Photochemistry of Polyhaloarenes. 8. The Photodechlorination of Pentachlorobenzene

Peter K. Freeman,* N. Ramnath, and Alan D. Richardson
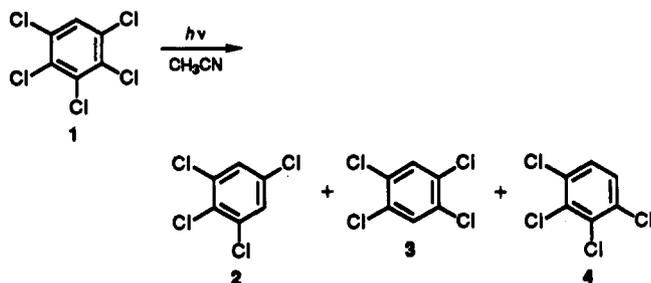
Department of Chemistry, Oregon State University, Corvallis, Oregon 97331-4003

Measurements of the intersystem crossing yield of pentachlorobenzene triplet, the quenching of photo-dechlorination of pentachlorobenzene with fumaronitrile, the dependence of the fluorescence lifetime, and the quantum yield of photodechlorination of pentachlorobenzene upon substrate concentration and the dependence of relative product concentration upon light intensity provide evidence for three pathways to product: direct fission of singlet and triplet and fragmentation of triplet excimer.

The photochemistry of aromatic halides has been studied with considerable interest in recent years due to the impact of these species in the environment and the need to devise practical waste management methods for their containment.[1,2] As part of our investigation into the photochemistry of a broad range of aromatic halides, we have previously reported on the photochemistry of pentachlorobenzene (1) in the presence and absence of electron donors.[2,3]

Direct irradiation of 1 in acetonitrile at 254 nm gives 1,2,3,5-tetrachloro (2), 1,2,4,5-tetrachloro- (3), and 1,2,3,4-tetrachlorobenzene (4) as the only products at low conversions of 1. In addition, the quantum yield of dis-

appearance of 1 was found to increase with increasing concentrations of 1 accompanied by a steady change in the relative ratios of the regioisomers.[3] Influenced by the report that the quantum efficiency of intersystem crossing of polychlorobenzenes in cyclohexane is close to one,[4] reaction from the singlet state was ruled out, initially, in favor of a reaction from the triplet state. Since the mechanism for the photochemical dechlorination of pentachlorobenzene represents a key model system in our studies of the photochemistry of haloarenes, we have devoted additional effort to an elucidation of the mechanistic pathways involved. As a starting point for discussion, a kinetic scheme showing possible reaction pathways is illustrated in Scheme I.

In order to underline the role of the triplet state, a butyrophenone ($E_T \approx 74$ kcal/mol)[5] sensitized irradiation of 1 at 350 nm was carried out and dechlorination and formation of the tetrachlorobenzenes was observed. Since 1 does not absorb at this wavelength range and butyrophenone absorbs all the incident light, the reaction clearly occurs through the intermediacy of the triplet state of 1

Scheme I
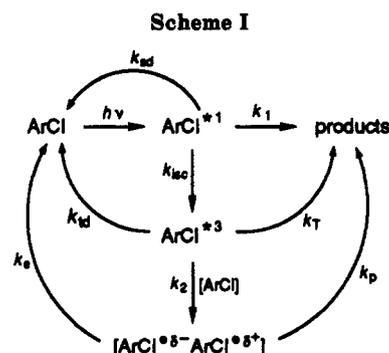
generated through triplet energy transfer from the butyrophenone triplet. The triplet state, however, might not appear to possess sufficient energy ($E_T = 74$ kcal/mol)[6] to break an aromatic C–Cl bond (DH$_{C–Cl}$ = 85–95 kcal/mol),[7,8] although homolysis could occur if contributions to the vibrational energy content of the excited state and strain relief (2.2 kcal/mol per ortho Cl–Cl bond interaction)[9] make up the deficit. This provides considerable encouragement for the proposal that the energy-demanding homolysis may be avoided through the formation of a triplet excimer[10] of the aryl halide through transfer of an electronic charge from the ground state of the halide to the excited triplet. The fact that the quantum yield of disappearance of 1 increased with increasing concentration of substrate supports this proposal.

