

in allene.^{16,17} The experimental uncertainties in the bond lengths also limit the significance of the difference in the two C=C bonds which might be caused by the fluorine substitution. The C-F bond distance (1.323 Å) is identical with that in H₂CCF₂.¹⁸ Although the listed value of the FC₁F angle (110.2°) is larger than that in H₂CCF₂ (109.1°),¹⁸ the experimental error again prevents any significance being placed on the difference. The structure of the methylene (CH₂) group in H₂CCF₂ is quite typical.¹⁷

In 1962, Bernstein¹⁹ showed a close relation between the averaged CH stretching frequency of a molecule and its CH bond length. In the absence of resonance, Duncan²⁰ has demonstrated the correlation between the separation of asymmetric and symmetric CH₂ stretching frequencies and the HCH angle in the =CH₂ group of a molecule. From the closeness of the CH₂ geometries of allene and 1,1-difluoroallene, one would, thus, expect little difference in their CH stretching frequencies.

It was concluded in the Coriolis coupling section that the $\nu(0,1)$ state has a lower energy than the $\nu(1,0)$ state. Both vibrational modes (B₁ and B₂) are antisymmetry with respect to the C₂ operation. For the same rotational transition, both satellites should have the same statistical weights. Our relative intensity measurement has indicated consistently for all three isotopic species that the $\nu(0,1)$ state has a lower energy

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than the $\nu(1,0)$ state. This result is in complete agreement with that obtained from the vibration and rotation interaction study.

The structural parameters employed in the chemical shift calculations for 1,1-difluoroallene were $r(C_1-C_2) = r(C_2-C_3) = 1.31$ Å, $r(C_1-F) = 1.33$ Å, and $r(C_3-H) = 1.08$ Å, and all angles were taken at 120.0°. The distances used for these calculations are comparable to those found in this study. However, there are significant differences between the angles employed in the calculations and those obtained in the microwave study. In particular, the $\angle FC_1F$ of $110.2 \pm 1.0^\circ$ is considerably smaller than 120° and it is expected that such a difference could lead to significant changes in the predicted shielding constants.

It should be of interest to compare the dipole moments and the structures for a series of fluorine-substituted allenes. Also, it appears that additional structure work on these molecules would be of interest in attempting to predict shielding constants. Therefore, further microwave work on some of these molecules is warranted and we hope to initiate such studies in the near future.

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Photochemistry of Bioactive Compounds. Photochemical Processes of Polychlorinated Biphenyls

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Abstract: Six symmetrical tetrachlorobiphenyls have been synthesized. Cyclohexane and methanol solutions of I-VI were irradiated at 300 nm and the products of the reaction identified. In both solvents dechlorination is the major reaction. Intersystem crossing quantum yields and quantum yields of reaction for I-VI have been determined in solution. The excited state responsible for photoreaction was found to be the triplet, and its lifetime was measured in cyclohexane and methanol. The rate constants for triplet decay and reaction were obtained using these data. The position of chloro substitution was found to have a marked effect on the photochemical properties of polychlorobiphenyls; an increase in ortho substituents decreased the lifetime and increased the reactivity of the excited state.

The photoreactions of polychlorobiphenyls (PCB) have acquired considerable environmental significance in recent years. In the absence of adequate metabolic pathways for PCB degradation in most organisms and the chemical stability of these compounds, ultraviolet radiation from sunlight remains as a possible route for their inactivation in the environment.

Few studies of PCB photochemistry have been re-

ported.^{4,5} All the work published thus far has been concerned with the nature of the photoproducts arising from reactions in various solvents (dechlorination and oxygenation).^{6,7} Neither the mechanism of the reaction nor the properties of the excited state(s) involved have

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been elucidated. The results of our study clearly detail the photochemical processes of PCB and also give useful information regarding a sterically hindered triplet geometry.

