

Further Studies on the Photoisomerization and Hydrolysis of Chlorobiphenyls in Water. Common Ion Effect in the Photohydrolysis of 4-Chlorobiphenyl

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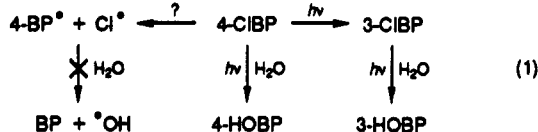
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The photochemistry of ^{14}C -labeled 2-chlorobiphenyl (2-CIBP) and 3-chlorobiphenyl (3-CIBP) in water was studied by isotopic dilution. 2-CIBP yielded 2-hydroxybiphenyl (2-HOBP) exclusively. 3-CIBP, on the other hand, yielded 3-HOBP, 2-HOBP, and 4-HOBP and a small amount of biphenyl (2%). Thus, 2-CIBP reacts exclusively by a heterolytic process, whereas 3-CIBP reacts not only by a heterolytic pathway but also by competing isomerization (to 2-CIBP and 4-CIBP) and homolytic pathways. The photochemistry of 4-CIBP in 80:20 (v:v) $\text{H}_2\text{O}-\text{CH}_3\text{CN}$ with added HCl or NaCl was also studied. These reactions were suppressed in the presence of HCl or NaCl. Further experiments demonstrated that the suppression was not due to any great extent to the ionic strength of the solution, spin orbit effects of heavy atoms, and proton quenching. These results are compatible with a mechanism originally proposed by Kropp in which the excited state of 4-CIBP, likely the triplet excited state, undergoes homolysis of the aryl carbon-chlorine bond to form a radical pair. Once formed the radical pair undergoes an electron transfer from the aryl radical to the chlorine atom to form a highly reactive aryl cation and chloride. Reaction of the aryl cation with added chloride then regenerates 4-CIBP. The overall reaction is equivalent to a common ion effect. The role of other mechanisms in the observed chemistry is also discussed.

Introduction

The photochemistry of aryl halides continues to receive attention, in part because the results may be relevant to the environment.¹⁻³ The chemistry is complex. Homolytic processes involving the bond dissociation of the aryl carbon-halogen bond dominate in nonpolar solvents.⁴ Heterolytic chemistry competes with the free-radical chemistry if the reactions are run in polar solvents.^{3,5} Dimerization reactions may also occur if the substrate concentration is sufficiently large.⁶ The photoisomerization of aryl halides is also now known.^{2,3,7}

We have previously studied the photochemistry of radiolabeled 4-chlorobiphenyl (4-CIBP) in water by isotopic dilution techniques.³ No biphenyl (BP), the product expected from free radical reactions, is formed. This negative result was anticipated because of the high dielectric constant and large oxygen-hydrogen bond dissociation energy of water. Instead, only products from heterolytic processes, 4-hydroxybiphenyl (4-HOBP) and 3-hydroxybiphenyl (3-HOBP), were formed. Additional experiments demonstrated that 3-HOBP resulted from the photohydrolysis of 3-chlorobiphenyl (3-CIBP), which had been generated by the photoisomerization of 4-CIBP.



(1) (a) Grimshaw, J.; deSilva, A. P. *Chem. Soc. Rev.* 1981, 10, 1981. (b) Davidson, R. S.; Goddin, J. W.; Kemp, G. *Adv. Phys. Org. Chem.* 1989, 20, 191. (c) Cornelisse, J.; DeGunst, G. P.; Havinga, E. *Adv. Phys. Org. Chem.* 1975, 11, 225.

(2) Dulin, D.; Drossman, H.; Mill, T. *Environ. Sci. Technol.* 1986, 20, 72.

(3) Pagni, R. M.; Moore, T. *J. Org. Chem.* 1987, 52, 770.

(4) Bunce, N. J.; Bergsma, J. P.; Bergsma, M. D.; DeGraaf, W.; Kumar, Y.; Ravanal, L. *J. Org. Chem.* 1980, 45, 3708.

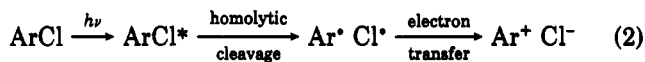
(5) (a) Ruzo, L.; Zabik, M. J.; Schuetz, R. D. *J. Am. Chem. Soc.* 1974, 96, 3809. (b) Soumillon, J. P.; DeWolf, B. *J. Chem. Soc., Chem. Commun.* 1981, 436. (c) Tissot, A.; Boule, P.; Lemaire, J. *Chemosphere* 1983, 12, 859. (d) Avila, V.; Gaponer, H. E. *J. Photochem.* 1984, 27, 163. (e) Previtali, C. M.; Ebbeson, T. W. *J. Photochem.* 1985, 30, 259. (f) Tissot, A.; Boule, P.; Lemaire, J. *Chemosphere* 1984, 13, 381. (g) Lemmetyinen, H.; Konijnenberg, J.; Cornelisse, J.; Varma, C. A. G. O. *J. Photochem.* 1985, 30, 315.

(6) (a) Ruzo, L.; Bunce, N. J. *Tetrahedron Lett.* 1975, 511. (b) Ruzo, L.; Bunce, N. J.; Safe, S. *Can. J. Chem.* 1975, 53, 688.

(7) Choudry, G. C.; Roof, A. A. M.; Hutzinger, O. *Tetrahedron Lett.* 1979, 2059.

How are the hydrolysis products formed from 4-CIBP and other aryl halides? Numerous mechanisms involving reactive intermediates such as arynes, σ complexes, addition products, aryl cations, and aryl radical cations have been proposed in the past. In the case of 4-CIBP in water we were able to show that the reaction did not occur through an aryne or addition-elimination mechanism.³

A mechanism which accounts nicely for both the homolytic and heterolytic chemistry observed for the photolysis of aryl halides is one originally proposed by Kropp for alkyl halides.⁸ In this scheme (as applied to aryl halides) an excited state of the aryl halide undergoes initial homolytic cleavage of the aryl carbon-halogen bond to form a radical pair which will yield radical products in nonpolar solvents. In polar solvents the radical pair undergoes an electron transfer from the aryl radical to the halogen atom to form an ion pair which will yield carbocationic products. If an aryl cation (Ar^+) is formed by this or another⁹ mechanism, added chloride should compete with water for the aryl cation and regenerate the aryl chloride.¹⁰ Thus, the quantum yield for the disappearance of the aryl chloride will be suppressed. This phenomenon is equivalent to the common ion effect observed in the solvolysis of numerous substrates.¹¹



The present work was undertaken to see if the photohydrolysis of 4-CIBP is subject to a common ion effect and to deduce if the other monochlorobiphenyls, 2-CIBP and 3-CIBP, undergo photoisomerization to other chlorobiphenyls.