In the absence of reaction from the singlet state ($k_1 = 0$), the steady-state assumption for the kinetic scheme represented in Scheme I gives eq 1, where $F = k_p/(k_p +$

$$\phi_{total} = \phi_{isc}\left(\frac{k_T + k_2[1]F}{k_T + k_{td} + k_2[1]}\right) \quad (1)$$

k_e), which was viewed as providing a satisfactory model.[2] Actual measurement of the quantum yield of intersystem crossing of 1 in acetonitrile using the cis–trans isomerization of *cis*-piperylene,[11] however, gave a value of 0.8, indicating that singlet reactivity cannot be ruled out entirely. Further, the reaction was quenched very efficiently

(1) Bunce, N. J.; Gallagher, J. C. *J. Org. Chem.* **1982**, *47*, 1955.
(2) Freeman, P. K.; Srinivasa, R.; Campbell, J-A.; Deinzer, M. L. *J. Am. Chem. Soc.* **1986**, *108*, 5531.
(3) Freeman, P. K.; Ramnath, N. *J. Org. Chem.* **1987**, *53*, 148.
(4) Bunce, N. J.; Hayes, P. J.; Lemke, M. E. *Can. J. Chem.* **1983**, *61*, 1103.
(5) Pitts, J. N.; Burley, D. R.; Mani, J. C.; Broadbent, A. D. *J. Am. Chem. Soc.* **1968**, *90*, 5900, 5902. Kochevar, I. E.; Wagner, P. J. *J. Am. Chem. Soc.* **1972**, *94*, 3859.

(6) Iwasaki, N.; Misra, T. N.; Kinoshita, M. *J. Lumin.* **1984**, *29*, 83.
(7) Bunce, N. J.; Bergsma, J. P.; De Graaf, W.; Kumar, Y.; Ravanal, L. *J. Org. Chem.* **1980**, *45*, 3708.
(8) Egger, K. E.; Cocks, A. T. *Helv. Chim. Acta* **1973**, *56*, 1516.
(9) Benson, S. W. *Thermochemical Kinetics*, 2nd ed.; Wiley: New York, 1976; p 281.
(10) See, for example Lim, E. C. *Acc. Chem. Res.* **1987**, *20*, 8. Takemura, T.; Aikawa, M.; Baba, H.; Shindo, Y. *J. Am. Chem. Soc.* **1976**, *98*, 2205. Locke, R. J.; Lim, E. C. *Chem. Phys. Lett.* **1989**, *160*, 28. Locke, R. J.; Lim, E. C. *Chem. Phys. Lett.* **1987**, *138*, 489. Nickel, B.; Rodriguez Prieto, M. F. *Chem. Phys. Lett.* **1988**, *146*, 125. Locke, R. J.; Lim, E. C. *J. Chem. Phys.* **1989**, *93*, 6017. Maciejewski, A. *J. Photochem. Photobiol. A* **1988**, *43*, 303.
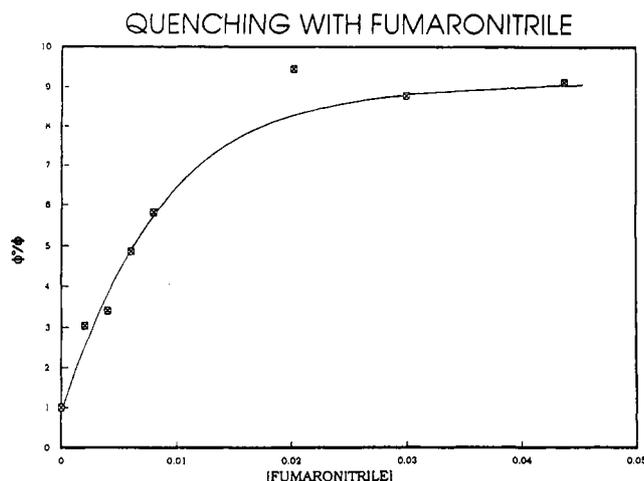(11) Lamola, A. A.; Hammond, G. S. *J. Chem. Phys.* **1965**, *43*, 2129.