The tetrachlorobiphenyls chosen for study (Table I)

Table I. Tetrachlorobiphenyls

PCB	Designation
3,3',4,4'-Tetrachlorobiphenyl	I
2,2',4,4'-Tetrachlorobiphenyl	II
3,3',5,5'-Tetrachlorobiphenyl	III
2,2',3,3'-Tetrachlorobiphenyl	IV
2,2',5,5'-Tetrachlorobiphenyl	V
2,2',6,6'-Tetrachlorobiphenyl	VI

are some of the more toxic constituents of commercially available PCB mixtures (Arochlors).⁸

Results

Photoproducts (Table II). We have found that the

Table II. Photoproducts in Hexane and in Methanol^a

PCB	Dechlorinated products	Methoxylated products ^b
I	3,4,4'-Trichlorobiphenyl	Trichloromethoxybiphenyl
	4,4'-Dichlorobiphenyl	
II	2,4,4'-Trichlorobiphenyl	Trichloromethoxybiphenyl
	4,4'-Dichlorobiphenyl	Dichlorodimethoxybiphenyl ^c
III	3,3',5-Trichlorobiphenyl ^c	
	2,3,3'-Trichlorobiphenyl	Trichloromethoxybiphenyl
IV	2,2',3-Trichlorobiphenyl ^c	
	3,3'-Dichlorobiphenyl	Dichlorodimethoxybiphenyl ^c
V	2,5,3'-Trichlorobiphenyl	Trichloromethoxybiphenyl
	3,3'-Dichlorobiphenyl	Dichlorodimethoxybiphenyl ^c
VI	3-Chlorobiphenyl ^c	
	2,2',6-Trichlorobiphenyl	Trichloromethoxybiphenyl ^c
	2,2'-Dichlorobiphenyl ^c	

^a Nondegassed solutions. Twenty hours irradiation. ^b Only major products are shown. ^c Compound represented less than 1% of reacted starting material.

major reaction undergone by I–VI in cyclohexane at 300 nm is stepwise dechlorination^{7,9} to yield tri- and dichlorinated biphenyls as major products. Monochlorobiphenyls were observed after 20 hr of irradiation (<1% of reacted PCB). Relative yields of the two main products were estimated by vpc analysis. In all cases one or both of these accounted for >98% of PCB reacted.

All PCB containing ortho chlorines yielded products arising from the loss of these. In their absence meta chlorines were cleaved. Some products (<1% of reacted PCB) arose from loss of a meta chlorine when an ortho chlorine was present. Chlorines in the para position (I and III) were not cleaved after 20 hr of irradiation. After irradiation periods >50 hr, 3,3',4,4'-tetrachlorobiphenyl (10^{-3} M) yielded 3,3',4-trichlorobiphenyl in addition to 3,4,4'-trichlorobiphenyl.

In methanol solution dechlorination was also found to be the major reaction; however, some methoxylated products were also observed (<3% of reacted PCB in all cases).

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All products in both solvents were identified by gas chromatography–mass spectrometry and by comparison of their vpc retention times with those of authentic samples. Mass balances based on reacted starting materials were obtained for the photolysis of I–VI.

Quantum yields of reaction (ϕ_r) were determined in degassed cyclohexane solutions of I–VI at 300 nm. Maximum conversions (PCB reacted) were kept below 10% to avoid sensitization or quenching of the reaction by the photoproducts. Concentrations of PCB's were such that >99.9% of the incident light was absorbed.

Actinometry was provided by parallel irradiation of benzophenone-sensitized solutions of *cis*-1,3-pentadiene in benzene. A quantum yield of 0.555 was used for the isomerization of the diene.¹⁰ Quantum yields for I–VI are listed in Table III.

Table III. Summary of Triplet State Reactivities of Polychlorobiphenyls in Cyclohexane

PCB	ϕ_r	τ , 10^{-8} sec	$1/\tau$, 10^7 sec ⁻¹	k_r , 10^7 sec ⁻¹ ^a	k_d , 10^7 sec ⁻¹ ^b
I	0.005	2.20	4.54	0.023	4.52
II	0.100	0.78	12.82	1.282	11.54
III	0.002	1.91	5.23	0.010	5.22
IV	0.007	0.77	12.99	0.091	12.90
V	0.010	0.67	14.92	0.149	14.77
VI	0.006	0.70	14.28	0.086	14.20

^a Obtained from eq 10. ^b Obtained from eq 4.

