The Photochemistry of Polyhaloarenes. 10. The Photochemistry of 4-Bromobiphenyl

Peter K. Freeman,* Jung-Suk Jang, and N. Ramnath

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

The photodebromination of 4-bromobiphenyl (BpBr) in a variety of solvents has been characterized by measurement of the dependence of quantum yield upon substrate concentration, concentration of quenchers cis-1,3-pentadiene and fumaronitrile, and determination of the quantum yield for intersystem crossing, ϕ_{isc}. The dependence of quantum yield upon light intensity reveals no evidence for biphotonic processes. The rate constant for triplet excimer formation (k_2) is dependent upon the polarity of the solvent as measured by E_T. By use of the linear solvation energy relationship of Abraham, Kamlet, and Taft, the rate constant for excimer formation is dependent upon the Hildebrand solubility parameter (δ_H^2) and solvent hydrogen bond acceptor basicity (β_1), $\log k_2 = 1.94 + 0.00242\delta_H^2 + 0.248\beta_1$. The rate constant for triplet excimer formation is much less sensitive to change in the E_T value of the solvent than is the rate constant (k_{ex}) for exciplex formation from BpBr[3] and triethylamine.

Polybrominated biphenyl mixtures are used widely as industrial fire retardants, for example, to retard the flammability of thermoplastics.[1] Through errors in handling, these materials have made their way into the environment and into the food supply,[2] which is a matter of concern as the potent biological effects of polybromobiphenyl have been revealed in a number of studies.[2,3] Since these substrates absorb in the sunlight range ($\lambda > 290$ nm)[4] and since toxicity depends on the number of bromines and their substitution pattern,[3] the mechanism of the photodebromination of these species is clearly of considerable interest. Although there have been a number of interesting studies on steric effects,[5] the quenching of triplet-state intermediates,[6,7] and reactions in the presence of an electron donor,[5] key mechanistic questions remain unresolved. For example, product-determining intermediates have not been completely characterized, and the importance of competing pathways in the singlet and triplet manifolds is not clearly understood. This background provided the impetus for an investigation of the photochemistry of the parent system, 4-bromobiphenyl (BpBr).

Results and Discussion

Irradiation of 4-bromobiphenyl at 300 nm in various protic and aprotic solvents led to the formation of biphenyl as the sole product. In an effort to provide a basis for the development of a mechanistic rationale, three kinetic schemes were considered. In the first case (Scheme I), the product is derived from the first excited singlet state. The kinetic expression for the inverse of quantum yield (eq 1),

$$\frac{1}{\Phi_{prod}} = \frac{k_p + k_{isc} + k_{sd}}{k_p} \tag{1}$$

based on the steady-state approximation, shows that the quantum yield of the reaction is independent of the substrate concentration. Thus, a plot of the inverse of the product quantum yield versus the inverse of the substrate

Scheme I

Scheme II
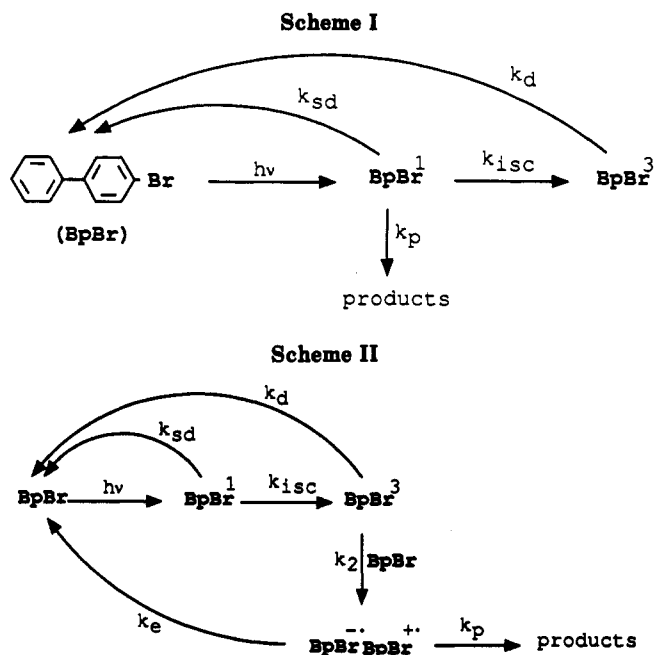
concentration should be linear with a zero slope.

4-Bromobiphenyl is expected to undergo efficient intersystem crossing due to the heavy-atom effect, and involvement of the triplet state of 4-bromobiphenyl has been shown earlier by various workers.[5,7,8] Since the reported quantum yield of the intersystem crossing process for biphenyl is 0.81,[9] BpBr was expected to have a quantum yield for intersystem crossing close to 1. Actual measurement of the quantum yield of intersystem crossing using Hammond's method[10] did indeed give a value of 0.98 ± 0.05. The triplet energy of 4-bromobiphenyl (66.9 kcal/mol)[11] is 12 kcal/mol lower than the phenyl C–Br bond fission energy (79.2 kcal/mol).[12] Thus, direct formation of product from the triplet state is unlikely. However, excimer formation through an electron-transfer process from the ground state to the triplet state of BpBr may provide an alternative pathway to the product. A second mechanistic picture reflecting these features is,

(1) Totter, W. J. *Bull. Environ. Contam. Toxicol.* **1977**, *18*, 726–732.
(2) (a) Miller, F. D.; Brilliant, L. B.; Copeland, R. *Bull. Environ. Contam. Toxicol.* **1984**, *32*, 125–133. (b) Robertson, L. W.; Parkinson, A.; Safe, S. *Biochem. Biophys. Res. Commun.* **1980**, *92*, 175–182.
(3) (a) Parkinson, A.; Safe, S. *Toxicol. Environ. Chem. Rev.* **1981**, *4*, 1. (b) Robertson, L. W.; Parkinson, A.; Campell, M. A.; Safe, S. *Chem.-Biol. Interact.* **1982**, *42*, 53.
(4) Ruzo, L. O.; Sundstrom, G.; Hutzinger, O.; Safe, S. *J. Agric. Food Chem.* **1976**, *24*, 1062–1065.
(5) Bunce, N. J.; Safe, S.; Ruzo, L. O. *Perkin Trans. 1* **1975**, 1607–1610.
(6) Ruzo, L. O.; Bunce, N. J. *Tetrahedron Lett.* **1975**, *8*, 511–514.
(7) Pedersen, C. L.; Lohse, C. *Acta Chem. Scand. B* **1979**, *33*, 649–652.