QUENCHING WITH FUMARONITRILE

Figure 1. Plot of inverse of relative quantum yield of photodechlorination ϕ°/ϕ vs concentration of fumaronitrile.

by the triplet quencher fumaronitrile.[12] Figure 1 shows the Stern–Volmer quenching plot for the reaction at 300 nm. The function is linear with an intercept of 1 at low quencher concentrations but as the concentration is increased is concave downward. By use of steady-state methods, it can be demonstrated that this quenching pattern signals the presence of both singlet and triplet reactions.[12] The plateau in Figure 1 thus represents the singlet reaction at 300 nm after the triplet reaction has been completely quenched by fumaronitrile. It thus appears that the observed quantum yield is the sum of the quantum yields of singlet and triplet processes.

The results from quenching by fumaronitrile clearly suggest the presence of a reactive singlet state. Reaction from the singlet state could occur through direct fission of the C–Cl bond, which is feasible in terms of the energy of the singlet state ($\sim$95 kcal/mol). In order to determine the possibility of reaction via a singlet excimer species similar to that depicted for the triplet state, the fluorescence lifetime of 1 was measured as a function of its concentration in ethanol. The lifetime ($\tau_s = 7.5$ ns) remained constant over a concentration range of 0.005–0.04 M,[13] and the singlet quantum yield does not increase with increasing substrate concentration in acetonitrile (vide infra), thus ruling out the intervention of a singlet excimer intermediate. The reaction from the singlet state thus occurs through the direct fission of the C–Cl bond. The contribution to the total quantum yield due to singlet reactivity ($\phi_{singlet}$) may be written as in eq 2, while the overall quantum yield ($\phi_{singlet} + \phi_{triplet}$) is provided in eq 3.

$$\phi_{singlet} = \frac{k_1}{k_1 + k_{isc} + k_{sd}} \tag{2}$$

$$\phi_{total} = \frac{k_1}{k_1 + k_{isc} + k_{sd}} + \phi_{isc}\left(\frac{k_T + k_2[1]F}{k_T + k_{td} + k_2[1]}\right) \tag{3}$$

A plot of the total quantum yield versus the concentration of pentachlorobenzene provides a very nice linear plot ($r = 0.995$; Figure 2), suggesting that $(k_T + k_{td}) > k_2[1]$. Thus, by extrapolation of [1] to zero, one can calculate the quantum yield independent of triplet excimer ($\phi_{singlet} + \phi_{triplet}$). Subtraction of the quantum yields for direct fission

(12) Turro, N. J. *Modern Molecular* Photochemistry, Benjamin Cummings: Menlo Park, 1978; p 254.
(13) Ethyl alcohol has a greater E_T value than acetonitrile (51.9 vs 46.0) and the rate constant for excimer formation of 4-bromobiphenyl is 60% greater in ethyl alcohol than in acetonitrile: Jang, J-S. Unpublished work.
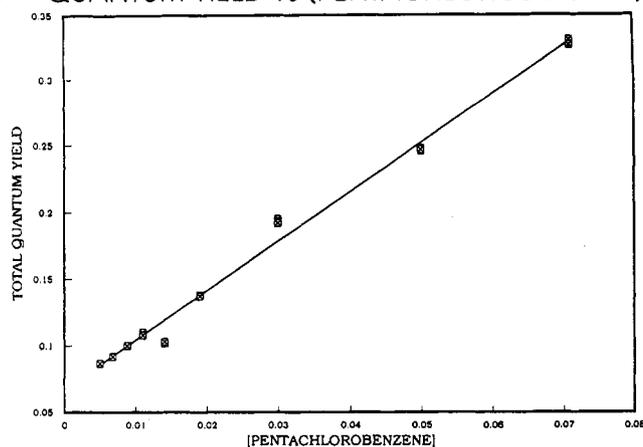
QUANTUM YIELD vs (PENTACHLOROBENZENE)

Figure 2. Plot of the quantum yield of photodechlorination vs the concentration of pentachlorobenzene.