Quantum yields of intersystem crossing (ϕ_{isc}) were by measuring the phosphorescence emission intensity obtained of biacetyl at 516 nm sensitized by either benzophenone or PCB. Compounds I, II, and III were tested and gave values of 1 ± 0.05 for ϕ_{isc} compared to benzophenone ($\phi_{isc} = 1$). No phosphorescence was observed for I, II, and III at 25° in degassed benzene solutions.

Quenching studies were performed on the photo-decomposition of I–VI in methanol and cyclohexane. Degassed solutions of PCB containing various concentrations of 1,3-cyclohexadiene ($E_t < 55$ kcal/mol) were irradiated to conversion $\leq 20\%$. Stern–Volmer plots were linear (Figures 1, 2, and 3). Assuming diffusion-controlled quenching ($k_q = 1.3 \times 10^{10}$ in methanol and 0.81×10^{10} in cyclohexane¹¹), triplet lifetimes (τ) were calculated (Table III). The values obtained for τ in both solvents were equal within experimental parameters, i.e., 0.78×10^{-8} sec for II in methanol and 0.85×10^{-8} sec in cyclohexane.

Discussion

Product Formation. The dechlorination products obtained from uv irradiation of I–VI appear to be formed by cleavage of the carbon–chlorine bond giving rise to a biphenyl free radical type species which then abstracts hydrogen from the solvent (Scheme I). Formation of hydrogen chloride was detected during photolysis in keeping with such a mechanism. The intermediary of such "free" radicals has been reported in many cases where carbon–iodine bonds are cleaved,^{12,13}

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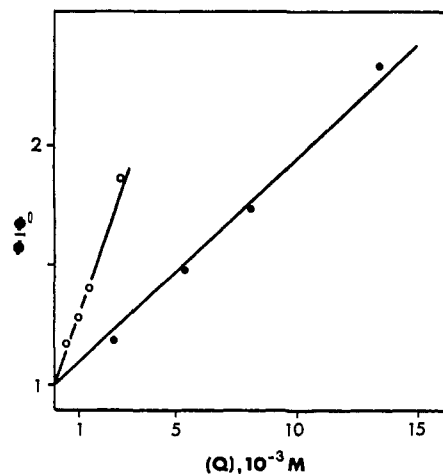


Figure 1. Stern-Volmer plots for (○) 3,3',4,4'- and (●) 2,2',3,3'-tetrachlorobiphenyls (I and IV) using 1,3-cyclohexadiene (Q) as quencher in methanol.

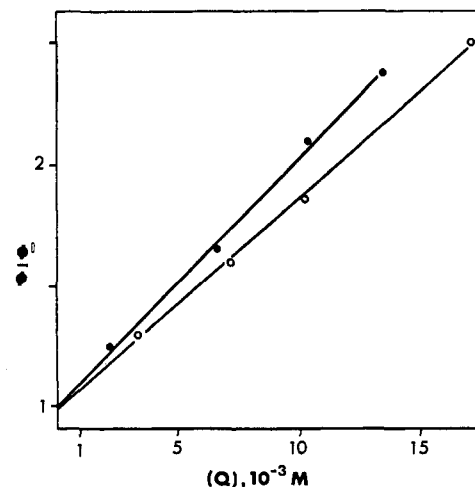
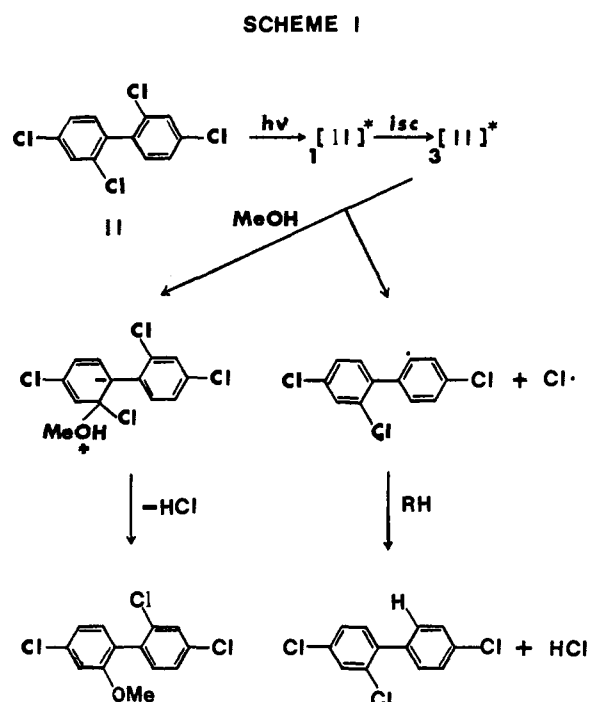