(8) Kropp, P. J.; Poindexter, G. S.; Pienta, N. J.; Hamilton, D. C. *J. Am. Chem. Soc.* 1976, 98, 8135.

(9) The ion pair could be formed directly from the aryl chloride excited state.

(10) This does not violate the principle of microscopic reversibility because the aryl cation is formed photochemically but reacts thermally.

(11) Jones, R. A. Y. *Physical and Mechanistic Organic Chemistry*, 2nd ed.; Cambridge University Press: Cambridge, 1984.

Table I. Photochemistry of ^{14}C -Labeled 2-CIBP and 3-CIBP in Water

reactant (molarity)	reaction conditions ^a	% reactant remaining	products, ^b mol ^c			
			BP	2-HOBP	3-HOBP	4-HOBP
2-CIBP (2.15×10^{-5})	12 h, N ₂	5.9	abs	1.12×10^{-5}	abs	abs
3-CIBP (2.18×10^{-5})	8 h, N ₂	70	1.4×10^{-7}	1.22×10^{-6}	1.5×10^{-7}	8.0×10^{-8}

^a Hanovia 450-W mercury lamp, vycor filter. ^b abs = absent. ^c From one liter of solution.

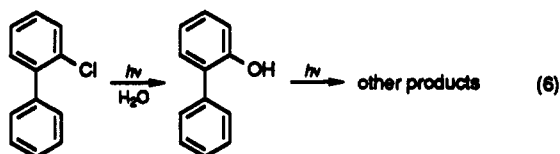
Table II. Photochemical Behavior of Monochlorobiphenyls in Water

reactant	reaction mode ^a	photoisomerization
2-CIBP	100% heterolysis	no
3-CIBP	2% homolysis; 98% heterolysis	yes, to 2-CIBP and 4-CIBP ^b
4-CIBP	100% heterolysis	yes, to 3-CIBP

^a Does not include photoisomerization. ^b See ref 18.

Results and Discussion

Photochemistry of 2- and 3-Chlorobiphenyl in Water. Because the chlorobiphenyls are poorly soluble in water,¹² isotopic dilution, a sensitive technique for identifying components in very low concentration, was used to follow the photochemistry of ^{14}C -labeled 2-CIBP and 3-CIBP. Typical results are shown in Table I. First of all it is clear that 2-CIBP is much more reactive than 3-CIBP. This observation is in line with the results of other researchers for reactions in $\text{H}_2\text{O}-\text{CH}_3\text{CN}^2$ and alkanes.¹³ The reaction of 2-CIBP is clean, however, yielding approximately 50% of 2-HOBP; no BP, 3-HOBP, or 4-HOBP is observed. The missing 50% of the material can be attributed to the secondary photolysis of 2-HOBP, a known process.^{2,14} The absence of BP and the rearranged phenols prove that the chemistry of 2-CIBP occurs exclusively by a heterolytic mechanism.



The photochemistry of 3-CIBP is more complex than that of 2-CIBP. Of the 30% of the 3-CIBP that had reacted in 8 h, 24% of the reacted substrate can be accounted for by four products: BP, 2-HOBP, 3-HOBP, 4-HOBP.¹⁵ The formation of biphenyl in this case is unique; neither 2-CIBP or 4-CIBP in water yielded this compound. Nonetheless, the amount of BP is small; biphenyl accounts for no more than 2% of the reacted 3-CIBP.^{16,17} Unlike BP which is formed by a homolytic mechanism involving free radicals, the three phenolic compounds are clearly formed through heterolytic pathways. Most interestingly, the formation of two of these compounds, 2-HOBP and 4-HOBP, suggests that 3-CIBP, in analogy to 4-CIBP,

photoisomerizes to 4-CIBP and 2-CIBP which then photolyze to give the observed phenols.¹⁸

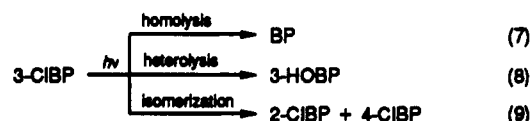


Table II summarizes the results for the photolysis of the monochlorobiphenyls in water. As expected for reactions in water, the substitution reactions occur primarily by heterolytic pathways. Because the oxygen-hydrogen bonds in water are strong, the abstraction of hydrogen from water by aryl radicals is endothermic; other reactions, i.e. heterolytic, become dominant. Photoisomerization also occurs for the two less reactive 3-CIBP and 4-CIBP, but not at all for the much more reactive 2-CIBP. Whether the correlation between reactivity and isomerization is mechanistically significant remains to be determined.

Several additional points are worth noting about these results. The higher reactivity of 2-CIBP than of 3-CIBP and 4-CIBP, for example, is striking and can be attributed to two factors:¹³ (1) the release of steric strain at the ortho positions of the biphenyl ring when the chlorine atom is released from the molecule, and (2) the larger triplet energies of ortho-substituted biphenyls. Bunce has shown that the bond homolysis of chlorobiphenyls from the corresponding triplet excited states is endothermic in all cases.¹³ Because 2-CIBP has the largest triplet energy, its bond homolysis is least endothermic and thus most efficient.

The mechanism by which 4-CIBP and 3-CIBP photoisomerize is not known but can be easily visualized to occur through intermediate benzvalene, Dewar benzene, and prismane intermediates, which are well-known products in the photochemistry of benzene derivatives.¹⁹

It is interesting that BP is formed in small amounts when 3-CIBP is irradiated in water but is undetected when 4-CIBP is photolyzed, even though 3-CIBP is a product of this latter photolysis. How is this possible? First of all, 4-CIBP not only yields 3-CIBP on photolysis but 4-HOBP as well. If a significant fraction of this reaction went through the 4-HOBP pathway, the amount of BP formed will clearly be less than when it arises from the direct photolysis of 3-CIBP. Even under these circumstances BP should likely be detected in the photolysis of 4-CIBP, provided the photochemical reactions are zero order in substrate (see Appendix 1). It is well known, however, that when the substrates are present in very low concentrations the photoreactions become first-order in substrate, a result we observed earlier in the photochemistry of chlorobiphenyls in water.²⁰ Under these circumstances it is easy to show that BP can be generated in one reaction but little BP generated in the other (see Appendix 1).

(12) (a) Mackay, D.; Mascarenhas, R.; Shiu, W. Y.; Valvani, S. C.; Yalkowsky, S. H. *Chemosphere* 1980, 9, 257. (b) Opperhulzen, A.; Gobas, F. A. P. C.; Van der Steen, J. M. D.; Hutzinger, O. *Environ. Sci. Technol.* 1988, 22, 638.