(8) Ruzo, L. O.; Zabik, M. J. *Bull. Environ. Contam. Toxicol.* **1975**, *13*, 181–182.
(9) Sandros, K. *Acta Chem. Scand.* **1969**, *23*, 2815–2829.
(10) Lamola, A. A.; Hammond, G. *J. Chem. Phys.* **1965**, *43*, 2129–2135.
(11) O'Donnell, C. M.; Harbaugh, K. F.; Fisher, R. P.; Winefordner, J. D. *Analyt. Chem.* **1973**, *45*, 609–611.
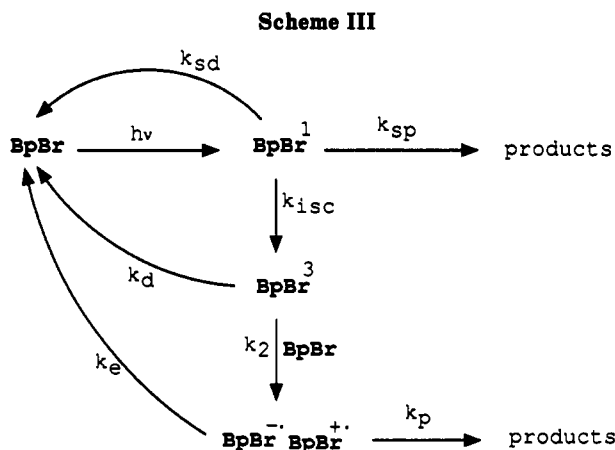(12) Egger, K. E.; Cocks, A. T. *Helv. Chim. Acta* **1973**, *56*, 1516–1535.

Scheme III

Table I. Photolysis of 4-Bromobiphenyl in Acetonitrile (300 nm)

[BpBr]$_i{}^a$ (M)	1/[BpBr]$_i$ (M^{-1})	$\phi_{prod}{}^b$	1/ϕ_{prod}
0.005 23	191	0.008 35	120
0.006 95	144	0.009 91	101
0.009 27	108	0.0130	76.7
0.012 10	82.6	0.0164	60.9
0.020 08	49.8	0.0263	38.0
0.030 20	33.1	0.0378	26.4
0.050 36	19.9	0.0743	13.5
0.086 23	11.6	0.146	6.85

^{a} Initial concentration of 4-bromobiphenyl. ^{b} Quantum yield of of product (biphenyl) formation: average of two determinations.

therefore, presented in Scheme II. Application of the steady-state assumption provides us with eqs 2 and 3.

$$\Phi_{prod} = \frac{k_2 FG[\text{BpBr}]}{k_d + k_2[\text{BpBr}]} \tag{2}$$

$$\frac{1}{\Phi_{prod}} = \frac{1}{F \cdot G} + \frac{k_d}{k_2 FG[\text{BpBr}]} \tag{3}$$

$$\text{where } F = \frac{k_p}{k_p + k_e} \qquad G = \frac{k_{isc}}{k_{isc} + k_{sd}}$$

Thus, a plot of the inverse of the quantum yield against the inverse of the concentration of BpBr will be linear with a positive slope.

If, however, the singlet forms product in competition with the triplet state (via the excimer), the plot of $1/\Phi_{prod}$ vs 1/[BpBr] will be curved. Scheme III depicts the kinetic scheme, while eq 4 represents the dependence of $1/\Phi_{prod}$

$$\frac{1}{\Phi_{prod}} = \frac{k_2 + k_d/[\text{BpBr}]}{G[k_{sp}k_2 + k_{isc}k_2 F + k_{sp}k_d/[\text{BpBr}]]} \tag{4}$$

$$\text{where } F = \frac{k_p}{k_p + k_e} \qquad G = \frac{1}{k_{sd} + k_{isc} + k_{sp}}$$

upon 1/[BpBr]. Thus, if this third mechanistic model is valid, as the concentration of BpBr increases, at some point $(k_{sp}k_2 + k_{isc}k_2F) \gg k_{sp}k_d/[\text{BpBr}]$ and a plot of the inverse of quantum yield versus 1/[BpBr] will be linear with a positive slope. However, as the concentration of BpBr decreases, the slope of the above plot will decrease and approach zero. Thus, the overall plot would be curved rather than linear.

It is clear that the dependence of the quantum yield upon concentration of the substrate is quite sensitive to changes in the mechanistic model. We chose, therefore, to focus, initially, on this dependence and found that the quantum yield of the reaction in any particular solvent
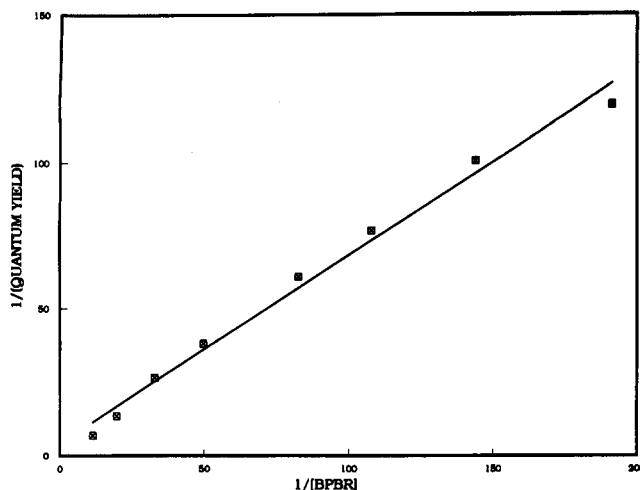

Figure 1. Plot of inverse of quantum yield of photodebromination of 4-bromobiphenyl in acetonitrile versus the inverse of the concentration of 4-bromobiphenyl.
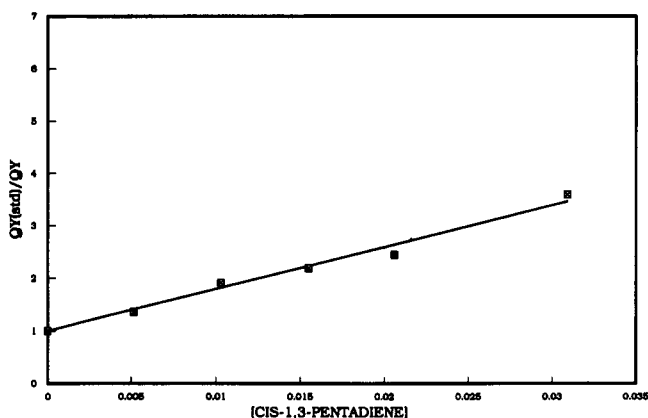