Figure 2. Stern-Volmer plots for (○) 2,2',5,5'- and (●) 2,2',4,4'-tetrachlorobiphenyls (V and II) using 1,3-cyclohexadiene (Q) as quencher in methanol.



but few studies have been devoted to photochemical cleavage of carbon-chlorine bonds.^{14,15} If a free radical is formed it be expected to yield oxygenated products through the formation of hydroperoxide intermediates. In the photolysis of aerated solutions of 2,2',4,4',6,6'-hexachlorobiphenyl such products have been observed.⁵

The methoxylated compounds shown in Table II would be formed by nucleophilic displacement of chlorine by methanol. Similar cases for several halobenzenes have been reported.¹⁶ An ionic intermediate has been postulated in the reaction of chlorobenzene with several nucleophiles at 280 nm.¹⁷

Nature of the Triplet. The properties of biphenyl and its derivatives in the ultraviolet have been ex-

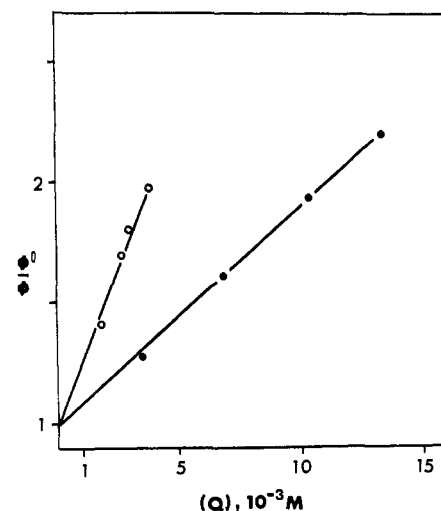


Figure 3. Stern-Volmer plots for (○) 3,3',5,5'- and (●) 2,2',6,6'-tetrachlorobiphenyls (III and VI) using 1,3-cyclohexadiene (Q) as quencher in methanol.

tensively studied.¹⁸⁻²⁰ Wagner in 1967 inferred a planar structure for the biphenyl triplet from its inefficiency in quenching several ketones.²¹ The evidence we have obtained supports this conclusion. Triplet lifetimes show a definite variation between ortho chlorinated PCB and the rest. This is probably the result of greater steric hindrance to the preferred excited state geometry. Crowded conditions created by ortho substituents result in greater twisting of the interring bond with a subsequent decrease in its double-bond character. The products obtained in greatest yields arise from the loss of ortho chlorines; thus the strain on that bond is relieved. No difference in τ is observed with the presence of two more chlorines in the 2, 2', 6, and 6' positions (VI). Apparently 2,2' disubstitution is efficient enough to minimize conjugation. The extinction coefficients (ϵ) for the 280-290-nm band for ortho chlorinated PCB are of the order of 10^2 while ϵ for I and III is of the order of 10^3 .