(13) Bunce, N. J.; DeSchutter, C. T.; Toone, E. J. *J. Chem. Soc., Perkin Trans. 2* 1983, 859.

(14) Sarakha, M.; Dauphin, G.; Boule, P. *Chemosphere* 1989, 18, 1391.

(15) The missing material is probably due to secondary reactions of the phenols.

(16) Biphenyl is photoinert in water,² whereas 4-HOBP,³ and 2-HOBP,^{2,14} and likely 3-HOBP are photoreactive. The 2% BP thus represents the maximum amount of this compound formed in the reaction.

(17) According to Pathfinder Laboratories, the ^{14}C -labeled 3-CIBP is uncontaminated by BP.

(18) In the photochemistry of 4-CIBP the formation of 3-HOBP was shown to arise from 3-CIBP. In the present study no attempt was made to find 2-CIBP and 4-CIBP during the photolysis of 3-CIBP.

(19) Turro, N. J. *Modern Molecular Photochemistry*; Benjamin/Cummings: Menlo Park, CA, 1978.

(20) Moore, T. A. M.S. Thesis, University of Tennessee, Knoxville, 1985.

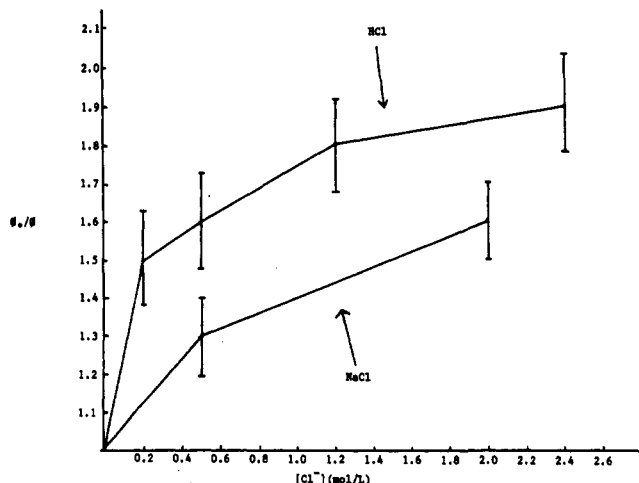


Figure 1. Relative quantum yields for the disappearance of 4-CIBP as a function of chloride concentration. The bars represent the error limits for the ϕ_0/ϕ values.

Reaction of 4-Phenylphenyl Cation with H₂O and Cl⁻. For the common-ion-effect experiment to be viable, the 4-phenylphenyl cation must react with Cl⁻ at rates comparable to those with H₂O. To see if this is true, the chemistry of 4-phenylbenzenediazonium ion in aqueous chloride was investigated. There is good reason to believe that this reaction will gauge the relative reactivity correctly. Swain has shown that aryldiazonium ions decompose in aqueous media to form aryl cations.²¹ Lewis studied the decomposition of benzenediazonium ion in aqueous chloride and found $k_{\text{Cl}}/k_{\text{H}_2\text{O}} = 2.5 \pm 0.13$ at 100 °C and 3.2 ± 0.3 at 50 °C, where k_{Cl} and $k_{\text{H}_2\text{O}}$ represent the rate constants for the reaction of C₆H₅⁺ with Cl⁻ and H₂O, respectively.^{22,23} Scaiano and Kim-Thuan generated aryl cations in aqueous media by flash photolysis of aryldiazonium ions and studied ion decay by indirect detection.²⁴ The phenyl cation was found to have a lifetime of 500 ps in pure water at room temperature. From these measurements, one calculates $k_{\text{Cl}}/k_{\text{H}_2\text{O}} \approx 290$.²⁵ The origin of the discrepancy between Scaiano and Kim-Thuan and Lewis is not clear. Because the large value for $k_{\text{Cl}}/k_{\text{H}_2\text{O}}$ is obtained by a more circuitous route, the smaller values

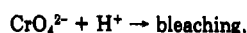
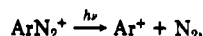
(21) (a) Swain, C. G.; Sheats, J. E.; Harbison, K. G. *J. Am. Chem. Soc.* 1975, 97, 783. (b) Swain, C. G.; Sheats, J. E.; Gorenstein, D. G.; Harbison, K. G. *J. Am. Chem. Soc.* 1976, 97, 791. (c) Swain, C. G.; Sheats, J. E.; Harbison, K. G. *J. Am. Chem. Soc.* 1975, 97, 796.

(22) Lewis, E. S. *J. Am. Chem. Soc.* 1958, 80, 1371.

(23) The error limits represent the standard deviation of the mean and were calculated by us.

(24) Scaiano, J. C.; Kim-Thuan, N. *J. Photochem.* 1983, 23, 269.

(25) The value for $k_{\text{Cl}}/k_{\text{H}_2\text{O}}$ can be computed in the following way. A Stern-Volmer plot of aryl cation yield versus [Cl⁻], where the cation is detected indirectly by the bleaching of CrO₄²⁻ as shown in the following three equations:



yields a slope of 5.3 M⁻¹. But

$$\text{slope} = 5.3 \text{ M}^{-1} = k_{\text{Cl}}\tau_{\text{H}_2\text{O}}$$

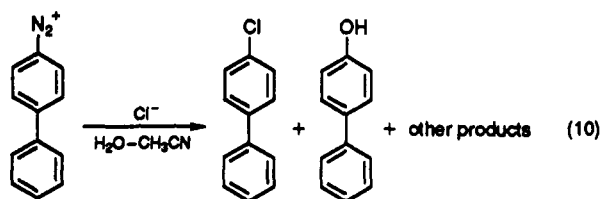
Since $\tau_{\text{H}_2\text{O}} = 1/k_{\text{H}_2\text{O}}[\text{H}_2\text{O}]$, it follows that

$$5.3 \text{ M}^{-1} = \frac{k_{\text{Cl}}}{k_{\text{H}_2\text{O}}[\text{H}_2\text{O}]}$$

Thus $k_{\text{Cl}}/k_{\text{H}_2\text{O}} = 5.3 \text{ M}^{-1}[\text{H}_2\text{O}] \approx 290$.

obtained by Lewis are more likely to be correct. It is obvious, nonetheless, that Cl⁻ can compete with H₂O for C₆H₅⁺.