Figure 2. Plot of the ratio of quantum yield of photo-debromination of 4-bromobiphenyl with and without quencher (QY(std)/QY) versus the concentration of cis-1,3-pentadiene.

increases with increasing concentration of BpBr, an example of which is shown in Table I for the acetonitrile system. Also, irradiation of a very dilute solution of BpBr (1 × 10^{-4} M) gave no biphenyl photoproduct. Moreover, a plot of the inverse of quantum yield versus the inverse of concentration of BpBr in acetonitrile was found to be linear with an excellent correlation coefficient of 0.994 (Figure 1), thereby suggesting that the reaction pathway is closest to that depicted in Scheme II. The involvement of only one excited state for debromination was supported by quenching studies using cis-1,3-pentadiene[10] and fumaronitrile[13] in acetonitrile solvent. Stern–Volmer plots obtained from both quenching studies were linear with positive slopes having r = 0.992 (Figure 2) and 0.984 (Figure 3), respectively. This result is in harmony with the view that the triplet excimer is the sole product-determining intermediate for the debromination of 4-bromobiphenyl. If reaction were to occur from the singlet state (in competition with reaction via the triplet excimer), the Stern–Volmer plot would be linear, with a positive slope, at low concentrations of the quencher but would flatten out as the concentration of the quencher increases. This is a likely outcome when all the triplet states are quenched at high concentrations of the quencher, while

(13) (a) Wagner, P. J. Acc. Chem. Res. 1971, 4, 168–177. (b) Wagner, P. J.; Kochevar, I. J. Am. Chem. Soc. 1968, 90, 2232–2238. (c) Wettack, F. S.; Renkes, G. D.; Renkly, M. G.; Turro, N. J.; Dalton, J. E. J. Am. Chem. Soc. 1970, 92, 1318–1326.
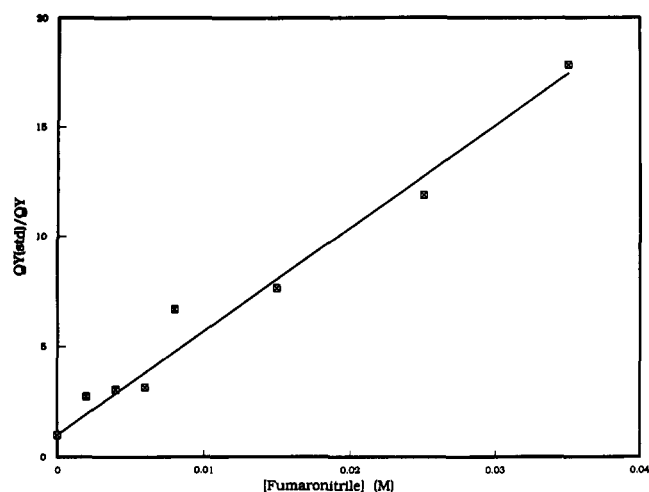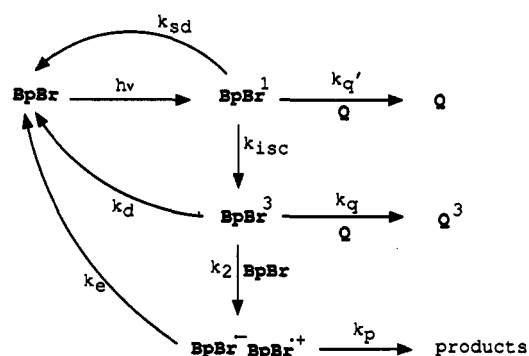
Figure 3. Plot of the ratio of quantum yield of photodebromination of 4-bromobiphenyl with and without quencher (QY(std)/QY) versus the concentration of fumaronitrile.

Figure 4. Plot of the inverse of the quantum yield, 1/QY(cis to trans), versus the concentration of cis-1,3-pentadiene.

Scheme IV

Scheme V

$$\Phi_{c \to t} = \frac{k_{isc}}{k_{isc} + k_{sd} + k_q'[Q]} \cdot \frac{k_q[Q]F}{k_d + k_2[\text{BpBr}] + k_q[Q]}$$

$$\frac{1}{\Phi_{c \to t}} = \frac{k_{isc} + k_{sd} + k_q'[Q]}{k_{isc}} \cdot \frac{k_d + k_2[\text{BpBr}] + k_q[Q]}{k_q[Q]F}$$

where F = fraction of Q^3 undergoing cis to trans isomerization

(a) $\phi_{prod} = \dfrac{k_2[\text{BpBr}]}{k_d + k_2[\text{BpBr}]} \cdot F$ \qquad $F = \dfrac{k_p}{k_p + k_e}$

(b) $\phi_{prod} = \dfrac{k_2[\text{BpBr}]}{k_d + k_2[\text{BpBr}]} \cdot G$ \qquad $G = \dfrac{If}{If + k_e}$

the singlet state continues to react. cis-1,3-Pentadiene (Q) has been shown to quench the singlet states of aromatic hydrocarbons.[14] In such a situation, the quantum yield of sensitized cis → trans isomerization will normally decrease with increasing concentrations of the diene (Scheme IV). In the case of pentachlorobenzene ($\phi_{isc} \cong 0.8$), quenching of singlet state was shown by the fact that the quantum yield of cis → trans isomerization of the cis-1,3-pentadiene sensitized by pentachlorobenzene showed a continuous decrease in the $\phi_{c \to t}$ with increasing concentrations of the diene and a plot of the inverse of $\phi_{c \to t}$ versus the concentration of 1,3-pentadiene shows a linear correlation with a positive slope. The 4-bromobiphenyl case contrasts clearly with this as the quenching of BpBr excited state gives a plot of $1/\phi_{c \to t}$ versus [cis-1,3-pentadiene] with negative slope at low concentrations which approaches
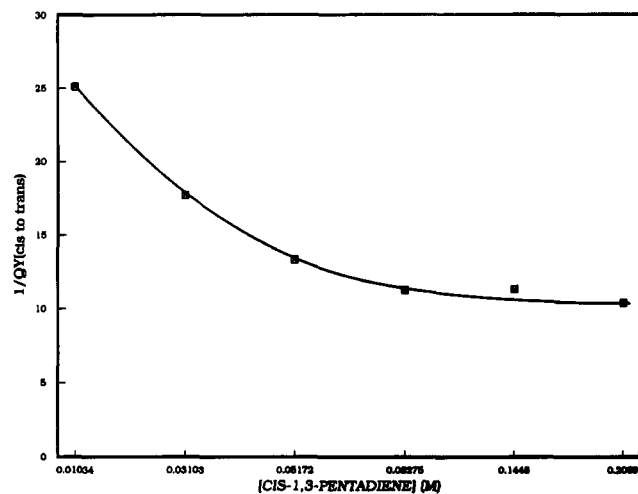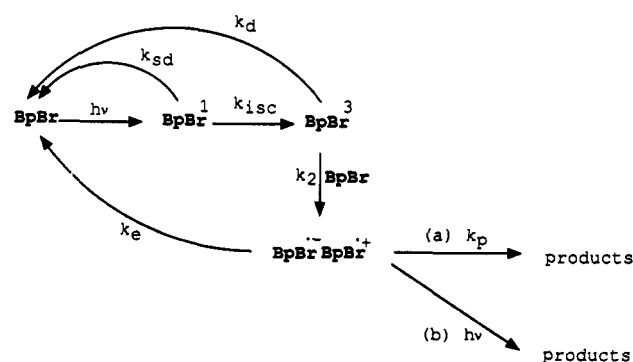
zero asymptotically at higher concentrations (Figure 4). These results indicate that while some of the pentadiene is quenching the singlet excited state of pentachlorobenzene in a nonchemical process, thereby reducing the extent of cis to trans isomerization of cis-1,3-pentadiene, there is no quenching of the singlet excited state of BpBr by cis-1,3-pentadiene.