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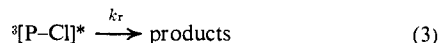
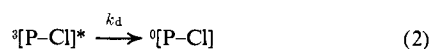
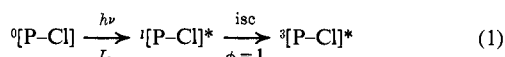
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Photochemical Mechanism. The following mechanistic scheme is drawn from our results



where ${}^0[\text{P-Cl}]$, ${}^1[\text{P-Cl}]^*$, and ${}^3[\text{P-Cl}]^*$ represent the PCB in its ground, excited singlet, and excited reactive triplet states. I_a is the quanta absorbed in the initial step and $P\cdot$ the biphenyl radical formed.

Normal kinetic analysis yields expressions 4–10.

$$\tau^{-1} = k_d + k_r \quad (4)$$

$$-d{}^0[\text{P-Cl}]/dt = I_a - k_d {}^3[\text{P-Cl}]^* \quad (5)$$

$$-d{}^3[\text{P-Cl}]^*/dt = 0 = k_d {}^3[\text{P-Cl}]^* + k_r {}^3[\text{P-Cl}]^* - I_a \quad (6)$$

$${}^3[\text{P-Cl}]^* = I_a/(k_d + k_r) \quad (7)$$

$$-(d{}^0[\text{P-Cl}]/dt)(I_a^{-1}) = \phi_r \quad (8)$$

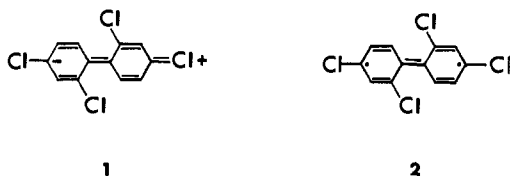
$$\phi_r = 1 - [k_d/(k_d + k_r)] \quad (9)$$

$$\phi_r = \phi_{isc} k_r (k_d + k_r)^{-1} \quad (10)$$

Expression 9 indicates that the quantum yields of reaction for PCB are independent of their concentration and dependent only on the lifetime of the excited triplet. This is evidence that reaction occurs in a primary rate-determining step process as would be expected for simple bond cleavage.

Using eq 10²² we have calculated values for the rate constants of decay and reaction (k_d and k_r), respectively, for I–VI (Table III).

As shown, k_d for all ortho chlorinated PCB is similar and greater by approximately a factor of 3 than those for I and III. The value for k_r is also much greater for II, IV, V, and VI. Both factors can be ascribed directly to the destabilizing effect of ortho substitution. The large difference in k_r between 2,2',4,4'-tetrachlorobiphenyl and the other compounds may be the result of increased double bond character of the inter-ring bond brought on by the para chlorine. Since it has been postulated¹⁹ that a para substituent may increase conjugation between the phenyl rings by electron donation, excited II may then be represented by structures 1 and 2.



This effect would bring about greater conjugation with an increased driving force to planarity resulting in faster chlorine cleavage.

Experimental Section

Chemicals. Spectrophotometric grade benzene (J. T. Baker Chemical Co., Phillipsburg, N. J.) was washed with sulfuric acid until no further coloration of the acid took place. Then the benzene was washed with water and dried by distillation from phos-

phorus pentoxide. Glass-distilled cyclohexane and methanol were obtained commercially (Burdick and Jackson Labs., Inc., Muskegon, Mich.)

cis-1,3-Pentadiene and 1,3-cyclohexadiene (chemical samples) were used as received. Benzophenone (Baker) was recrystallized from pentane until pure by vpc. Biacetyl was kindly supplied by Dr. P. J. Wagner at this University. *n*-Alkanes used as internal standards were obtained from Aldrich Chemical Co. and used as received.

Tetrachlorobiphenyls (I–V) were prepared by reacting the corresponding dichloriodobenzenes with copper powder in refluxing dimethylformamide²³ for 4–12 hr. Then the reaction mixture was poured into ice and allowed to stand overnight. The solid was collected and extracted with boiling acetone, the solvent evaporated, and the PCB recrystallized twice from methanol. All compounds prepared were >99.5% pure by vpc.

