolysis of heptachlor in mixtures of acetone and hexane, cyclopentane, and ethylacetate.



R = cyclohexyl, cyclopentyl, hexyl, etc

VI

The formation of the solvent adduct at carbon 1 shows that the sensitized triplet reaction or cage formation involves excitation of the 2,3 double bond. Since the photodechlorination involves excitation of the 5,6 double bond, the two reactions are not closely related but proceed through two, separate and discrete transition states. It is understandable, therefore, that the two reactions have not been found to occur simultaneously.

Identification of the Cyclohexyl Adduct

The identification of the major product formed by the irradiation of heptachlor at 3000A in mixtures of acetone and cyclohexane was made on the basis of the mass spectrum, nuclear magnetic resonance spectrum and infrared spectrum of the pure compound. (The sample was collected as a viscous liquid from the gas chromatograph. Reinjection of the sample under a different set of conditions into a different column showed only one peak.)

Some of the key features of the mass spectrum are summarized in Table III. The expected values for the isotope effects should be considered as only qualitative due to the complexity of the molecule. Additional large peaks, for which isotope effects were not calculated due to the complexity of the spectra, appear at m/e values of 300 (F_8 = $C_{10}H_5Cl_5^+$), 299 (F_9 = $C_{10}H_4Cl_5^+$), 265 (F_{10} = $C_{10}H_5Cl_4^+$), 264 (F_{11} = $C_{10}H_4Cl_4^+$) and 65 (F_{12} = C_5H_5).

The presence of these fragments can be explained by the following scheme.

$F_1 \longrightarrow F_2 + Cl\cdot$

$F_2 \longrightarrow F_3 + HCl$

$F_1 \longrightarrow F_4 + C_6H_{11}\cdot$ (cyclohexyl) F_7

$F_1 \longrightarrow F_5 + F_6$ (reverse Diels-Alder)

$F_4 \longrightarrow F_8 + \cdot Cl$

$F_4 \longrightarrow F_9 + HCl$

$F_8 \longrightarrow F_{10} + Cl\cdot$

TABLE III

Mass Spectrum of the Cyclohexyl Adduct of Heptachlor

	M/e	Percent of P (found)	Percent of P (expected)	P^+ ion
P+6	424	81	70	
P+4	422	176	161	F_1 $C_{18}H_{18}Cl_6^+$
P+2	420	204	196	
P	418	100	100	
P+6	389	37	35	
P+4	387	106	106	F_2 $C_{18}H_{18}Cl_5^+$
P+2	385	161	163	
P	383	100	100	
P+6	353	23	14	
P+4	351	69	64	F_3 $C_{18}H_{15}Cl_4^+$
P+2	349	116	131	
P	347	100	100	
P+6	341	69	70	
P+4	339	157	161	F_4 $C_{10}H_5Cl_6^+$
P+2	337	173	196	
P	335	100	100	
P+6	241	41	35	
P+4	239	91	106	F_5 $C_5Cl_5^+$
P+2	237	149	161	
P	235	100	100	
P+2	150	0.95	0.67	
P+1	149	11.8	12.1	F_6 $C_{11}H_{18}^+$
P	148	100	100	
P+2	85	0.13	0.19	
P+1	84	8.2	6.7	F_7 $C_6H_{11}^+$
P	83	100	100	

$$F_8 \longrightarrow F_{11} + HCl$$

or

$$F_9 \longrightarrow F_{11} + Cl\cdot$$

and $$F_6 \longrightarrow F_{12} + F_7$$

The mass spectrum of heptachlor (8) shows a very similar fragmentation pattern including a large contribution of the retro Diels-Alder type of cleavage giving peaks at m/e = 270 ($C_5Cl_6^+$) analagous to F_5 and at m/e = 100 ($C_5H_5Cl^+$) analogous to F_6.

Further support for the assignment of carbon 1 as the site of reaction is given by the complete absence in the mass spectrum of the adduct of any fragments at m/e's of 318 ($C_{11}H_{11}Cl_5^{++}$) and 283 ($C_{11}H_{11}Cl_4^+$). These fragments would certainly be formed by the retro Diels-Alder cleavage of the adduct if the cyclohexyl group replaced any chlorine other than the one attached to carbon 1.