One possible explanation for bond fission from an energy-deficient excimer species involves a biphotonic process in which the excimers formed from a triplet excited state of BpBr absorb an additional photon and are excited to a higher electronic state, which, then, undergoes the debromination process (Scheme V). In the case of a biphotonic process (case b), ϕ_{prod} will be a function of "I" (intensity of light), where "f" is the probability of light absorption. At low intensity of light where $k_e \gg If$, ϕ_{prod} will be a linear function of "I". On the other hand, when k_e and If are of approximately the same order of magnitude, the plot will have a positive slope and be concave downward. It is, in fact, possible to calculate what the dependence of quantum yield upon intensity should be using the intercept of the plot of Figure 1 as a measure of G in (b), Scheme V. The calculated values of ϕ_{prod} are given in column three in Table II. A biphotonic process can be ruled out since ϕ_{prod} does not increase with in-

(14) (a) Stephenson, L. M.; Hammond, G. S. *Pure Appl. Chem.* 1968, *16*, 125–136. (b) Stephenson, L. M.; Whitten, D. G.; Vesley, G. F.; Hammond, G. S. *J. Am. Chem. Soc.* 1966, *88*, 3665–3667.

Table II. Effect of Light Intensity on ϕ_{prod} of BpBr[a] in Acetonitrile

[intensity] (Einstein/min)	ϕ_{prod}[b]	ϕ_{prod}[c] (if biphotonic process)
0.000 021	0.009 47	0.000 38
0.000 033	0.009 98	0.000 59
0.000 187	0.008 91	0.003 09
0.000 639	0.008 64	0.008 64

[a] 0.005M. [b] Quantum yield of product formation: average of two determinations. [c] Calculated from the intercept in Figure 1 according to eq b in Scheme V.

creasing light intensity (Table II). To satisfy the energy requirement for conversion of excimer to product, a process similar to delayed luminescence[15] involving generation of singlet- and ground-state species via a triplet–triplet annihilation process was also considered. However, such a case can be ruled out since $1/\phi_{prod}$ would be a nonlinear function of 1/[BpBr] and the rate of product formation would be a nonlinear function of the intensity.

On the matter of product formation from excimer, the nature of the hydrogen incorporation into product biphenyl is revealed in experiments carried out in CH_3OD and CD_3OD. While the quantum yields are identical within experimental error, ϕ (CH_3OD) = 0.023 ± 0.0008 and ϕ (CD_3OD) = 0.024 ± 0.002 (both at 0.01 M BpBr), the biphenyl product formed in CH_3OD contained 0% d_1, while that formed in CD_3OD contained 99% d_1. This is consistent with the mechanism of Scheme II and fragmentation of excimer to aryl radical which then abstracts hydrogen atom from solvent.

Since the excimer is a key intermediate in Scheme II, it was of considerable importance to provide additional characterization of this species. Evidence bearing on the extent of charge separation in the excimer was obtained by determining the dependence of the rate constant for the formation of excimer (k_2) upon solvent polarity. Solvents of differing polarity based on the E_T polarity scale[16] were chosen (Table III), and the quantum yields were determined as a function of concentration of BpBr for each solvent, plots of the inverse of the quantum yield vs the inverse of the concentration of BpBr exhibiting a linear relationship for each solvent system. This is illustrated for the reaction using acetonitrile as the solvent (Figure 1). Using the least-squares method, the best fitted first-order equation correlating the inverse of quantum yield and the inverse of concentration for each solvent system was obtained. The above equation was then used to obtain a standard quantum yield (Φ_0) at an arbitrary reference concentration ([BpBr]₀ is equal to 0.01 M) for each system (eq 5). By taking the ratio of the standard quantum yield (Φ_0) to the observed quantum yield (Φ_{prod}), the slope of a plot of Φ_0/Φ_{prod} against 1/[BpBr] will give k_2 as a function of k_d (eqs 6 and 7).
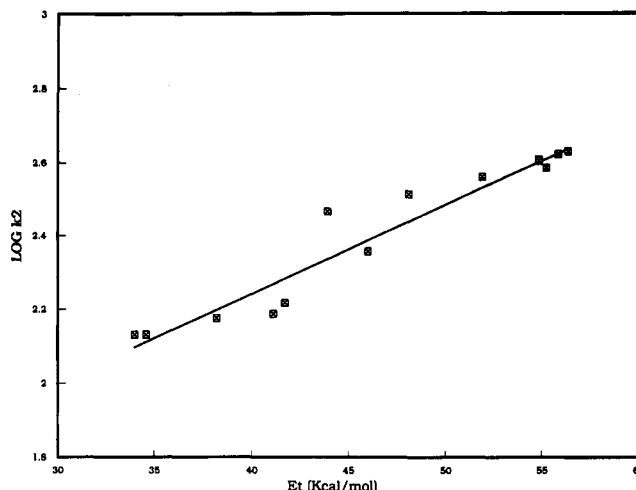
$$\Phi_0 = \frac{k_2 FG[BpBr]_0}{k_d + k_2[BpBr]_0} \quad (5)$$

$$\frac{\Phi_0}{\Phi_{prod}} = \frac{[BpBr]_0}{k_d + k_2[BpBr]_0}\left[k_2 + \frac{k_d}{[BpBr]}\right] \quad (6)$$

$$k_2 = k_d\left[\frac{1}{slope} - \frac{1}{[BpBr]_0}\right] \quad (7)$$

(15) Birks, J. B. In *Photophysics of Aromatics*; Wiley: New York, 1970; p 254.