All tri-, di-, and monochlorobiphenyl standards and 2,2',6,6'-tetrachlorobiphenyl (VI) were obtained from Analabs, Inc. and recrystallized from ethanol.

Preparation of Samples for Irradiation. Solutions containing known concentrations of PCB, internal standard, and any other additive were prepared in volumetric flasks. Then 3.0-ml portions of these solutions were syringed into separate, constricted, 100 × 13 mm Pyrex culture tubes. The tubes used did not transmit >1% of the radiation below 287 nm. The samples were degassed by three freeze-pump-thaw cycles and sealed *in vacuo*.

Irradiation of Samples. Irradiations were performed in a "merry-go-round"²⁴ apparatus with a Rayonette Reactor (The Southern N. E. Ultraviolet Co.) fitted with RUL 3000 lamps having a peak (90%) output energy at 300 ± 10 nm. The "merry-go-round" ensures that the same intensity of radiation impinges on each sample of a set of simultaneously irradiated samples. The irradiation chamber temperature was 30°.

Quantum Yields. All quantum yields for the reaction of I–VI were determined in cyclohexane in concentrations of 0.1–0.5 *M* to ensure 99.9% absorption of light in the 290–310-nm region. Benzophenone (0.2 *M*) sensitized *cis* → *trans* isomerization of 1,3-pentadiene (0.4 *M*) was used as an actinometer and samples irradiated in parallel with those of I–VI. Conversions were kept below 10%. In cases where quantum yields for PCB reaction were very low several different actinometer samples in staggered succession had to be used due to the length of time the irradiation was carried out.

Quantitative Analysis. All analyses for PCB disappearance were performed on a Beckman GC-4 gas chromatograph equipped with a flame ionization detector. A 50-ft stainless steel SE-30 S.C.O.T. column (Perkin-Elmer) was used for separations. The column oven was maintained isothermally in the 160–200° range with a nitrogen carrier gas flow of 6 ml/min. Detector and inlet temperatures were 300 and 250°, respectively.

For analyses of *cis*- to *trans*-1,3-pentadiene conversion a 25% 1,2,3-tris(cyano)ethoxypropane on gas Chromosorb Q 32 ft × 1/8 in. stainless steel column was used. Nitrogen carrier gas flow was 15 ml/min and an oven temperature of 40° was maintained isothermally.

Mass spectrometry was carried out with a Du Pont 21-490 spectrometer interfaced with a Beckman GC-65 gas chromatograph equipped with a 15% QF1-10% DC200 on gas Chromosorb Q, 6 ft × 1/8 in. stainless steel column. The oven temperature was maintained at 220°, with a nitrogen carrier gas flow of 25 ml/min.

Quenching with 1,3-Cyclohexadiene. Methanol and cyclohexane PCB solutions (0.02–0.06 *M*) were mixed with varying amounts of quencher solutions (0.02–0.08 *M*) in 10-ml volumetric flasks. Three 3-ml samples of each quencher concentration were degassed and photolyzed. Each run consisted of at least four sets of samples with different quencher concentration and one set with no quencher added.

PCB Sensitized Phosphorescence of Biacetyl. Benzene solutions of I–IV (0.07 *M*) and of benzophenone (0.08 *M*) each containing 0.1 *M* biacetyl concentrations were degassed in 13 × 100 mm Pyrex tubes. Excitation was induced at 315 nm on an Aminco-Bowman spectrofluorometer. Phosphorescence emissions at 516 nm were measured. The ratio of intensities obtained with either PCB or benzophenone provided a measure of intersystem crossing. After each degassed sample was measured, the tube was opened. The emission intensity of the aerated sample was subtracted from

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the original intensity reading to correct for impurity or by-product emission.

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ministration DHEW under Contract FDA 71-285 and the Michigan Agricultural Experiment Station, Michigan Agricultural Experiment Station Journal Article No. 6786.