Examination of the infrared spectrum of the adduct (above 1200 cm^{-1}) shows it to be almost a superimposition of the spectra of cyclohexane on that of heptachlor (Figure 11 and Table IV). Close analysis of Table IV and Figure 11 shows two significant features. First of all, the 1610 cm^{-1} absorption of heptachlor (ν C=C) is also present in the spectrum of the adduct indicating that the double bonds are unaffected by the reaction. Secondly, 3070 cm^{-1} absorption (ν C-H) of heptachlor is shifted to lower frequency (3050 cm^{-1}) in the adduct. This is accompanied by a shift of the 2890 cm^{-1} and 2800 cm^{-1} (ν-CH) bands by cyclohexane to higher

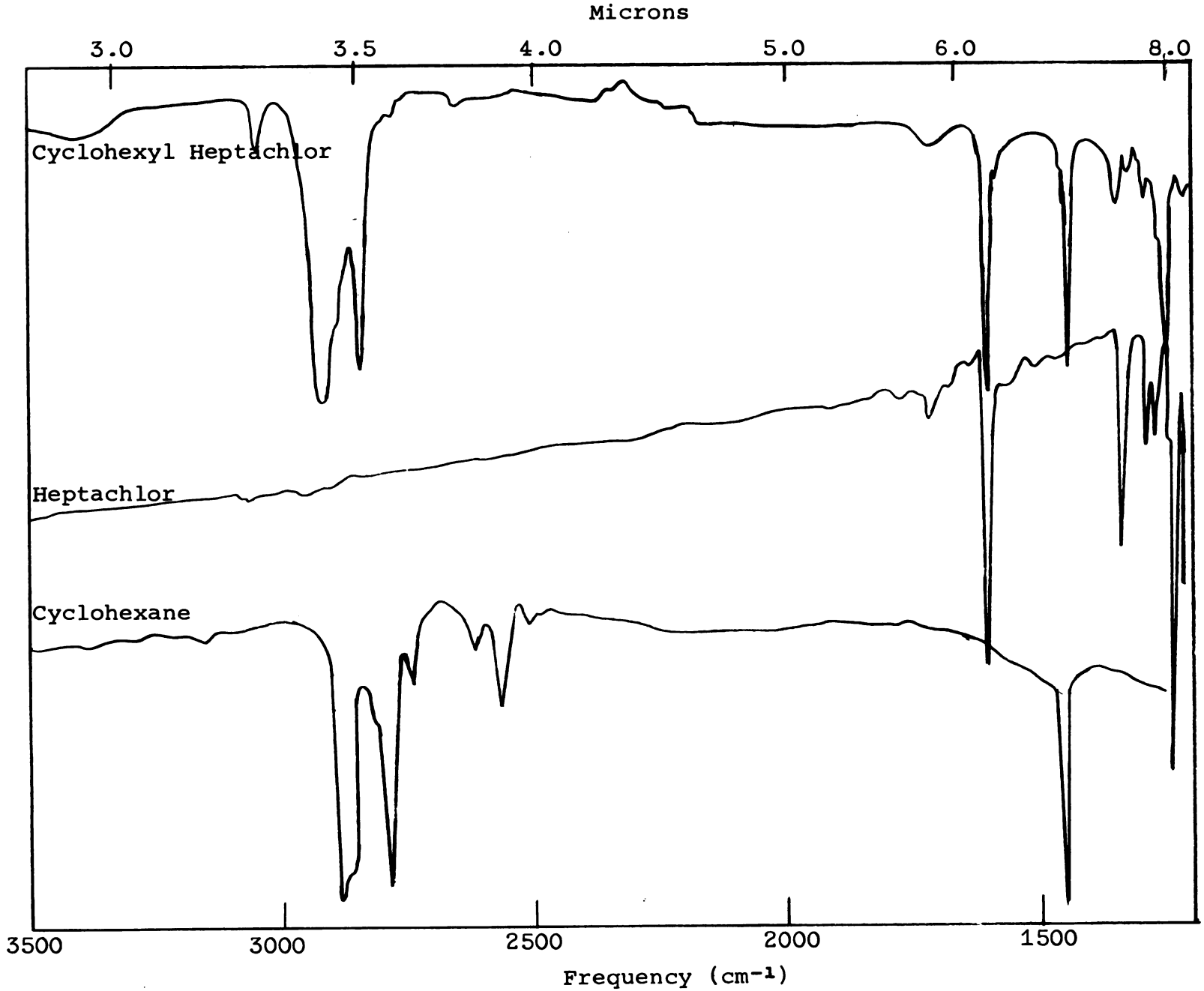


Figure 11. Comparison of the IR spectra of cyclohexyl heptachlor, heptachlor and cyclohexane.