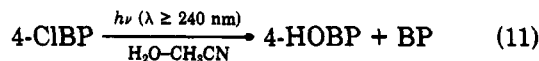
The measurement of $k_{\text{Cl}}/k_{\text{H}_2\text{O}}$ from the decomposition of 4-phenylbenzenediazonium ion proved to be difficult. Solubility considerations of both 4-phenylbenzenediazonium chloride and chloride salts made it difficult to measure the amounts of products, especially 4-CIBP, accurately by HPLC. Often mixed solvents (H₂O-CH₃CN) and HCl were used to overcome these problems, but these species are not always compatible (possible hydrolysis of CH₃CN), especially at high temperature. Furthermore, homolytic processes sometimes competed in the mixed solvents. For example, photolysis of the diazonium ion in HCl-H₂O-CH₃CN always produced some biphenyl. Even laser photolysis at 334 nm, where 4-CIBP and 4-HOBP do not absorb light, yielded several unknown products.



All of the modes of decomposition that were tried—thermal at various temperatures, photochemical in H₂O or H₂O-CH₃CN, with KCl or HCl—yielded $k_{\text{Cl}}/k_{\text{H}_2\text{O}}$ values which were typically greater than one, but varied erratically. The cleanest reaction occurred in the decomposition of the diazonium ion in a solution of CH₃CN-H₂O (1:1 by volume), which was 4.1 M in HCl, over a period of 1 week in the dark at room temperature. This gave $k_{\text{Cl}}/k_{\text{H}_2\text{O}} = 2.1$, a value not too different from those determined by Lewis²² for the decomposition of the benzenediazonium ion. Therefore, because the experiments demonstrated that Cl⁻ can compete with H₂O for the 4-phenylphenyl cation, the common-ion-effect experiment was attempted.

Photohydrolysis of 4-CIBP. Because the common-ion-effect experiment only required monitoring the unreacted 4-CIBP, the photolyses were performed on unlabeled 4-CIBP and analyzed by HPLC. To increase the amount of material analyzed, these experiments were performed in 4:1 (v:v) H₂O-CH₃CN, where 4-CIBP is more soluble than in H₂O.

The photoreaction of degassed solutions which were 10⁻⁵–10⁻⁴ M in 4-CIBP is largely heterolytic, with 4-HOBP being the major product at short reaction times. Small amounts of BP are also produced, but no 4-biphenylacetamide, a plausible product from the reaction of the aryl cation with CH₃CN in H₂O, is formed. Because 4-HOBP is photoactive under these conditions³ and BP is not,² the ratio of BP to 4-HOBP increased as the photolysis of 4-CIBP proceeded. These results are similar to those observed by Mill for the photolysis of aerated solutions of 4-CIBP in 9:1 H₂O-CH₃CN except no BP is formed in their reaction.^{2,26}



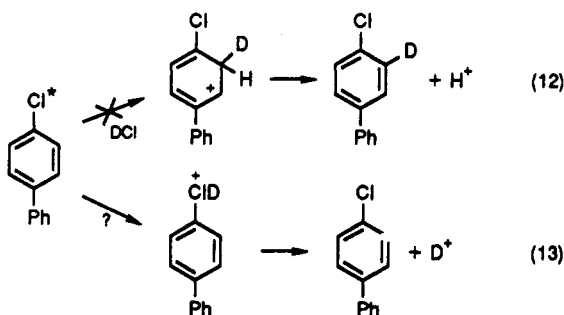
When the photolyses were repeated in a series of degassed, precision bore quartz tubes (on a merry-go-round apparatus) containing varying concentrations of HCl²⁷ or NaCl, the relative quantum yields for the disappearance

(26) For our system O₂ quenched the reaction without altering its course.

(27) Experiments described in the Experimental Section show that CH₃CN is stable under the reaction conditions.

of 4-CIBP were measured. The results of these experiments are shown graphically in Figure 1 in which ϕ_0/ϕ , the ratio of the quantum yield for the disappearance of 4-CIBP in the absence and presence of chloride is plotted against the formal chloride ion concentration. Because $\phi_0/\phi > 1$ when Cl^- is present, the reaction is being quenched by Cl^- , but the effect is not linear. Also, HCl is more effective at retarding the reaction than is NaCl. Is the quenching, however, due to Cl^- or is it due to H^+ or Na^+ ?

Because Cl^- is common to the HCl and NaCl solutions, the excess quenching by the HCl solution may be due to quenching by protons. Quenching of the excited states of molecules by protons is a well-established phenomenon.²⁸ To test this idea, the photolysis of 4-CIBP was repeated in a 1.2 M DCl in $\text{D}_2\text{O}-\text{CH}_3\text{CN}$ (80:20, v:v) solution. Recovered 4-CIBP contained no deuterium by high-field ^1H NMR in the presence of the Ag(fod)/Yb(fod) shift reagent²⁹ or mass spectrometry. Quenching by protonation at the nine hydrogen-containing carbons clearly does not occur.³⁰ Quenching at the three ipso carbons or the chlorine atom is still possible, however. This question was examined by a molecular orbital calculation,³¹ which showed the chlorine atom to have the largest negative charge in both 4-CIBP's ground state and lowest excited state. Thus, if any quenching occurs by protonation, it likely does so on the chlorine atom.³²



The quenching of the photodecomposition of 4-CIBP by NaCl could be explained by a spin orbit effect in which either Na^+ or Cl^- , ions possessing large atomic numbers, accelerates the rates of reactions involving changes of spin multiplicity. The effect, if it exists, should also be concentration dependent. Depending on which reaction is affected by the spin orbit effect, the quantum yield for the disappearance of 4-CIBP could go up or down. If the rate of intersystem crossing went up, for example, the quantum yield would go up because the triplet excited state is the reactive state. If the lifetime of the reactive triplet state were shortened, the quantum yield would go down. In an example to be described later Ruza et al. found the photodecomposition of a series of haloarenes in methanol to

(28) Pincock, J. A.; Redden, P. R. *Can. J. Chem.* 1989, 67, 227, 710.

(29) Wenzel, T. J.; Bettes, T. C.; Sadlowski, J. E.; Sievers, R. E. *J. Am. Chem. Soc.* 1980, 102, 5903.

(30) A referee has suggested that D^+ may not quench the reaction even though H^+ does. We did not specifically look for quenching by D^+ in the manner we did for H^+ , but consider this extraordinary isotope effect highly unlikely. The acidity functions for HCl/ H_2O and DCl/ D_2O are identical up to concentrations of 1 M in solute: Högfeldt, E.; Bigeleisen, J. *J. Am. Chem. Soc.* 1960, 82, 15. It seems highly unlikely that H^+ and D^+ will behave much differently with the base (the excited state of 4-CIBP) in our system.

(31) The geometry of 4-CIBP was optimized by a molecular mechanics calculation. The geometry was then used as the input for a MNDO calculation. We thank Professor John Bartmess for his assistance with the calculation.