INVERSE OF TRIPLET QUANTUM YIELD vs
INVERSE OF [PENTACHLOROBENZENE]
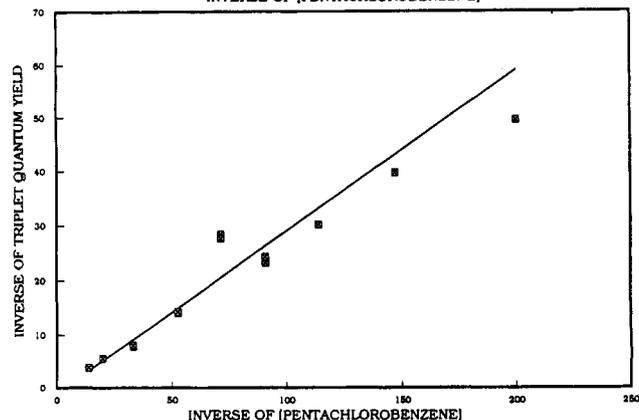
Figure 3. Plot of the inverse of the triplet excimer quantum yield $1/\phi_{ex}$ vs the inverse of pentachlorobenzene concentration.

from singlet and triplet states ($\phi_{singlet} + \phi_{triplet}$) from ϕ_{total} provides the expression for the dependence of the remainder (ϕ_{ex}) upon concentration (eq 4). If this mechanistic picture is correct, a plot of the reciprocal ($1/\phi_{ex}$) versus the reciprocal of the concentration of the substrate should be linear. We find, indeed, that there is a reasonable linear correlation ($r = 0.950$), which is illustrated in Figure 3.

$$\phi_{ex} = \phi_{isc}\frac{k_2[1]F}{k_T + k_{td} + k_2(1)} \tag{4}$$

In reconsidering the energy requirements for conversion of triplet (ARCl*[3]) or excimer ($\text{ArCl}^{\delta-}\text{ArCl}^{\delta+}$) to product, a process similar to delayed luminescence[14] involving generation of higher energy singlet species via triplet–triplet annihilation processes is conceivable. Such processes, however, can be ruled out as in each case the rate of product formation would be a nonlinear function of the intensity, whereas a plot of relative product concentration versus intensity is linear ($r = 0.995$; Figure 4), which is consistent with the expression for ϕ_{total} given in eq 3. Excitation of (ArCl*[3]) or excimer ($\text{ArCl}^{\delta-}\text{ArCl}^{\delta+}$) with a second photon can be ruled out on a similar basis. A third alternative that might be considered at this point is the suggestion that the interaction of triplet (ArCl*[3]) with

(14) Birks, J. B. *Photophysics of Aromatic Molecules*; Wiley: New York, 1970; p 372.

Figure 4. Plot of the relative product concentration (tetrachlorobenzenes) vs intensity (in Einsteins).

Table I. Relative Contributions of the Three Major Mechanistic Reaction Pathways in the Photodechlorination of Pentachlorobenzene (1)