TABLE IV

The IR Spectra of Heptachlor, Cyclohexane and Cyclohexylheptachlor

Cm^{-1} Adduct	Cm^{-1} Heptachlor	Cm^{-1} Cyclohexane
3050 (m)	3070 (w)	
2960 (sh)	2960 (w)	
2925 (vs)		2890 (vs)
2900 (sh)		2860 (sh)
2850 (vs)		2800 (vs)
		2725 (w)
2790 (w)		2600 (w)
2660 (w)		2560 (m)
		2500 (w)
1720 (w)	1725 (w)	
1610 (vs)	1610 (vs)	
1455 (vs)		1445 (vs)
1350 (m)	1340 (s)	
1300 (w)	1295 (m)	
1275 (sh)	1280 (m)	
1260 (vs)	1240 (vs)	

(w) = weak; (m) = medium; (s) = strong; (vs) = very strong; (sh) = shoulder.

frequencies (2925 cm^{-1} and 2850 cm^{-1}, respectively). This is consistent with the replacement of the chlorine attached to carbon 1 in heptachlor (I) by a cyclohexyl radical to form the adduct (VI).

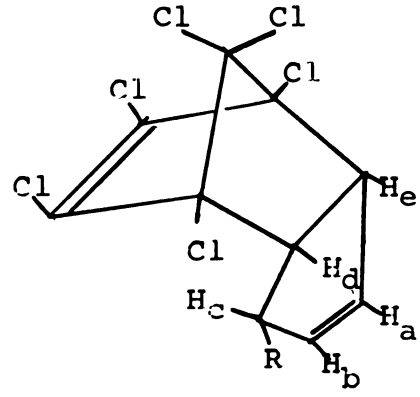
Final and conclusive proof that carbon 1 is the reaction site is provided by a comparison of the nuclear magnetic resonance spectrum of heptachlor with that of the adduct (Table V). The addition of a broad multiplet at 8.55 τ having an area indicative of eleven hydrogens together with the splitting of H_b and the drastic upfield shift (toward higher tau values) of H_c show quite unequivocally, when taken along with the mass and infrared spectral evidence, that the chlorine attached to carbon 1 in heptachlor (I) is replaced by an unrearranged cyclohexyl group to form VI.

n-Hexyl Adduct

The acetone sensitized photolysis of heptachlor in n-hexane is not so simple as that in cyclohexane due to the ease of rearrangement of the n-hexyl radical. Indeed the reaction yields at least three major adducts in proportions which vary depending on the exact reaction conditions, e.g., length of irradiation and amount of air in contact with the reaction mixture. The first product shows a parent peak in the mass spectrum at M/e = 420 and appears to be a rather straightforward substitution product similar to that formed in the cyclohexyl case. (Although this product has not been completely characterized, it is probable that n-hexyl

TABLE V

The NMR Chemical Shifts of Heptachlor and Its Cyclohexyl Adduct



I R= Cl

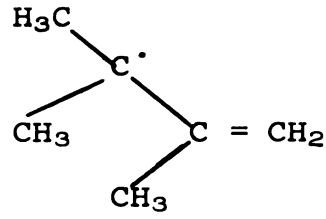
VI R= Cyclohexyl

Proton	Chemical Shift (tau)	
	Heptachlor	Adduct
H_a	4.1 (s) (2H)	4.73 (s) (1H)
H_b		4.28 (m) (1H)
H_c	5.20 (m) (1H)	7.55 (m) (1H)
H_d	6.50 (m) (1H)	6.90 (m) (1H)
H_e	5.90 (m) (1H)	6.20 (m) (1H)
H_R		8.55 (m) (11H)

(m) = multiplet

(s) = singlet

radical has rearranged.) The second product is what appears to be, from its infrared and mass spectra, an alcohol formed by a partial oxidation following the substitution reaction. The third product is quite interesting in that it shows a drastic rearrangement of the n-hexyl radical along with unsaturation. Its mass spectrum shows a parent peak at M/e = 418 instead of M/e = 420; its infrared spectrum shows the presence of a terminal methylene group; and its nmr spectrum shows the presence of two equivalent vinyl protons and three methyl groups, two of which are equivalent. This evidence points to a structure such as VII for the hexyl radical.



VII

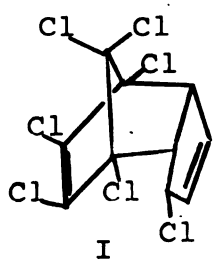
Reaction Mechanisms

On the basis of the evidence presented above it is possible to postulate mechanisms for both the photodechlorination and cage formation photoreactions of heptachlor.