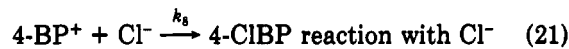
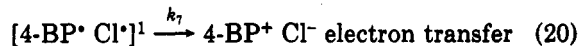
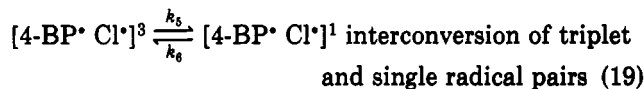
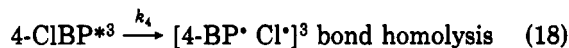
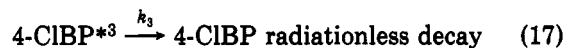
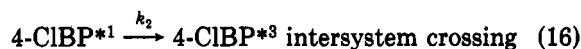
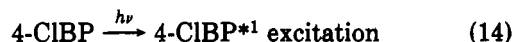
(32) The reaction of the excited state of 4-CIBP with a proton to give a ground state intermediate such as a sigma complex should be exothermic. In such cases, electron density should determine the site of protonation.

be retarded by I^- and Br^- , but not by Cl^- .³³ To test this idea on the 4-CIBP system, 4-CIBP in $\text{H}_2\text{O}-\text{CH}_3\text{CN}$ (80:20, v:v) was decomposed in the presence of 2.0 M LiCl or 2.0 M CsCl. Because spin orbit effects depend on atomic number, Li^+ should not affect the reaction, Cl^- could affect the reaction, but is common to both solutions, and Cs^+ , the ion with largest atomic number, should yield the largest effect. In fact, the extent of reaction was identical in both cases. Therefore, cations, and likely anions, do not influence our observations by a spin orbit effect.³⁴

Ionic strength is known to influence the rate of heterolytic reactions such as solvolysis reactions.^{11,35} Because the photohydrolysis reactions were not run at constant ionic strength, this effect could have influenced the results. This did not seem to be the case, however. First of all, ionic strength alone should accelerate the photohydrolysis of 4-CIBP, which is the opposite of what is observed. Secondly, changing the ionic strength had only a minimal effect on the reaction. When a series of degassed 8.70×10^{-5} M 4-CIBP solutions in the standard solvent were photolyzed for five hours, solutions containing 1.2 M HCl yielded $(7.30 \pm 0.03) \times 10^{-5}$ M of recovered 4-CIBP, while solutions containing 1.2 M HCl + 2.0 M LiClO_4 yielded $(7.50 \pm 0.02) \times 10^{-5}$ M of recovered 4-CIBP. One assumes here, of course, that LiClO_4 did not alter the reaction by some other effect.

The above experiments clearly show that chloride anions are the primary source for the observed quenching of the photohydrolysis of 4-CIBP in aqueous acetonitrile. An expanded version of the Kropp mechanism as applied to 4-CIBP, which is shown below (Scheme I), will account for

Scheme I



chloride quenching. In this scheme, the 4-CIBP triplet excited state undergoes homolytic cleavage to form a triplet geminate radical pair consisting of the 4-phenylphenyl radical (4-BP *) and a chlorine atom.³⁶ Bunce and others

(33) Ruza, L. O.; Sundström, G.; Hutzinger, O. *Recl. Trav. Chim. Pays-Bas* 1977, 96, 249.

(34) One way to avoid potential spin orbit problems would be to use $(n\text{-Bu})_4\text{NCl}$. Unfortunately, use of this salt introduces new problems. It is well-known that as the amount of CH_3CN in the mixed $\text{H}_2\text{O}-\text{CH}_3\text{CN}$ solvent increases, the fraction of reaction yielding free-radical products also increases. Thus, one wants to minimize organic species in the system. The solvent used in this study is approximately 3.8 M in CH_3CN and 11.4 M in abstractable hydrogen. 1.0 M $(n\text{-Bu})_4\text{NCl}$ is 36 M in abstractable hydrogen.

(35) Winstein, S.; Robinson, G. C. *J. Am. Chem. Soc.* 1958, 80, 169.

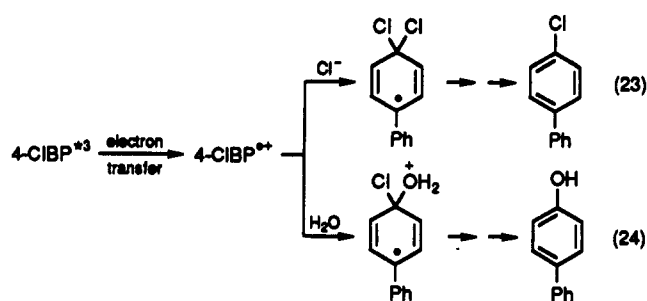
have shown that the photochemistry of chlorobiphenyls in other solvents is initiated from the triplet excited state, probably by homolysis of C-Cl bond.⁴⁵ There is no reason to believe that this does not occur in water or water-acetonitrile. The formation of BP is a further indication that free radicals are formed in the reaction. In the scheme the triplet radical pair is assumed to equilibrate with a singlet radical pair which undergoes spin-allowed electron transfer to yield Cl⁻ and the aryl cation (4-BP⁺). Although the electron transfer is endothermic in the gas phase by around 145 kcal/mol,³⁷ it should be exothermic in aqueous solution because the heat of solution of Cl⁻ in water is -85 kcal/mol³⁸ and the heat of solution of 4-BP⁺ in water should likewise be very large.³⁹ Once 4-BP⁺ is formed, it will react with Cl⁻ at close to the rate of diffusion²⁴ to regenerate 4-CIBP and with water to form 4-HOBP.

The above scheme yields the equation $\phi_0/\phi = 1 + k_3[\text{Cl}^-]/k_2[\text{H}_2\text{O}]$, where $k_3/k_2 = k_{\text{Cl}}/k_{\text{H}_2\text{O}}$ as described earlier. Figure 1 clearly shows that the ϕ_0/ϕ versus $[\text{Cl}^-]$ is not linear, as is required by the Kropp mechanism if one assumes $[\text{H}_2\text{O}]$ to be constant. Even when one replots the data in the more correct ϕ_0/ϕ versus $[\text{Cl}^-]/[\text{H}_2\text{O}]$ form, the resulting line is still curved. Why should these Stern-Volmer-like quenching plots be curved? There are several possibilities. Curved Stern-Volmer plots are known to occur when two excited states of different lifetimes undergo the same reaction.^{40,41} A long-lived triplet is quenched by low concentrations of quencher and a short-lived singlet is quenched by higher concentrations of the quencher. A similar situation is plausible here in which the singlet and triplet excited states of 4-CIBP react to give the aryl cation. This scheme, unfortunately, also predicts a straight line plot for ϕ_0/ϕ versus $[\text{Cl}^-]/[\text{H}_2\text{O}]$.