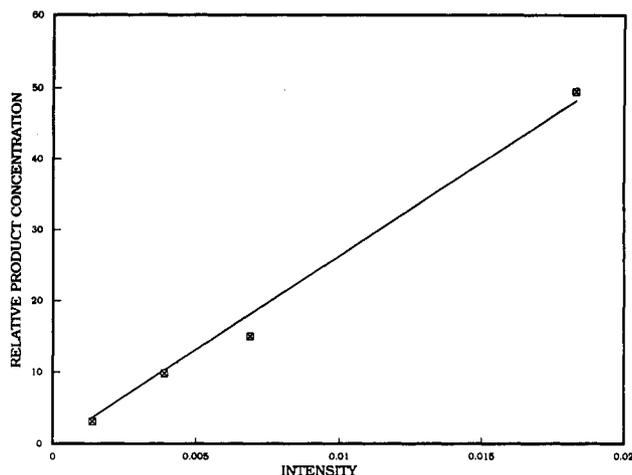| [1] (M)	ϕ_{total}	ϕ_{ex} (%)	$\phi_{triplet}$ (%)	$\phi_{singlet}$ (%)
0.0050	0.087	0.0202 (23.2)	70.8	6.00
0.0068	0.092	0.0252 (27.3)	67.0	5.70
0.0088	0.100	0.0332 (33.2)	61.6	5.20
0.0110	0.108	0.0412 (38.1)	57.0	4.90
0.0140	0.103	0.0362 (35.1)	59.8	5.10
0.0190	0.138	0.0712 (51.6)	44.6	3.80
0.0300	0.193	0.126 (65.4)	31.9	2.70
0.0500	0.247	0.180 (72.9)	24.9	2.10
0.0710	0.329	0.262 (79.7)	18.7	1.60

ground-state ArCl results in direct formation of aryl radical and a Cl• atom π-complex of pentachlorobenzene (eq 5).

$$\text{ArCl}^{*3} \xrightarrow{\text{ArCl}} \text{Ar}\bullet + \text{Cl} \leftarrow \text{ArCl} \qquad (5)$$
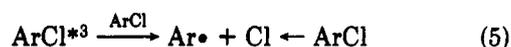
This variation seems most unlikely, since such a chlorine atom complex would be stabilized to a very small extent, if at all, by an electron deficient arene such as C_6HCl_5. The substitution of one nitro group on the benzene ring reduces the selectivity (S^m) for tertiary/primary hydrogen abstraction from 2,3-dimethylbutane from 5.1 to 1.0. For comparison, free Cl• atoms in neat 2,3-dimethylbutane give an S^m value of 0.63.[15] Since pentachlorobenzene would be a weaker π-base than nitrobenzene, the process illustrated in eq 5 would provide no help in the fission.

Although all questions are not answered, we are now able to propose an improved mechanistic scheme for the photodecomposition of the useful model polychlorobenzene substrate. It seems clear that the simplest picture is that of a three-way competition that involves direct homolysis of singlet and triplet states and C–Cl fragmentation of the radical anion-like moiety of the excimer. The competition of these three reaction pathways is illustrated in Table I. The major routes to product are via direct fission of triplet state and reaction through the intermediacy of excimer with only a minor contribution of singlet.

Experimental Section

General Procedures. Reagent-grade acetonitrile (EM Science or Baker Chemical Co.) was freshly distilled from phosphorus pentoxide, and its purity was greater than 99% by GLC analysis. Pentachlorobenzene (Aldrich) was recrystallized from ethanol and dried in a vacuum oven before use. cis-1,3-Pentadiene (Albany

International Chemicals Division, 99%), fumaronitrile (Aldrich, 98%), and butyrophenone (Lancaster Synthesis, 98%) were used without further purification. UV–vis spectra were obtained on Hewlett-Packard Models 8451A and 8452a diode array spectrometers. Fluorescence and phosphorescence spectra were determined by laser flash spectroscopy with an excitation wavelength of 266 nm. The laser source was a pulsed Nd-YAG laser. Lifetime profiles were obtained by classical PMT, boxcar integration, and digitalization.

General Procedure for Photolysis. The irradiation of 1 has been described elsewhere.[2,3] At the wavelength of irradiation (254 nm), the optical density of the acetonitrile solutions of 1 used for determining the dependence of quantum yield of disappearance of 1 on the concentration of 1 was >2 over the entire range of concentrations used (0.005–0.071 M; $\epsilon^{254}(CH_3CN = 1800)$. This ensured uniform absorption of light at all the concentrations employed. The fate of the chlorine lost during the photolysis was determined by titrating photolyzed 0.02 M solutions of 1 against a standard NaOH solution. Hydrogen chloride formation (12.4% ± 0.8) compares favorably with the amount of 1 consumed during the irradiation as determined by GC analysis (14.6% ± 0.6). Sensitized irradiations and quenching studies were conducted at 350 and 300 nm, respectively, with the appropriate lamps.