(16) (a) Dimroth, K.; Reichardt, C.; Seipman, T.; Bohlman, F. *Liebig Ann. Chem.* 1963, *661*, 1. (b) Reichardt, C. *Ibid.* 1971, *752*, 64. (c) Reichardt, C. *Angew. Chem., Int. Ed. Engl.* 1965, *4*, 29.

Figure 5. Plot of log of k_2 versus solvent polarity (E_T).

The vlaue of k_d (the inverse of the lifetime of the triplet state) was obtained from the determination of triplet lifetimes by measuring the decay of phosphorescence in three solvents of differing polarity (Table IV). These solvents were chosen due to their ability to form glasses at 77 K while providing different polarities, which were determined according to the method of Dimroth et al.[16] by measuring the solvatochromic band shifts of 2,6-diphenyl-4-(2,4,6-triphenyl-N-pyridinio)phenolate in each solvent. Perusal of Table IV suggests that the lifetime of the triplet state of BpBr is unaffected by solvent polarity. It was thus possible to obtain the value of k_2 for each solvent by using an average value for the lifetime (28.5 ms). The phosphorescence spectra in these three solvents are also very similar, thus suggesting that the polarity of the solvent has little effect on the triplet excited state of BpBr. Therefore, any change in the value of the slope of eq 6 reflects the influence of the solvent on the rate constant for formation of the excimer species of BpBr. The k_2 values derived from eq 7 increased with increasing polarity of the solvent suggesting the development of a species with some charge separation. A linear least-squares fit of a plot of log k_2 against E_T showed a dependency on the solvent polarity (Figure 5) with a correlation coefficient of r = 0.968.

At this point, it seemed worthwhile to attempt to improve this correlation and to study the nature of the excimer through the use of the linear solvation energy relationship described by Abraham, Kamlet, Taft and coworkers.[17] In their studies of the solvent effects on the solvolysis rate of *tert*-butyl halides, a best correlation for the solvolysis rate constants (k) was obtained through the use of eq 8 with four different solvation parameters: (i)

$$\log k = (\log k)_0 + h\delta_H{}^2 + s\pi_1{}^* + a\alpha_1 + b\beta_1 \quad (8)$$

$\delta_H{}^2$ or the square of the Hildebrand solubility parameter (solvent cohesive energy density), (ii) $\pi_1{}^*$ or solvent dipolarity or polarizability (solvent ionizing power), (iii) α_1 or solvent hydrogen-bond-donor acidity (solvent electrophilic assistance), and (iv) β_1 or solvent hydrogen-bond-acceptor basicity (solvent nucleophilic assistance).

Table V shows the solvatochromic parameters used with eq 8. For those deuterated and aqueous methanolic systems the parameters were measured according to reported methods.[18-22] The usefulness of each of these parameters,

(17) Abraham, M. H.; Doherty, R. U.; Kamlet, M. J.; Harris, J. M.; Taft, R. W. *Ibid.*, 1987, 1097–1101, 913–920.

Table III. Correlation between log k_2 and Polarity of Solvents

solvents	$E_T{}^a$	slope[b]	$k_2{}^c(\times 10^{-2})$	log k_2
i-Pr$_2$O	34.0	0.009 63 ± 0.000 45	1.35 ± 0.06	2.13 ± 0.02
Et$_2$O	34.6	0.009 63 ± 0.000 95	1.35 ± 0.13	2.13 ± 0.04
(CH$_3$OCH$_2$)$_2$	38.2	0.009 59 ± 0.000 37	1.50 ± 0.06	2.18 ± 0.01
CH$_2$Cl$_2$	41.1	0.009 58 ± 0.000 31	1.54 ± 0.05	2.19 ± 0.01
(CH$_2$Cl)$_2$	41.7	0.009 55 ± 0.000 67	1.65 ± 0.12	2.22 ± 0.03
CH$_3$CN	46.0	0.009 39 ± 0.000 40	2.28 ± 0.10	2.36 ± 0.02
t-BuOH	43.9	0.009 23 ± 0.000 63	2.93 ± 0.20	2.47 ± 0.03
i-PrOH	48.1	0.009 14 ± 0.000 68	3.26 ± 0.24	2.51 ± 0.03
EtOH	51.9	0.009 56 ± 0.000 71	3.64 ± 0.35	2.56 ± 0.04
CH$_3$OH	55.2	0.009 01 ± 0.000 63	3.86 ± 0.27	2.59 ± 0.03
CH$_3$OD	54.8	0.008 96 ± 0.000 56	4.07 ± 0.28	2.61 ± 0.03
CD$_3$OD	54.8	0.008 97 ± 0.000 62	4.03 ± 0.28	2.61 ● 0.02
90% aq CH$_3$OH	55.8	0.008 93 ± 0.000 56	4.21 ± 0.27	2.62 ± 0.03
80% aq CH$_3$OH	56.3	0.008 91 ± 0.001 01	4.29 ± 0.49	2.63 ± 0.05

a Polarity scale (kcal/mol). *b* See text for details. *c* Rate constant for excimer formation.

Table IV. Phosphorescence Lifetime of 4-Bromobiphenyl

	solvents	E_T (kcal/mol)	τ (ms)
1	EtOH	51.9	28.7 ± 1.0
2	EPA^a	47.5	28.5 ± 0.6
3	97.5% Et$_2$O 2.5% EtOH	39.7	28.4 ± 0.3

a Mixture of ethanol, isopentane, and diethyl ether in a 2:5:5 (v/v) ratio.