Other explanations for the curvature are possible and will be discussed briefly. First, the above scheme is incomplete because the aryl radicals abstract hydrogen from acetonitrile to form BP and the Cl⁻ reacts efficiently with Cl⁻ to form Cl₂⁻.⁴² Proper account of these reactions, which is difficult because the ultimate fate of all the transitory species is not known, might explain the curvature. Second, if Cl⁻ not only quenched the reaction as described above but also accelerated intersystem crossing, a leveling effect, as observed in Figure 1, is expected. This unfortunately requires a spin orbit effect which has been ruled out. Third, because salts do not have ideal behavior in water and presumably in H₂O-CH₃CN for most of the concentrations used, the plot in Figure 1 should properly be for ϕ_0/ϕ versus the activity of the solution components. Such behavior could explain the observed results. It is interesting to note that HCl and NaCl do not have the same activities in water. Fourth, ion pairing may play a role in the nonlinear effect of ϕ_0/ϕ versus $[\text{Cl}^-]/[\text{H}_2\text{O}]$.

Several other studies which involve the interaction of excited states with salt solutions are worth noting. As

Scheme II



discussed earlier, Ruzo and co-workers have observed that the photochemistry of aryl chlorides including chlorobiphenyls in methanol is quenched by I⁻ and Br⁻, but not by Cl⁻.^{6,33} It is interesting to note that some monoanions in methanol quench the photoreactions of chlorobiphenyls whereas cations in H₂O-CH₃CN do not. Furthermore, Cl⁻ in methanol does not quench the reaction, but Cl⁻ in H₂O-CH₃CN does. How is this possible? The chemistry in the two solvents is different. In methanol the chlorine of the aryl chloride is predominantly replaced by hydrogen; in water it is predominantly replaced by OH. Although Ruzo et al. propose a different mechanism than ours, one can interpret their results by the Kropp mechanism (Scheme I). If true, once the aryl radical is formed, it efficiently abstracts a hydrogen atom from the relatively weak C-H bond of methanol. An analogous hydrogen abstraction from water is not possible, and the aryl radical goes on to form the aryl cation. Thus Ruzo et al. do not observe quenching of their reaction by Cl⁻ because there is no spin orbit effect and the quenchable aryl cation is never formed in methanol.

Can the observed chemistry be due to a mechanism involving 4-CIBP^{•+}, the radical cation of 4-CIBP (Scheme II)? Electron transfer from the excited state of 4-CIBP to a solvent having a large dielectric constant is reasonable. If 4-CIBP^{•+} were formed by this process, it could react with H₂O to form 4-HOBP and with added Cl⁻ to regenerate 4-CIBP. Chloride salts do react with radical cations at a fast rate.⁴³ Thus Cl⁻ will quench the reaction by this mechanism. This cannot be correct, however, because the electron transfer should be subject to a salt effect, i.e. the electron transfer will become more efficient in the presence of the salt.⁴⁴ This means that the quenching effect of Cl⁻ will be offset by the effect of salt solutions on the electron transfer.

Chloride and other anions are known to quench the fluorescence of aromatic molecules in water-ethanol by electron or charge transfer from the anion to the aromatic molecule.⁴⁵ If this reaction were to occur in our system, it would yield Cl[•] and 4-CIBP⁻, the radical anion of 4-CIBP, or an exciplex (Scheme III). Wubbels has rationalized the HCl-catalyzed photoreactions of 4-bromonitrobenzene through such an intermediate.⁴⁶ At first glance, it would appear that the excited state quenching by Cl⁻

(36) Chlorine atoms react with Cl⁻ to form Cl₂⁻ at close to the rate of diffusion: Ross, A. B.; Neta, P. *Natl. Stand. Ref. Data (U.S. Natl. Bur. Stand.)* 1979, NSRDS-NBS 65. The possible complicating factor in the Kropp scheme will not be considered in this paper.

(37) ΔH , (electron transfer) = ionization potential of C₆H₅[•] - electron affinity of Cl[•] = 145 kcal/mol.

(38) Rashin, A. A.; Honig, B. *J. Phys. Chem.* 1985, 89, 5588.

(39) The direct heterolysis of the C-Cl bond from 4-CIBP^{•+} is also possible. This reaction should also be exothermic in water.

(40) Dalton, J. C.; Dawes, K.; Turro, N. J.; Weiss, D. S.; Barltrop, J. A.; Coyle, J. D. *J. Am. Chem. Soc.* 1971, 93, 7213.

(41) For an extensive discussion of energy transfer and Stern-Volmer quenching, see: Wagner, P. In *Creation and Detection of the Excited State*; Lamola, A. A., Ed.; Marcel Dekker: New York, 1971; Vol. 1, part A, p 173. Several situations in which curved Stern-Volmer plots, either upward or downward, are discussed.

(42) Citation in ref 36.

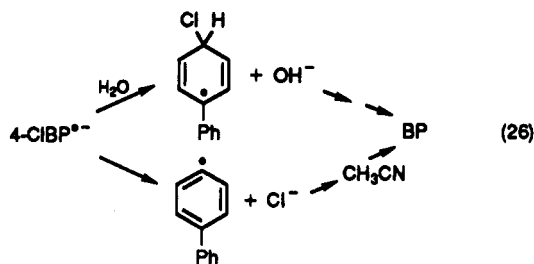
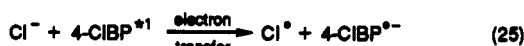
(43) Yamamoto, Y.; Aoyama, T.; Hayashi, K. *J. Chem. Soc., Faraday Trans. 1* 1988, 84, 2209.

(44) Strictly speaking the electron transfer reaction is reversible. In the presence of salt solutions the reverse reaction is impeded because the ions are stabilized by solvation with the salt solutions. Thus the fraction of 4-CIBP^{•+} reacting with nucleophiles will go up in the presence of salts. This effect is well-documented in the literature. See: Mizuno, K.; Ichinose, N.; Otsuji, Y. *Chem. Lett.* 1985, 455. Kawanishi, Y.; Kitamura, N.; Tazuke, S. *J. Phys. Chem.* 1986, 90, 6034.

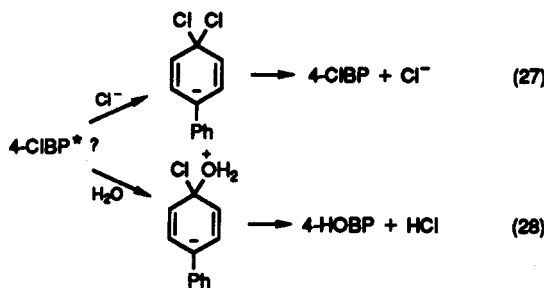
(45) Shizuka, H.; Nakamura, M.; Morita, T. *J. Phys. Chem.* 1980, 84, 989.