Sensitized Irradiation of Pentachlorobenzene (1). A stock solution containing a mixture of 0.0532 and 0.0496 M of 1 and butyrophenone, respectively, was prepared in acetonitrile. A blank solution of 1 of the same concentration was also made in acetonitrile. All solutions contained hexadecane as internal standard for GLC analysis (typically, one-third of the mass of 1 in the solution). Two sets of each solution (1 mL) were degassed in Pyrex tubes (Ace Glass, 170 × 15 mm) and irradiated in a Rayonet merry-go-round reactor equipped with eight 3500-Å Rull lamps. The percentage conversion of 1 was typically 10–15%. The percentage conversion of 1 in the blank solution was less than 1%.

Irradiation of Pentachlorobenzene in the Presence of Quenchers. (a) cis-1,3-Pentadiene. A stock solution of 1 (with hexadecane as internal standard) and the diene (0.0393 and 0.0691 M, respectively) were prepared in acetonitrile. Appropriate volumes of the diene solution were pipetted into 5-mL volumetric flasks containing 2 mL each of the stock solution of 1 and diluted up to the mark. The concentration of the pentadiene was thus varied between 0.00 and 0.0415 M at a constant concentration of 0.0157 M of 1. Two sets of each solution (1 mL) were degassed and irradiated at 300 nm for 60 min in the Rayonet reactor as usual. The solutions were irradiated in the presence of three sets of azoxybenzene[16] actinometer solutions (1 mL; ~0.006 M). **(b) Fumaronitrile.** Solutions of 1 (with hexadecane as internal standard) and fumaronitrile were made as described previously such that the concentrations of fumaronitrile varied from 0.00 to 0.0437 at a constant concentration of 0.0158 M of 1. Two sets of each solution of 1 mL each were degassed and irradiated in the presence of azoxybenzene actinometer at 300 nm for 60 min.

Determination of Quantum Yield of Intersystem Crossing (ϕ_{isc}) of Pentachlorobenzene (1). The cis → trans isomerization of cis-1,3-pentadiene was used to determine the quantum yield of intersystem crossing of 1 according to the method of Lamola and Hammond.[11] The cis/trans ratio of the isomers was determined by irradiating several degassed 1-mL samples of a solution containing a mixture of 0.0127 M of 1 and 0.103 M of the diene over various lengths of time (0.5–40 h). The irradiations were carried out at 300 nm in the Pyrex tubes described previously. The ratio at the photostationary state was determined to be cis/trans = 1.80. The quantum yield of cis → trans isomerization was corrected for any quenching of the singlet state of 1 by the ground state according to the method of Stephenson and Hammond.[17] Accordingly, the quantum yield of the isomerization

(15) Ingold, K. U.; Lusztyk, J.; Raner, K. D. *Acc. Chem. Res.* **1990**, *23*, 219. Raner, K. D.; Lusztyk, J.; Ingold, K. U. *J. Am. Chem. Soc.* **1989**, *111*, 3652.

(16) Bunce, N. J.; LaMarre, J.; Vaish, S. P. *Photochem. Photobiol.* **1984**, *39*, 531.

(17) Stephenson, L. M.; Whitten, D. G.; Vesley, G. F.; Hammond, G. S. *J. Am. Chem. Soc.* **1966**, *88*, 3665. Stephenson, L. M.; Whitten, D. G.; Hammond, G. S. *Chemical Ionization Excitation.* Proceedings of a Conference on Radiation Chemistry and Photochemistry, 1966, University of Newcastle-upon-Tyne, 1967; pp 35–42. Stephenson, L. M.; Hammond, G. S. *Pure Appl. Chem.* **1968**, *16*, 125.

was determined at a constant concentration of 1 (0.0127 M) with the diene concentrations varying from 0.0101 to 0.203 M. The quantum yield of isomerization decreased with increasing concentration of the diene and reached a constant quantum yield after the concentration of the diene in the mixture increased above 0.081 M, thus showing some quenching of the singlet state of the halide. The quantum yield of isomerization corrected for singlet quenching was determined by plotting the inverse of the quantum yield of isomerization versus the corresponding pentadiene concentration and extrapolating the linear portion of the curve to zero concentration of the diene.