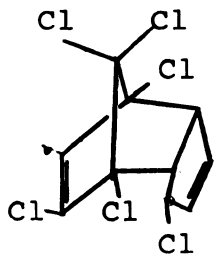
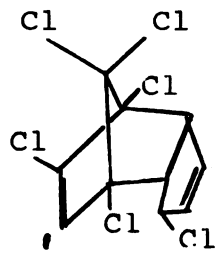
Photodechlorination

The monodechlorination of heptachlor under the influence of ultraviolet light can be viewed as a simple

non-chain free radical process. Heptachlor (I) is activated

1)  $\xrightarrow{h\nu}$ I^* $\longrightarrow$

I

 or  + Cl·

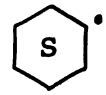
I_b I_a

by high energy ultraviolet light ($<$2800A) to give the activated complex I^*. The exact nature of I^* is only speculation at this time. Although it is probably a singlet state, a high energy triplet ($E_T > 86$ Kcal/mole) cannot be eliminated. This excited state can then decompose to yield either free radical I_a or I_b and a chlorine radical. Radicals I_a and I_b can then abstract a proton from the solvent (cyclohexane)

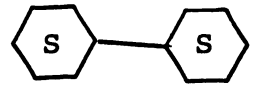
2) I_a +  $\longrightarrow$ II +  ·

3) I_b +  $\longrightarrow$ III +  ·

to give the monodechlorination isomers II and III respectively plus solvent radicals. The chlorine radicals can likewise

4) $Cl\cdot$ +  ⟶ HCl + 

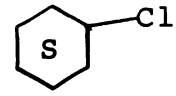
abstract a proton from the solvent to give hydrogen chloride and a solvent radical. Finally, two cyclohexyl radicals can combine to form bicyclohexyl. Processes such as those

5) 2  ⟶ 

shown in equations 6 through 9 are unlikely in that they

6)  ⟶  + H·

7) $Cl\cdot$ + I ⟶ I_a or I_b + Cl_2

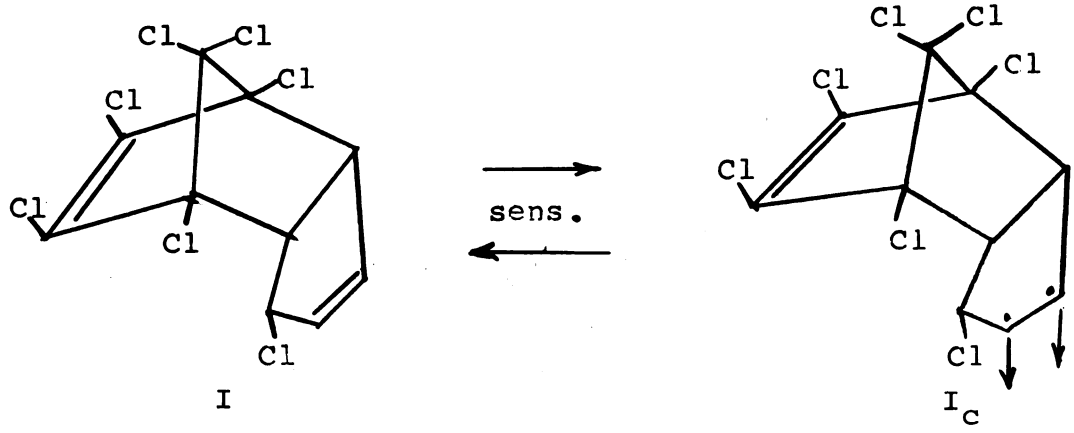
8)  + I ⟶ I_a or I_b + 

9) H· + I ⟶ I_a or I_b + HCl

would lead to a chain process and result in a quantum yield much higher than that observed (ϕ = 0.025).

