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## THE PHOTOCHEMISTRY OF THREE TETRACHLORONAPHTHALENES<sup>1</sup>

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Summary: The regiochemistry of the photolysis of three tetrachloronaphthalenes is sharply dependent upon the presence of triethylamine. Analysis of the steady state kinetics in the presence and absence of quenchers and of triethylamine provides a mechanistic rationale in terms of triplet, triplet excimer, and singlet exciplex.

Polychloronaphthalenes have a number of industrial uses analogous to those of polchlorobiphenyls and represent similar environmental threats to human health.<sup>2</sup> Since the polychloronaphthalenes all absorb in the sunlight range, the mechanisms of photodegradation are of considerable interest. Due to the excellent prospects for distinguishing mechanistic alternatives based on regiochemical differences, we chose to evaluate the photochemical hydrodehalogenation of 1,2,3,4-tetrachloro- (1), 1,4,6,7-tetrachloro- (2) and 1,3,5,8-tetrachloronaphthalene (3)



The photochemical hydrodechlorinations of tetrachlorides 1, 2, and 3 were carried out in acetonitrile at 300 nm with the extent of conversion maintained so that monodechlorination was assured. In the direct irradiation of tetrachloro 1, monodechlorination favored replacement of chlorine at C-2 over C-1, producing a ratio of 1,3,4-trichloronaphthalene (1-2H) to 1,2,3-trichloronaphthalene (1-1H) of 4.0:1.0, while photolysis of tetrachloro 2 generated an identical ratio of 4.0:1.0 for 2-1H:2-6H. Analogous photochemical hydrode-chlorination of tetrachloro 3 produces 1,3,5-trichloronaphthalene (3-8H) and 1,4,6-trichloronaphthalene (3-1H) in a ratio of 2.3:1, accompanied by small amounts of two additional trichlorides (always less than 10% and presumably 3-3H and 3-5H). The photochemical hydrodehalogenation of tetrachloro 1, 2, and 3 at 300 nm in acetonitrile in the presence of triethylamine, using concentrations of tetrachloronaphthalene and triethylamine such that all the light was absorbed by the napthalene substrate, provided rather remarkable changes in the regiochemistry. Amine induced photodechlorination of 1 provides an enhanced ratio of 10:1 of 1-2H:1-1H, while 2 generates a 50:1.0 ratio of 2-6H:2-1H, which represents a 200 fold switch in the regiochemistry. Parallel treatment of tetrachloro 3 provides a 25:1.0 ratio of monodechlorination products 3-1H and 3-8H, a 63 fold switch in the relative rates of hydrodechlorination.

Additional insight is provided by analysis of the steady state kinetics of the phototransformations of tetrachlorides 1, 2, and 3. In each case the quantum yield increased with substrate concentration (ArCl). Plots of 1/ $\phi$  versus 1/(ArCl) were very similar in each case and are illustrated for 1 in Fig 1. At high concentrations of ArCl the plot is linear with a positive slope, while as the concentration is decreased the plot is concave downward and approaches a linear plot with a zero slope. This is consistent with the mechanistic picture presented in Scheme I. At high concentrations of ArCl excimer formation is dominant,  $k_2(ArCl)F >> k_p$  and equation 1, derived using the steady state assumption, pertains. As the concentration of substrate is reduced excimer formation drops off and fission directly from the triplet provides a constant contribution. The view that the triplet state provides the branching point leading to product by direct fission or via excimer formation is supported by the quantum yield for intersystem crossing for 1,<sup>3</sup>  $\phi_{isc}$ = 1.00 ± 0.04, oxygen quenching, and linear Stern-Volmer plots of  $\phi_0/\phi$  versus concentration of triplet quencher 1,3-pentadiene for tetrachloro 1, 2, and 3.



Figure 1. Plot of 1/\$\$ for product formation for photolysis of 1,2,3,4-tetrachloronaphthalene (1).

In the photodechlorinations carried out at 300 nm in acetonitrile in the presence of triethylamine (A), the quantum yields are enhanced and the plots of  $1/\phi$  versus 1/(A) at the high end of the amine concentration range are linear, illustrated for 1 (Fig 2), which is consistent with the mechanism presented in Scheme II and a bimolecular generation of exciplex which is dominant over intersystem crossing, and with steady state eq 2. At the low end of the amine concentration range there are constant contributions to product via the triplet state according to Scheme I.

Scheme II



Figure 2. Plot of 1/¢ versus 1/(triethylamine) for photolysis of 1 at 300nm.

In Scheme II electron transfer to singlet state is portrayed. The plot of Fig 2 is also consistent for a process which involves electron transfer to the triplet state. However, using the values of the (slope)/(intercept) of Fig 2 and similar plots for the tetrachlorides 2 and 3 in the exciplex dominant region and the values of the triplet lifetimes obtained from phosphorescence measurements (112, 36, and 29 msec), values of  $k_{ex} \approx 10-10^2$  M<sup>-1</sup> s<sup>-1</sup> are obtained which are too low. Estimating the inherent radiative lifetime from the molar absorptivity,  $k_{isc}$  must be  $10^9-10^{10}$  s<sup>-1</sup>, since no detectable fluorescence was observed. The slope over the intercept using eq 2

now yields values  $10^9 - 10^{10} \text{ M}^{-1} \text{ s}^{-1}$  for k<sub>ex</sub> which seems much more reasonable.<sup>4</sup>

Thus, without amine, regiochemistry is directed by fission of triplet and triplet excimer and with amine by fission of singlet exciplex. Earlier in studies on pentachlorobenzene, we have provided evidence for fragmentation of a solvent separated or completely unencumbered radical anion in the product determining step.<sup>5</sup> In addition, we have suggested that a useful model for the fragmentation transition state is a radical anion with a carbon-halogen bond (bent out of the plane of the arene ring) and a localized radical center at the point of fission, similar in nature to the intermediate for aromatic nucleophilic substitution.<sup>6</sup> This would lead to transition state I for fragmentation at C-1 in the radical anion of 2, for example. The stability of the transition states for the competing fragmentation pathways in the present study might be assessed by summing the charge densities at carbons containing chlorine in the NBMO ( $\Sigma c_{iX}^2$ ) using the Longuet-Higgins rule.<sup>7</sup> As Burdon has suggested for nucleophilic aromatic substitution, the interaction between the the charge on carbon and the filled p-orbital of chlorine can be viewed as a destabilizing interaction.<sup>8</sup> Thus one chooses the lowest sum as representing the favored transition state and site of fragmentation. Table I lists the values for  $\Sigma c_{iX}^2$ , which for each substrate, predict the major reaction pathway successfully. Thus, with a back-of-the-envelope calculation, one can rationalize the key pathways invoked in these phototransformations.

Table I.	Assessment	of Relative	Stabilities	of Competing	g Transition	States
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	Parent Cpd	Localized Radical Pos	Σc <sub>iX</sub> <sup>2</sup>
CI SUM S	1	1	0.7272
		2	0.6252
	2	1	0.4545
ci		6	0.2501
0- 10	3	1	0.0909
I		3	0.1250
		5	0.5454
		8	0.3636

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## **References and Notes**

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