Photochemistry of Polyhaloarenes. 9. Characterization of the Radical Anion Intermediate in the Photodehalogenation of Polyhalobenzenes

P. K. Freeman* and N. Ramnath

Department of Chemistry, Oregon State University, Corvallis, Oregon 97331-4003

Received August 28, 1990

The product-determining intermediate in the photodehalogenation of polyhalobenzenes has been characterized by generating excimers and radical anions within a micellar core and by formation of corresponding radical anions by electron transfer from lithium *p,p'*-di-*tert*-butylbiphenyl radical anion (LiDBB). The photodechlorination of pentachlorobenzene (1; 254 nm, CH_3CN) produces 1,2,3,5-tetrachloro- (2), 1,2,4,5-tetrachloro- (3), and 1,2,3,4-tetrachlorobenzene (4). The regiochemistry of this reaction is compared with that observed in the photodechlorination of 1 in a micellar solution of hexadecyltrimethylammonium bromide (CTAB) with occupancy numbers (*n*) principally <2 and ≥2. Further comparisons with photodechlorination of 1 in a micellar CTAB solution (*n* < 2) in the presence of triethylamine, as well as photodechlorination in CH_3CN in the presence of triethylamine, were used to characterize unencumbered radical anions. The regiochemistries observed in photolytic dehalogenations of 1, 2, 1,2,4-trichlorobenzene, and pentafluorobenzene in the presence of triethylamine are in good agreement with those realized in the radical anion fragmentations induced by electron transfer from LiDBB.

The mechanistic aspects of the photochemistry of monochloroarenes have been studied in detail in the presence of electron donors.[1] Polychlorobenzenes exhibit enhanced and efficient photodechlorination to their corresponding lower homologues in the presence of electron donors.[2,3] This reaction offers a potentiality for development as a powerful tool for toxic waste disposal methods and thus the mechanistic pathways followed are of considerable interest.

Irradiation of pentachlorobenzene (1) in acetonitrile at 254 nm leads to its dechlorination. At low conversions (15–20%) of 1, 1,2,3,5-tetrachlorobenzene (2) is formed as the major product along with 1,2,4,5- and 1,2,3,4-tetrachlorobenzene (3 and 4, respectively) as minor products (Scheme I).[2,3] In the presence of triethylamine (TEA), irradiation at 254 nm leads to a reversal in the regiochemistry of dechlorination of 1 so that 1,2,4,5-tetrachlorobenzene (3) is now formed as the major product with 2 and 4 generated as minor components as shown in Scheme I.[2,3]

The reversal in regiochemistry in the presence of triethylamine is likely the consequence of reaction of the radical anion of 1 generated through the transfer of an electron from triethylamine to an excited state of 1. The pattern of monodechlorination observed is consistent with that expected from a radical anion of 1, on the basis of a transition state analogous to the intermediate for nucleophilic aromatic substitution.[2] As noted, the regiochemistry of the photodechlorination in the absence of triethylamine

Scheme I

2, 50.1% + 3, 37.3% + 4, 12.6%

2, 25.3%　　　3, 66.2%　　　4, 8.5%

Scheme II

contrasts sharply with that in the presence of triethylamine and the dependence of quantum yield upon substrate concentration and quencher is consistent with product formation via the triplet and triplet excimer as major

---

(1) Bunce, N. J.; Gallagher, J. C. *J. Org. Chem.* 1982, *47*, 1955.
(2) Freeman, P. K.; Srinivasa, R.; Campbell, J.-A.; Deinzer, M. L. *J. Am. Chem. Soc.* 1986, *108*, 5531.
(3) Freeman, P. K.; Ramnath, N. *J. Org. Chem.* 1987, *53*, 148.