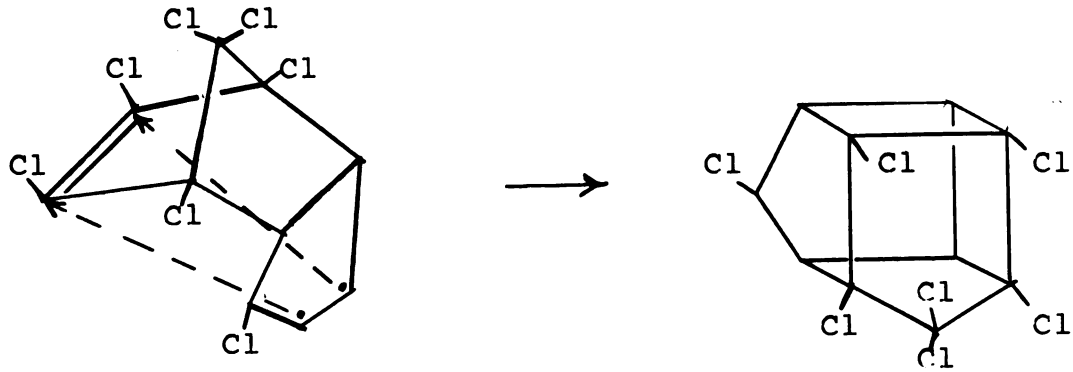
Cage Formation and Adduct Formation

The sensitized triplet reaction of heptachlor to form cage compound or add solvent radical can be viewed as proceeding by a mechanism such as the following. Heptachlor (I)

10) 

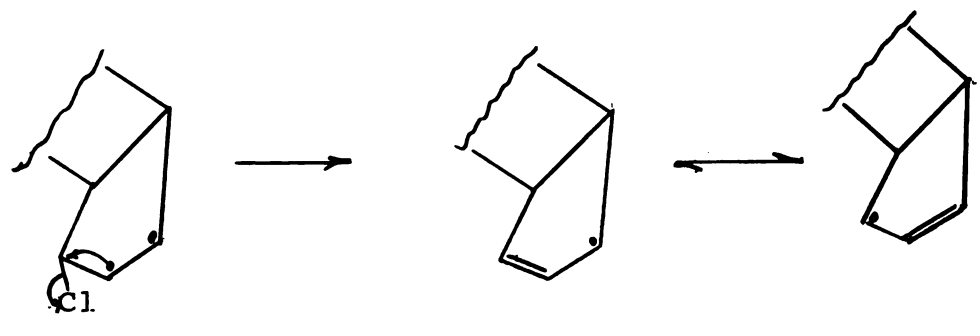
I I_c

is activated by ultraviolet light through the sensitizer to form the triplet biradical I_c. I_c can do either of two things then; it can close to form the cage compound IV

11) 

I_c IV

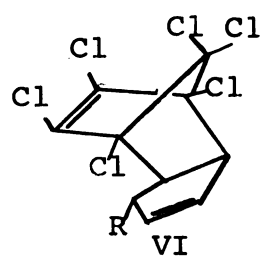
(equation 11) or it can eliminate a chlorine radical to form the stable allyl radical I_d (equation 12). The allyl radical

12) 

I_c I_d

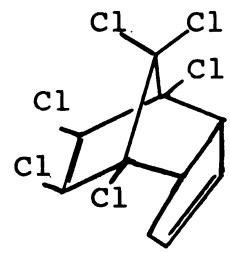
(I_d) can then react with a solvent radical, formed by the abstraction of a proton by the chlorine radical, to form

13) $Cl\cdot + R\text{-}H \longrightarrow HCl + R\cdot$

14) $I_d + R\cdot \longrightarrow$ 

VI

the solvent adduct VI (equations 13 and 14). The radical I_d is, evidently, stable enough that it allows for rearrangement of an n-hexyl radical (R = n-hexyl). Consequently proton abstraction by I_d from the solvent is not expected and, indeed, products such as VIII have not been found. This mechanism has also been written as a non-chain process

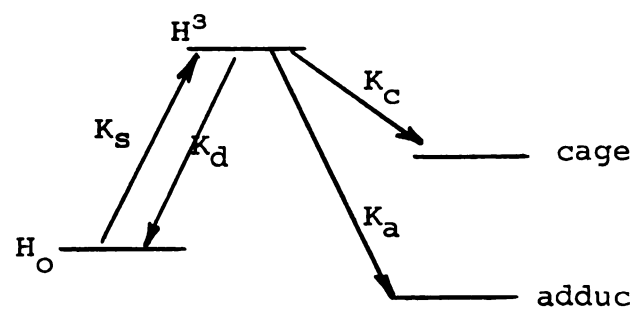
15) $I_d + R.H \longrightarrow$  $+ R\cdot$

VIII

because of the low quantum efficiency with which it proceeds.