(46) Wubbels, G. G.; Snyder, E. J.; Coughlin, E. B. *J. Am. Chem. Soc.* 1988, 110, 2543.

Scheme III



Scheme IV



would retard the hydrolysis of 4-CIBP. It would, of course, if the reverse electron transfer were efficient. One would expect, however, 4-CIBP^{•-} to be very reactive, either by expulsion of Cl⁻ or by protonation with H₂O. Both pathways would yield new products. In other words, Cl⁻ will accelerate the destruction of 4-CIBP, as was observed by Wubbels for 4-bromonitrobenzene.⁴⁶

Prior work has shown that the photohydrolysis of 4-CIBP in H₂O does not proceed through an arylene intermediate or an addition-elimination (+ H₂O, -HCl) mechanism.³ The present study has suggested that the reaction in H₂O-CH₃CN does not involve 4-CIBP radical ions (Schemes II and III). The Kropp mechanism (Scheme I) accounts for the Cl⁻ quenching quite nicely. Is there any mechanism besides the Kropp mechanism which accounts for the chloride quenching? In fact a mechanism in which 4-CIBP^{*3} or 4-CIBP^{*1} reacts directly with Cl⁻ and H₂O to form σ complexes which then decompose to 4-CIBP and 4-HOBP, respectively, will yield results very similar in character to what is expected for the Kropp mechanism (Scheme IV). We favor the Kropp mechanism over the new mechanism for the simple reason that the Kropp mechanism accounts for the formation of BP in H₂O-CH₃CN. The mechanism in which Cl⁻ and H₂O attack the excited state of 4-CIBP to form σ complexes cannot do this.

One final comment is worth noting. It has been suggested that the best way to support the Kropp mechanism (Scheme I) is to run the photohydrolysis of 4-CIBP in the presence of NaCl³⁵ or NaCl³⁷ and look for incorporation of the chlorine label into 4-CIBP. In addition to the enormous expense of the experiment⁴⁷ the results will not give definitive results. For example, the mechanism involving the direct attack of chloride on the excited state of 4-CIBP (Scheme IV) would result in both quenching of the reaction and incorporation of the label even though this mechanism can be ruled out on other grounds. Surprisingly, it can be shown (Appendix 2) that the Kropp mechanism will lead to little or no incorporation of label even though the reaction is quenched by chloride. Thus,

whether the label is incorporated or not does not unambiguously distinguish mechanisms.

In conclusion, the photochemistry of the monochlorobiphenyls, 2-CIBP and 3-CIBP, in water has been determined and compared to the previously studied 4-CIBP.³ Both 3-CIBP and 4-CIBP undergo competing hydrolysis and isomerization pathways. 3-CIBP also yields a small amount of homolysis product (BP). 2-CIBP by contrast is the most reactive of the molecules and undergoes hydrolysis exclusively. The photohydrolysis of 4-CIBP in H₂O-CH₃CN (80:20 by volume) is subject to a common ion effect which is most easily accommodated by the Kropp mechanism involving radical and ion pairs. The cause for the nonlinear quenching by Cl⁻ remains to be determined.

Experimental Section

Isotopic Dilution Experiments. The labeled chlorobiphenyls were obtained from Pathfinder Laboratories. Unlabeled chlorobiphenyls were obtained from Overlook Industries Inc. The purity of the liquid 3-chlorobiphenyl was confirmed by gas chromatography. 2-Chlorobiphenyl was recrystallized to constant melting point. Methods for performing the isotopic dilution experiments are found in an earlier publication.³ Details for the photochemical experiments may also be found in an earlier paper,³ further details are also found below.

4-Biphenyldiazonium Chloride. The compound was synthesized from 4-aminobiphenyl (Aldrich) by standard procedures.⁴⁸ The compound's purity was checked by high-field NMR in D₂O. Thermal decomposition in H₂O also gave the predicted amount of HCl.

4-Phenylacetanilide. The compound was prepared from 4-aminobiphenyl (Aldrich) by treatment with acetic anhydride in acetic acid; mp 100–104 °C (lit.⁴⁹ mp 104 °C). The compound yielded a single peak by HPLC.

Methods for Reaction Analysis. The hydrolysis of 4-biphenyldiazonium chloride and the photoreactions of 4-chlorobiphenyl in H₂O/CH₃CN were followed at 254 nm by chromatography on a Varian 5000 liquid chromatograph using a C-18/10, 0.46 × 25 cm Partisil ODS-3, analytical column with a Varian 2050 variable wavelength detector (solvent: 20% H₂O in CH₃OH (v/v); flow rate: 1.5 mL/min. Standard curves (area vs concentration) were obtained for biphenyl, 4-chlorobiphenyl, and 4-hydroxybiphenyl and analyzed by least-square methods. Substrates were removed quantitatively from reaction mixtures by repeated extraction with ethyl acetate.

Photochemical Experiments. The photohydrolysis of 4-chlorobiphenyl in H₂O/CH₃CN was performed in specially prepared tubes on a merry-go-round apparatus using a 450-watt, water-cooled, medium-pressure, Hanovia mercury lamp (vycor glass filter) as light source. Each photolysis tube (1/4 × 10 in.) was prepared from precision bore quartz (Galbrath Laboratories) and contained a ground-glass stopcock at its top. Experiments demonstrated that the stopcocks did not leak gases. Other experiments proved that the tubes gave the same extent of photolysis (±2%) under identical reaction conditions. Most photolyses were performed under an atmosphere of prepurified N₂ that had been deoxygenated by the procedure of Meites and Meites.⁵⁰

Laser-Induced Decomposition of 4-Biphenyldiazonium Chloride. A neodymium: YAG-pumped dye laser (pump laser, DCR-2A10; dye laser, PDL-2; Quanta Ray, Mountain View, CA) with a wavelength extender was used to decompose 4-biphenyldiazonium chloride at ambient temperature. The dye laser contained 225 mg of LDS-698/L of CH₃OH in the oscillator and 28.75 mg/L of the same components in the amplifier. The laser was run at a rate of 2 mJ/pulse at 333.75 nm.

Stability of CH₃CN to Aqueous HCl. The behavior of CH₃CN in aqueous HCl was followed by high field ¹H NMR on solutions of CH₃CN in DCl/D₂O. No decomposition of CH₃CN was ever observed under any of the reaction conditions.

(47) The NaCl³⁷ required to prepare 100 mL of a 1.0 M aqueous solution costs approximately \$3800.