**Table V. Excimer Formation Rate Constants and Solvatochromic Parameters Used in the Correlations**

solvents	$\delta_H{}^2$	$\pi_1{}^*$	α_1	β_1	log k_2
i-Pr$_2$O^a	51.4	0.27	0.00	0.49	2.13
Et$_2$O^a	54.8	0.53	0.00	0.47	2.13
(CH$_3$OCH$_2$)$_2$^{a}	64.0	0.27	0.00	0.41	2.18
CH$_2$Cl$_2$^{a}	94.1	0.82	0.30	0.00	2.19
(CH$_2$Cl)$_2$^{a}	94.5	0.81	0.00	0.00	2.22
CH$_3$CN^a	141.6	0.75	0.19	0.31	2.36
t-BuOH^a	106.1	0.41	0.68	1.01	2.47
i-PrOH^a	132.3	0.48	0.76	0.95	2.51
EtOH^a	161.3	0.54	0.85	0.77	2.56
CH$_3$OH^a	210.3	0.60	0.99	0.62	2.59
CH$_3$OD	204.5	0.60	0.97	0.58	2.61
CD$_3$OD	198.8	0.60	0.97	0.62	2.61
90% aq CH$_3$OH	231.0	0.72	1.00	0.55	2.62
80% aq CH$_3$OH	265.7	0.80	1.13	0.51	2.63

a Solvatochromic parameters taken from refs 18–22 with the remainder determined in the present study according to the methods described therein.

either by itself or in combination with one or more of these parameters, has been evaluated by considering the correlation coefficient and the confidence level (CL%) for the corresponding parameters. These are listed in Table VI.

When all four solvatochromic parameters are employed (Table VI, eq A), only the terms in $\delta_H{}^2$ and β have a confidence level greater than 95%, which is generally viewed

as the minimum confidence level that is required to justify the inclusion of any given term in a multiple parameter linear equation.[17] Dropping the solvent dipolarity term $\pi_1{}^*$, since it exhibits the lowest confidence level in equation A, provides eq B. The confidence level for the participation of hydrogen-bond-donor term α_1 increases, but is still clearly less than 95%, so solvent electrophilic assistance is not established. Omitting both the $\pi_1{}^*$ and α_1 terms provides eq D, which underscores the importance of the solvent cohesive energy density and solvent nucleophilic assistance. A comparison of eq D with E and G reveals that the cavity term is more important than nucleophilic solvent participation since there is a considerably greater decrease in the correlation coefficient when the cavity term is omitted. The positive term in $\delta_H{}^2$ is consistent with the reorganization of solvent–solute and solvent–solvent interactions in the formation of triplet excimer. As the BpBr[3] and BpBr components approach each other to form an excimer, for example A, a layer of solvent molecules on the inside faces of the two benzene rings would be stripped away providing a larger number of solvent-solvent interactions. A small amount of charge transfer might well induce the solvent nucleophilic assistance illustrated in A.

A
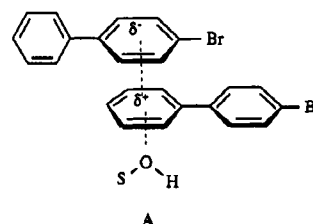
A comparison with the solvolysis of *tert*-butyl halides is revealing. For *tert*-butyl halides, solvolysis/dehydrohalogenation rates in 21 protic and aprotic solvents were best correlated by eqs 10–12.[23] A strong dependence on

$$\log k_2 = 1.94 + 0.00242\delta_H{}^2 + 0.248\beta_1 \qquad (9)$$

$$r = 0.9765 \qquad sd = 0.0438$$

$\log k_{t\text{-BuCl}} =$
$$-14.60 + 0.0048\delta_H{}^2 + 5.10\pi_1{}^* + 4.17\alpha_1 + 0.73\beta_1 \quad (10)$$

$$r = 0.9973 \qquad sd = 0.242$$

$\log k_{t\text{-BuBr}} =$
$$-11.97 + 0.0031\delta_H{}^2 + 5.77\pi_1{}^* + 3.16\alpha_1 + 0.46\beta_1 \quad (11)$$

$$r = 0.9947 \qquad sd = 0.280$$

$\log k_{t\text{-BuI}} =$
$$-9.60 + 0.0003\delta_H{}^2 + 6.07\pi_1{}^* + 2.43\alpha_1 - 0.34\beta_1 \quad (12)$$

$$r = 0.9905 \qquad sd = 0.311$$

(18) (a) Taft, R. W.; Kamlet, M. J. *J. Chem. Soc., Perkin Trans. 2* 1979, 1723–1729. (b) Kamlet, M. J.; Taft, R. W. *Ibid.* 1979, 349–356. (c) Taft, R. W.; Kamlet, M. J. *J. Am. Chem. Soc.* 1976, *98*, 2886–2894.
(19) (a) Taft, R. W.; Gramstad, T.; Kamlet, M. J. *J. Org. Chem.* 1982, *47*, 4557–4563. (b) Taft, R. W.; Pienta, N. J.; Kamlet, M. J.; Arnett, E. M. *Ibid.* 1981, *46*, 661–667. (c) Kamlet, M. J.; Taft, R. W. *J. Am. Chem. Soc.* 1976, *98*, 377–383. (d) Yokoyama, T.; Taft, R. W.; Kamlet, M. J. *Ibid.* 1976, *98*, 3233–3237.
(20) (a) Kamlet, M. J.; Hall, T. N.; Boykin, J.; Taft, R. W. *J. Org. Chem.* 1979, *44*, 2599–2604. (b) Kamlet, M. J.; Abboud, J. L.; Taft, R. W. *J. Am. Chem. Soc.* 1977, *99*, 6027–6038. (c) Abboud, J. L.; Kamlet, M. J.; Taft, R. W. *Ibid.* 1977, *99*, 8325–8327.
(21) (a) Kamlet, M. J.; Carr, P. W.; Taft, R. W.; Abraham, M. H. *J. Am. Chem. Soc.* 1981, *103*, 6062–6066. (b) Barton, A. F. M. *Chem. Rev.* 1975, *75*, 731–753.
(22) (a) Kamlet, M. J.; Taft, R. W. *Acta Chem. Scand. B* 1985, *39*, 611–628. (b) Kamlet, M. J.; Doherty, R. M.; Abboud, J.-L. M.; Abraham, M. H.; Taft, R. W. *Chemtech September* 1986, 566–576.