Reaction of Amines with Haloalkanes. III. The Stability and Photochemical Decomposition of the Complex Formed by *n*-Butylamine with Carbon Tetrachloride

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Contribution from the Department of Chemistry and the Laboratory for Research on the Structure of Matter, University of Pennsylvania, Philadelphia, Pennsylvania 19174. Received September 6, 1973

Abstract: The formation constant for the 1:1 complex of *n*-butylamine and carbon tetrachloride has been measured by determination of its absorbance at 240–250 nm in *n*-hexane at 25°. The value of K_f was found to be $0.032 M^{-1}$, a value placing the complex in the range of low stability shown by other aliphatic amine-haloalkane pairs. The limitation of the accuracy of that K_f value is discussed. An induction period in the photochemical decomposition of the complex aided the measurement of both K_f and the kinetics of the decomposition. The kinetic studies have been carried out in *n*-hexane at 25°, using both spectroscopic and chemical measurements. The results are in agreement with a mechanism proposed by Stevenson and Coppinger and by Mulliken for the decomposition of the weak complex and with a mechanism proposed for the photochemical initiation of chain reaction between the amine and haloalkane.

The photochemical initiation of reaction between amines and haloalkanes probably takes place by completion of charge transfer in the electron donor-acceptor interaction of the reactant molecules.^{1–3} Spectroscopic measurements have shown that the complexes formed by that charge-transfer interaction are so loose as to approach the nature of contact pairs⁴ when the amines are aliphatic and CCl_4 is the acceptor,^{1,3,5,6} but no quantitative estimate of the strength of the complex involving a primary aliphatic amine has been made previously. Furthermore, although a reasonable mechanism for the decomposition of the excited complexes that form on light absorption has been suggested^{1,2} and has been related³ to the ensuing chain reaction, no experimental test of that mechanism has been made heretofore.

Since the complexes also appear to play an important role in dark initiations of the amine-haloalkane reactions,^{3,7,8} and since primary aliphatic amines have been used most frequently in the study of the reactions, we have made quantitative measurements of the stability and photochemical decomposition of the complex formed between *n*-butylamine and CCl_4 .

Experimental Section

Materials. Carbon tetrachloride and *n*-butylamine were prepared as before.³ Spectroquality *n*-hexane and chloroform (Matheson Coleman and Bell) were used as received. Prepurified nitrogen (Air Products, Inc.) was passed over Drierite before use. Ammonia gas (Air Products, Inc.) was used directly from a lecture bottle.

n-Butylamine hydrochloride (Eastman Organic Chemicals) was recrystallized from anhydrous ether. Hexachloroethane (Baker Chemical Co.) was used without further purification. *n*-Butylidenebutylamine was prepared by the method of Day and Stein⁹ (bp 141–145° (lit.¹⁰ 140–145°); n_D^{20} 1.4217 (lit.¹⁰ n_D^{20} 1.4211)). Potassium ferrioxalate was prepared by mixing three volumes of 1.5 *M* $K_2C_2O_4$ with one volume of 1.5 *M* $FeCl_3$ in the dark. The green precipitate was recrystallized three times from water and was stored in the dark.

Apparatus and Procedures. Dry prepurified nitrogen was bubbled through the amine and the CCl_4 for 2 hr to remove oxygen immediately before preparation of the solutions. The solvent used was *n*-hexane in all cases. Solutions were prepared in the dark and under nitrogen. Trials of degassing by several freeze-pump-thaw cycles produced no changes in the observations.

Concentrations were determined by weighing procedures. Smaller amounts of the reactants were delivered by syringes chosen to be free of initiating metals or salts.

A Cary Model 14 recording spectrophotometer was employed for all of the spectroscopic measurements. The stoppered cuvettes were kept at constant temperature by circulating water from a Wilkens-Anderson Lo Temp thermostat through their jackets. A stream of nitrogen was used to purge the cell compartment and to drive a magnetic stirrer placed under the cuvettes.

The intensity of the light entering the cells in the kinetic runs was determined by ferrioxalate actinometry suitable to the low intensity¹¹ used.

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