(48) Vogel, A. *Vogel's Textbook of Practical Organic Chemistry*; Longman House: New York, 1978; p 688.

(49) Reference 48, p 684.

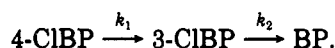
(50) Meites, L.; Meites, T. *Anal. Chem.* 1948, 20, 984.

Photolysis of 4-Chlorobiphenyl in DCl/D₂O/CH₃CN. The photolysis of 4-chlorobiphenyl in D₂O/CH₃CN (80:20, v:v), which was 1.2 M in DCl, was run to partial conversion, and unreacted 4-chlorobiphenyl isolated. Because the ¹H NMR spectrum of 4-chlorobiphenyl is uninterpretable even at high fields, the photolyzed sample was subjected to the shift reagent Agfod/Yb(fod)₃²⁹ and compared to the ¹H NMR spectrum of unphotolyzed 4-chlorobiphenyl, similarly treated. There were no differences in the spectra at any of the five unique hydrogen sites. Mass spectrometry confirmed that no deuteration had occurred on the irradiated molecule.

Acknowledgment. This research was partially supported by the Energy, Environment and Resources Center of the University of Tennessee.

Appendix 1

Consider the simplified reaction scheme



In this scheme it is possible to start the reaction with 4-ClBP, i.e. [4-ClBP] = [4-ClBP]₀ and [3-ClBP] = 0 at *t* = 0, or with 3-ClBP, i.e. [4-ClBP] = 0, [3-ClBP] = [3-ClBP]₀ at *t* = 0. The reactions may be either zero-order or first-order. The following possibilities will arise.

A. Zero-Order Reactions

1. Reaction Starting with 4-ClBP. The following equations are true.

$$[4\text{-ClBP}] = [4\text{-ClBP}]_0 - k_1 t$$

$$[3\text{-ClBP}] = (k_1 - k_2)t$$

and

$$[\text{BP}] = k_2 t$$

2. Reaction Starting with 3-ClBP. Here the following equations are true.

$$[3\text{-ClBP}] = [3\text{-ClBP}]_0 - k_2 t$$

and

$$[\text{BP}] = k_2 t$$

It is clear the BP's formation depends only on *k*₂ in both cases. It is reasonable then that BP should be observed in reactions beginning with 4-ClBP and 3-ClBP.

B. First-Order Reactions

1. Reaction Starting with 4-ClBP. It is easy to show that the concentration of BP will be governed by

$$[\text{BP}] = [4\text{-ClBP}]_0 \left(1 - \frac{k_2}{k_2 - k_1} e^{-k_1 t} + \frac{k_1}{k_2 - k_1} e^{-k_2 t} \right)$$

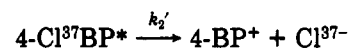
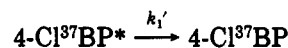
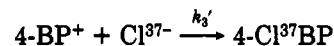
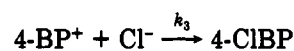
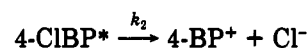
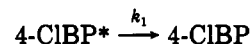
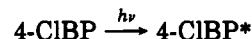
2. Reaction Starting with 3-ClBP. Here the concentration of BP is governed by

$$[\text{BP}] = [3\text{-ClBP}]_0 (1 - e^{-k_2 t})$$

Clearly the amount of BP generated in the two pathways will differ and will depend on [4-ClBP]₀ and [3-ClBP]₀, which should be similar in water, and *k*₁ and *k*₂. Provided *k*₁ > *k*₂, the amount of BP from the second pathway will always be larger than that generated from the first pathway. For example, if [4-ClBP]₀ = [3-ClBP]₀, *k*₁ = 10*k*₂ and *k*₂ = 1*t*⁻¹, one will get greater than 20 times more BP from the second pathway at *t* = 0.01.

Appendix 2

For the sake of argument consider the following, somewhat simplified, scheme for the photohydrolysis of 4-ClBP in the presence of Cl³⁷⁻.



It is easy to show that the following equation is true:

$$\frac{\phi_0}{\phi} = 1 + \frac{k_3[\text{Cl}^-] + k_3'[\text{Cl}^{37-}]}{k_4[\text{H}_2\text{O}]}$$

where

$$\frac{k_3}{k_4} = \frac{k_{\text{Cl}}}{k_{\text{H}_2\text{O}}} \text{ and } \frac{k_3'}{k_4} = \frac{k_{\text{Cl}^{37}}}{k_{\text{H}_2\text{O}}}$$

It can also be shown that

$$[4\text{-Cl}^{37}\text{BP}] = \frac{k_2}{k_1 + k_2} \left[\frac{k_3'[\text{Cl}^{37-}]}{k_3'[\text{Cl}^{37-}] + k_3[\text{Cl}^-] + k_4[\text{H}_2\text{O}]} \right] I t - \frac{k_2'}{k_1' + k_2'} \left[\frac{k_3[\text{Cl}^-] + k_4[\text{H}_2\text{O}]}{k_3'[\text{Cl}^{37-}] + k_3[\text{Cl}^-] + k_4[\text{H}_2\text{O}]} \right] I t$$

where *I* represents the intensity of light. When [Cl³⁷⁻] = 0, the first term of the above equation is zero because the numerator is zero, and the second term is zero because *k*₁' , *k*₂' and *k*₃' only exist when Cl³⁷⁻ is present. Thus [4-Cl³⁷BP] = 0 when [Cl³⁷⁻] = 0.

If one neglects isotope effects, which should be very small for chlorine, *k*_{*n*} = *k*_{*n*'}, where *n* = 1, 2, 3. Thus

$$[4\text{-Cl}^{37}\text{BP}] \approx \frac{k_2}{k_1 + k_2} \left[\frac{k_3[\text{Cl}^{37-}] - k_3[\text{Cl}^-] - k_4[\text{H}_2\text{O}]}{k_3[\text{Cl}^{37-}] + k_3[\text{Cl}^-] + k_4[\text{H}_2\text{O}]} \right] I t$$

Unless *k*₃[Cl³⁷⁻] > *k*₃[Cl⁻] + *k*₄[H₂O], [4-BPCl³⁷] will be zero or negative. Since a concentration cannot be negative, this means that there will be no accumulation of 4-Cl³⁷BP in the reaction. For reasonable values of *k*₃/*k*₄ (2 to 3) and concentrations ([Cl³⁷⁻] = 1 M, [H₂O] = 55 M, [Cl⁻] ≤ 1 M), the above inequality is not valid. Therefore there will be no buildup of 4-Cl³⁷BP even though the reaction is quenched by Cl³⁷⁻.