Table VI. Correlation of Rate Constants for Excimer Formation

$$\log k_2 = (\log k_2)_0 + h\delta_H{}^2 + s\pi_1{}^* + a\alpha_1 + b\beta_1$$

	$(\log k_2)_0$ $(\pm)$	$100h$ $(\pm)$	s $(\pm)$	a $(\pm)$	b $(\pm)$	r	sd	confidence level (CL%)			
								$\delta_H{}^2/100$	$\pi_1{}^*$	α_1	β_1
A	1.95 (0.09)	0.152 (0.056)	0.097 (0.115)	0.137 (0.102)	0.216 (0.091)	0.9787	0.0417	97.5	57.5	79.0	95.9
B	2.01 (0.06)	0.160 (0.055)		0.155 (0.098)	0.165 (0.066)	0.9793	0.0411	98.5		85.5	96.8
C	1.87 (0.07)	0.219 0.027)	0.128 (0.117)		0.303 (0.066)	0.9769	0.0434	100	70.1		99.9
D	1.94 (0.03)	0.242 (0.018)			0.248 (0.043)	0.9765	0.0438	100			>99.9
E	2.03 (0.05)	0.268 (0.034)				0.9101	0.0843	100			
F	2.17 (0.44)			0.438 (0.032)		0.9672	0.0516			100	
G	2.21 (0.10)				0.392 (0.166)	0.5100	0.1749				99.9

$\pi_1{}^*$ and α_1 is consistent with a transition state that is well on its way to a fully developed ion pair.[24,25] The fact that in the present case $\pi_1{}^*$ exhibits a poor correlation for excimer formation probably indicates that very little charge separation occurs at the transition state for excimer formation. In fact for the two parameter correlation (eq D), comparison with the *tert*-butyl halide cases reveals that solvent effects for excimer formation are quite muted.

The effect of the electron donor triethylamine (D) on the photoreactivity of BpBr was also investigated in order to observe the effect of the solvent polarity on the rate constant for the formation of an exciplex formed via an electron transfer from triethylamine to an excited state of BpBr. The photolysis of BpBr at 300 nm in acetonitrile in the presence of triethylamine forms biphenyl. The concentrations of BpBr and triethylamine were such that all the incident light was absorbed by BpBr. The quantum yield of the reaction increased with increasing concentrations of triethylamine at a fixed concentration of BpBr. Product formation could occur by electron transfer to triplet-state or singlet-state BpBr. If the branching point is the triplet state, product formation will result from the competing steps of excimer and exciplex formation as illustrated in Scheme VI.

Using the steady state assumption, the quantum yield according to this scheme is represented by eq 13. As the

$$\Phi_{prod} = \frac{Fk_2[BpBr] + Gk_{ex}[D]}{k_2[BpBr] + k_d + k_{ex}[D]} \quad (13)$$

$$\frac{1}{\Phi_{prod}} = \frac{1}{G} + \frac{k_d + k_2[BpBr]}{Gk_{ex}[D]} \quad (14)$$

$$F = \frac{k_p}{k_p + k_e} \qquad G = \frac{k_p{}'}{k_p{}' + k_e{}'}$$

concentration of triethylamine is increased, at some point $Fk_2[BpBr] \ll Gk_{ex}[D]$ so that eq 13 simplifies to eq 14. This picture is consistent with the plot obtained for the inverse of the quantum yield versus the inverse of triethylamine concentration (Figure 6). At high concentrations of triethylamine, the plot is linear with a positive slope (in agreement with eq 14), whereas with decreasing concentrations of triethylamine there is a competition between excimer and exciplex formation, the slope decreases and the plot becomes concave downward (in
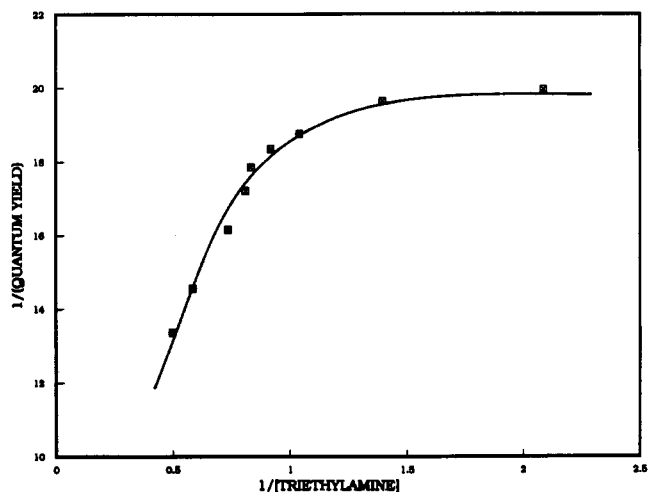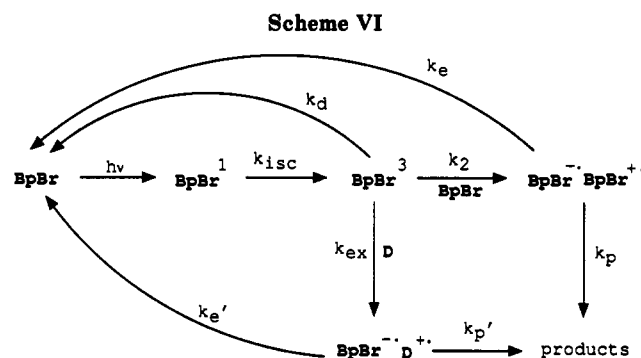
(23) Abraham, M. H.; Grellier, P. L.; Nasehzadeh, A.; Walker, R. A. C. *J. Chem. Soc., Perkin Trans. 2* **1988**, 1717–1724.

(24) Abraham, M. H.; Abraham, R. J. *J. Chem. Soc., Perkin Trans. 2* **1974**, 47.

(25) Abraham, M. H. *Prog. Phys. Org. Chem.* **1974**, *11*, 1.

Scheme VI

Figure 6. Plot of the inverse of the quantum yield of the photodebromination of 4-bromobiphenyl in acetonitrile in the presence of triethylamine versus the inverse of the triethylamine concentration.

agreement with eq 13). If the branching point in product formation is singlet-state BpBr, equations similar to 13 and 14 are derived from the steady-state assumption and are also consistent with the experimental plot.[26] The reaction was carried out in such a way that less than 4% of BpBr was allowed to react so that the concentration of BpBr could be considered constant. Using that portion of the plot where exciplex formation is dominant and eq 14 holds,

(26) Where k'_{ex} is the rate constant for exciplex formation from singlet in the region where exciplex formation is dominant

$$\frac{1}{\phi} = \frac{1}{G} + \frac{k_{isc}}{k'_{ex}G(D)}$$

where G is the fraction of exciplex that goes on to product.

one can calculate k_{ex} using the ratio of the slope to the intercept, k_d and k_2, obtained from the reaction without triethylamine. Upon changing from diisopropyl ether to the more polar solvent, MeOH, there was a 7.5-fold increase in k_{ex} compared to the 2.9-fold increase in k_2. (If the singlet mechanism is operative, the increase in the rate constant is 5.7, assuming no change in k_{isc} with solvent.) In a recent study,[27] we have compared the regiochemistry of photodehalogenation of pentachlorobenzene in the presence of triethylamine with the regiochemistry obtained via the radical anion of pentachlorobenzene generated in a nonphotochemical process with lithium *p,p'*-di-*tert*-butylbiphenylide. The regiochemistries were found to be remarkably similar and have been ascribed to the generation of exciplexes in which the radical anion and cation are solvent separated. Thus, the variations in k_{ex} and k_2 in diisopropyl ether and MeOH support the idea that the fully charge-separated exciplex is more sensitive to solvent polarity whereas the excimer of BpBr is less sensitive due to a smaller charge separation.