Kinetic Mechanism for the Triplet Reaction

The above mechanism for the triplet reaction can be rewritten in a little different manner as follows:



(This diagram is not meant to indicate relative energy levels except in a qualitative and intuitive way.) The equations for each of the separate steps can be written:

16) $H_o \xrightarrow{k_s} [H^3]$ rate = k_s = R_s

17) $[H^3] \xrightarrow{k_d} H_o$ rate = $k_d [H^3]$ = R_d

18) $[H^3] \xrightarrow{k_c}$ Cage rate = $k_c [H^3]$ = R_c

19) $[H^3] \xrightarrow{k_a}$ Adduct rate = $k_a [H^3]$ = R_a

where H_o refers to the ground state heptachlor and H^3 is the excited triplet biradical. (The rate constant for sensitization is dependent, to some extent, on the amount of sensitizer and the viscosity of the solution as has been discussed previously.) If a steady state approximation is now applied to the triplet state,

$$20) \quad \frac{d[H^3]}{dt} = 0 = k_s - k_d[H^3] - k_c[H^3] - k_a[H^3] ,$$

the concentration of the triplet state, $[H^3]$, can be expressed as

$$21) \quad [H^3] = k_s/(k_a + k_c + k_d).$$

The rate of formation of cage compound (equation 18) can now be written as

$$22) \quad R_c = k_s k_c/(k_a + k_c + k_d).$$

In like manner the rate of adduct formation and the rate of decay of heptachlor can be written as

$$23) \quad R_a = k_s k_a/(k_a + k_c + k_d) \qquad \text{and}$$

$$24) \quad R_{H-} = k_s - k_d k_s/(k_a + k_c + k_d).$$

Dividing equation 22 by equation 24 gives

$$25) \quad R_c/R_a = \frac{k_c}{k_a} \cong 0.045,$$

where the values for the reaction with 10% acetone are used for R_c and R_a. Two additional terms must now be introduced: ϕ_c the quantum yield of cage compound and ϕ_{H-} the quantum efficiency of decay for heptachlor.

$$26) \quad \phi_c = k_c/(k_a + k_c + k_d)$$

$$27) \quad \phi_{H-} = k_s/(k_s + k_a + k_c + k_d)$$

If it is now assumed that the rate of decay from the triplet to the ground state heptachlor is much faster than the other rates:

$$28) \quad k_d >> k_s, k_a, k_c$$

then

$$29) \quad \phi_c \cong \frac{k_c}{k_d}$$

and

$$30) \quad \phi_{H-} \cong \frac{k_s}{k_d}$$

Now, dividing equation 29 by equation 30 and substituting the values obtained for the 10% acetone solution

$$31) \quad \phi_c/\phi_{H-} \cong \frac{k_c}{k_s} \approx \frac{8.25 \times 10^{-5}}{1.93 \times 10^{-3}} \approx .0427$$

or

32) $k_c \approx .0427\ k_s$

Now, since, $k_c \approx 0.045\ k_a$, from equation 25,

33) $k_a = \frac{.0427}{.045}\ k_s = 0.946\ k_s$ and from

30) $k_d \approx k_s/\phi_{H-} = 518\ k_s$

all of the rate constants can be written in terms of k_s:

30) $k_d \cong 518\ k_s$

32) $k_c \approx 0.0427\ k_s$

33) $k_a \cong 0.946\ k_s$

If these values are substituted into equation 24 and the rate determined for the 10% acetone solution is used for R_{H-}, one obtains a value for k_s of

34) $k_s \approx 1.243 \times 10^{-3}$ moles/liter·minute.

The values of these constants for all the reactions carried out in mixed solvents (cyclohexane-acetone) are summarized in Table VI.

That the sensitization step is not diffusion controlled in this case can be seen by the low value for k_s even though the rate of diffusion does have some effect on this step as seen above. For a truly diffusion controlled reaction, the value of k_s should be on the order of 10^{10} as predicted by the Debye equation (9).

TABLE VI

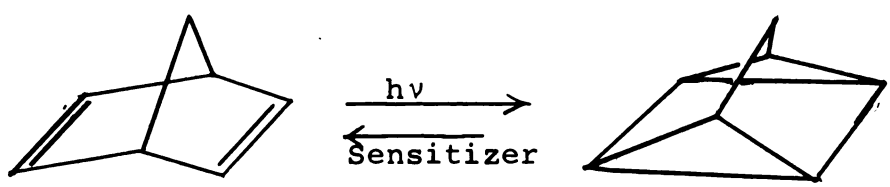
Specific Rate Constants for the Triplet Sensitized Photodecomposition of Heptachlor

	Percent Acetone				
	10	20	30	40	50
k_s	1.24×10^{-3}	1.08×10^{-3}	9.70×10^{-4}	8.70×10^{-4}	8.25×10^{-4}
k_a	9.0×10^{-4}				
k_c	7.5×10^{-5}				
k_d	6.46×10^{-1}				

Reversibility of Cage Formation

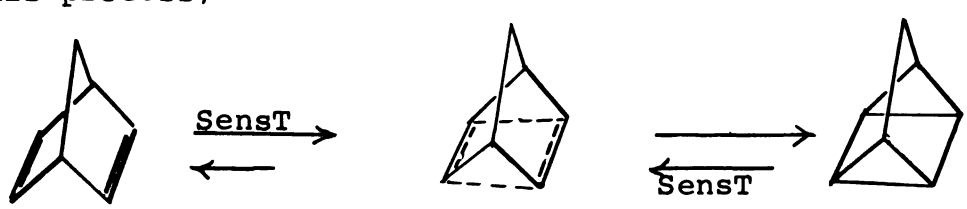
Irradiation at 2000A of a mixture of cage compound and heptachlor in cyclohexane, without the addition of sensitizer, yielded a decrease in the concentration of the cage compound and a corresponding increase in the concentration of the heptachlor. This reaction proceeds at a rate of 3.22×10^{-7} moles/liter·minute (Figure 12), giving a quantum yield of 0.195 based on absorption of 2.3% of the 1.6×10^{17} quanta/minute available energy.

Although this is the first demonstration of the reversibility of cage formation in pesticide systems it has been shown in somewhat related systems. Hammond et al. (13) have shown the photoisomerization of [2.2.1]-bicycloheptane (IX) to [2.2.1.$0^{2,6}$.$0^{3,5}$] tetracycloheptane (X) to be a reversible reaction with a quantum efficiency of 0.08 for the cage



IX X

opening. The authors have proposed two possible mechanisms for this process;



IX IXa X

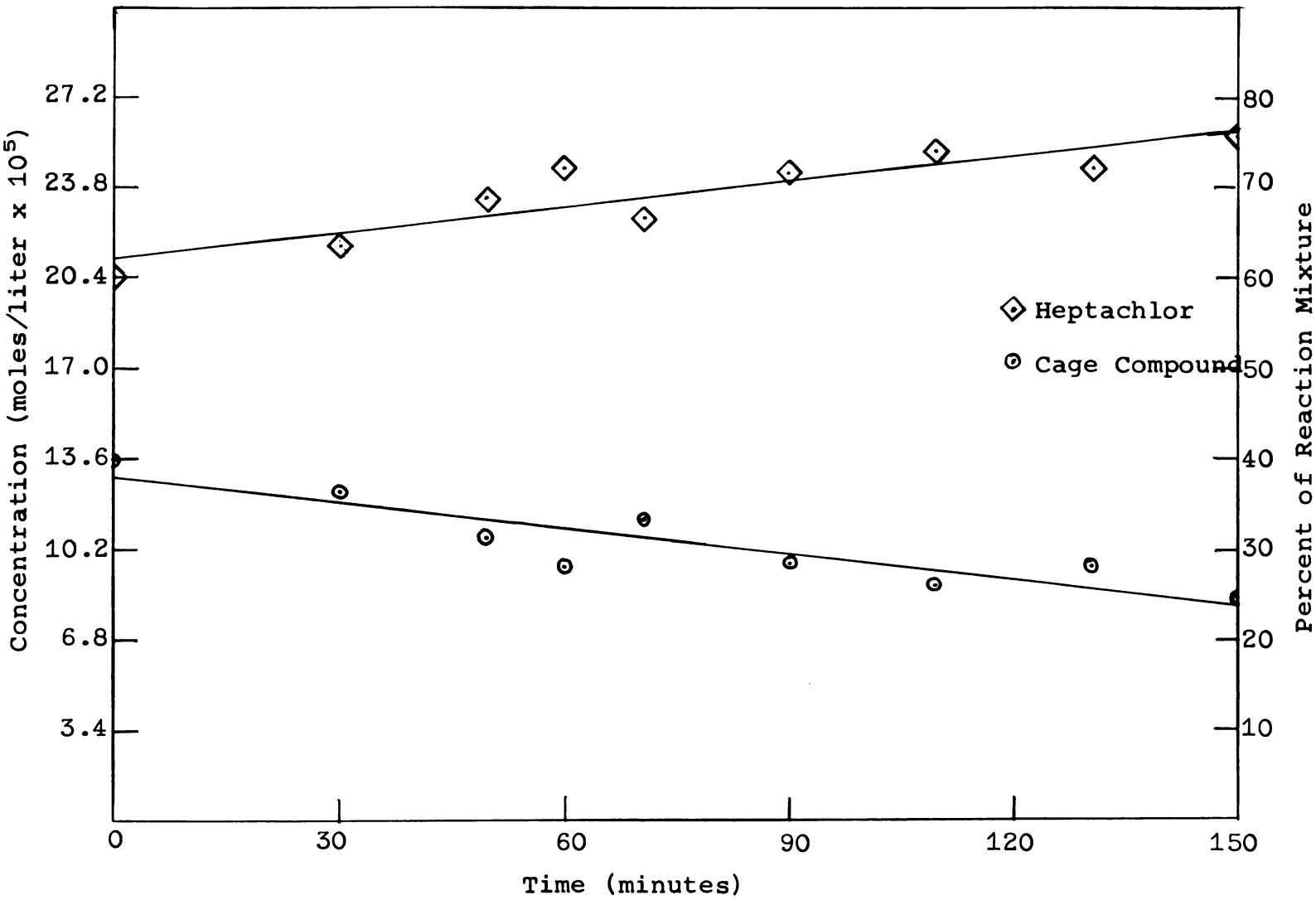
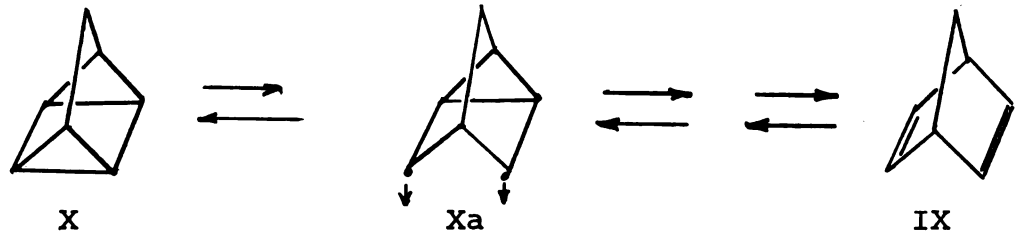


Figure 12. Rate of cage opening at 2000A.

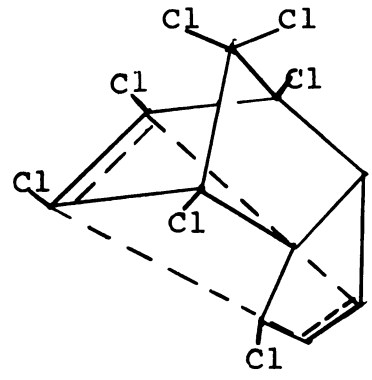
or



X Xa IX

Although Hammond shows both forward and reverse processes to be sensitized reactions, it must be noted that he gives no data on reactions carried out in the absence of sensitizer. Indeed our investigation has shown that the reverse process, cage opening, proceeds in the absence of sensitizer in the heptachlor system.

Our investigation has also shown that in the heptachlor system the classical, nondelocalized biradical I_c, analogous to Xa, is more probable than a delocalized transition state (I_e) analogous to IXa. If an intermediate such as I_e were



I_e

important in the reaction mechanism, one would be hard pressed to account for the photodechlorination and cage

formation being independent from one another and for the loss of chlorine from carbon 1 in forming the solvent adduct. Since a stable, delocalized system would be already present there would be no tendency to form an allyl free radical by the loss of chlorine from carbon 1.

PRACTICAL IMPLICATIONS

The results of these investigations have contributed a great deal to the understanding of the phenomena observed in the photodegradation of chlorinated policyclic pesticides. The differentiation between mechanism of photodechlorination and that of cage formation has explained the failure to observe these reactions concurrently. Indeed, the failure to observe photodechlorination under environmental conditions is understandable in view of the energy requirements for this process. The inability to react by this mode coupled with the requirement for a sensitizer with a relatively high triplet energy explains, to a large degree, the persistency of these pesticides under environmental conditions.

This investigation has also opened up new paths of applied research in the pesticide area. It would, for example, be of great potential value to investigate the effect of sensitizers added to the spray formulations on the persistency of the pesticides. Another area of interest would be the ability of these pesticides to form products, similar to the solvent adducts, with compounds commonly found in nature, especially those found in plant surfaces.

This study has, however, been only a step, although an important one, toward the ultimate goal of pesticide research; the ability to produce a pesticide which is toxic to insects but harmless to animal life. The attainment of this goal must await, for the most part, the better understanding of the relationship between the structures of these compounds and their toxicity.

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