Conclusion

BpBr undergoes photoreduction from the triplet state with no detectable product formation from the singlet state. This observation is supported by the near unity of ϕ_{isc} as well as by quenching studies. The variation in the quantum yield of reaction of BpBr does indicate the formation of an excimer. In the absence of singlet reactivity, it may be concluded that this excimer is a triplet excimer. However the linear solvation energy parameters for this reaction appear to indicate only a weak polarization of the excimer species suggesting a weak radical anion and cation character for the respective moieties that make up the excimer. The different sensitivities of the rates of solvent separated exciplex formation and excimer formation support the conclusion that there is a smaller charge separation in the BpBr excimer than in the BpBr·NEt$_3$ exciplex.

Experimental Section

General. 4-Bromobiphenyl (Aldrich) was recrystallized from methyl alcohol. The solvents used in the photolysis were purified by distillation. Anhydrous *i*-Pr$_2$O and CH$_2$Cl$_2$ (Aldrich) were used as obtained, and their purity was greater than 99% by GLC analysis. Triethylamine was freshly distilled prior to its use. The indicators for the measurement of the solvatochromic parameters (α_1, β_1, π_1^*, and δ_H^2) were used as obtained: 4-nitroanisole (Aldrich), *N,N*-diethyl-3-nitroaniline, *N,N*-diethyl-4-nitroaniline (Frinton), 4-nitroaniline (JT Baker), and 4-methoxy-β-nitrostyrene (Trans World Chemical).

2,6-Diphenyl-4-(2,4,6-triphenyl-*N*-pyridinio)phenolate was prepared according to the procedure of Dimroth.[16a] Photolysis mixtures were analyzed by GLC on a Varian 3300 and/or 3400 capillary gas chromatograph equipped with an FID, a 30 m × 0.25 mm capillary column (J&W Scientific Inc.) and a Spectra physics 4290 integrator. The capillary columns used were DB-5 (5% phenyl-methylsilicone), DB-17 (50% phenyl-methylsilicone) and DB-225 (50% (cyanopropyl)phenyl-methylsilicone). Helium was used as carrier gas at 30 mL/min. The photoproduct was identified by comparing its GC retention time with that of an authentic sample coupled with mass spectral analyses carried out with a Finnigan 4023 mass spectrometer equipped with a Finnigan 9610 or Varian 3400 capillary gas chromatograph.

General Procedure for Photolysis. Irradiation of the samples in duplicate was carried out in a Rayonet merry-go-round reactor (The Southern New England Co.) equipped with eight lamps (300 nm) while being cooled by an overhead fan to maintain a constant temperature of ca. 30 °C. The photolysis samples (1 mL) were placed in Pyrex tubes (Ace Glass, 170 mm × 15 mm), each screwed to a nylon adapter bushing containing a Pyrex glass

Table VII. Stern–Volmer Quenching of BpBr^a with cis-1,3-Pentadiene

[1,3-pentadiene] (M)	ϕ_{prod}^b	ϕ_{std}/ϕ_{prod}
0	0.0221	1.00
0.005 15	0.0162	1.36
0.0103	0.0115	1.91
0.0155	0.0101	2.19
0.0206	0.009 04	2.44
0.0309	0.006 14	3.59

^{a} 0.0100 M. ^{b} Quantum yield of product formation, average of two determinations.

Table VIII. Stern–Volmer Quenching of BpBr^a with Fumaronitrile

[fumaronitrile] (M)	ϕ_{prod}^b	ϕ_{std}/ϕ_{prod}
0	0.0230	1.00
0.002 00	0.008 39	2.74
0.004 01	0.007 52	3.06
0.006 01	0.007 30	3.15
0.008 01	0.003 44	6.69
0.015 03	0.003 01	7.64
0.025 04	0.001 93	11.89
0.035 06	0.001 29	17.83

^{a} 0.0100 M. ^{b} Quantum yield of product formation, average of two determinations.

sliding stopper valve and degassed through three or four freeze–pump–thaw cycles. The tubes were sealed under vacuum and irradiated at 300 nm for the desired time period. Quantum yields of products were determined by using 3 azoxybenzene[28] actinometer solutions (1 mL each).

Quantum Yield Dependence of BpBr on Concentration of BpBr. Appropriate amounts of BpBr were weighed into 5-mL volumetric flasks, and the solutions were made up to the mark with CH$_3$CN to obtain the concentrations shown in Table I. At the concentrations employed for both BpBr and the actinometer solutions, the optical densities were greater than 2, thus ensuring complete absorption of incident light. Two samples of each of the solutions were degassed and irradiated at 300 nm in the presence of an azoxybenzene actinometer. Three actinometer tubes each containing 1 mL of azoxybenzene solution (ca. 0.006 M) were used for each irradiation run. A stock solution of dodecane internal standard (0.0178 M) was prepared by weighing 30.4 mg into a 10 mL volumetric flask and diluting to the mark. After irradiation was completed (1 h), appropriate volumes of the solution of internal standard (dodecane) were added so that the ratio of the initial concentration of BpBr to the concentration of the internal standard was around 1.1. Quantum yields of products were determined by using 3 sample tubes of azoxybenzene[28] actinometer (1 mL each). GLC analyses were carried out using a DB 225 capillary column and initial temperature/holding time/rate of increase in °C per min/final temperature = 60/10/25/220 with injector/detector temperature = 300/350 °C. Reported quantum yields are averages of two samples for each BpBr concentration.

Stern–Volmer Quenching of the Photodebromination of 4-Bromobiphenyl with cis-1,3-Pentadiene[10] and Fumaronitrile.[13] Appropriate amounts of cis-1,3-pentadiene and fumaronitrile were dissolved in 0.0100 M solution of 4-bromobiphenyl in acetonitrile to get the concentrations shown in Tables VII and VIII, respectively. BpBr absorbs all the incident light at this concentration. Photolysis (300 nm, 60 min) and product analyses were carried out as described above in the general procedure for photolysis and product analyses. Quantum yields of products were determined by using three solutions of azoxybenzene actinometer (1 mL each). The Stern–Volmer plots were obtained by plotting the ratio of quantum yield of reaction in the absence of the quenchers to that in the presence of the quenchers

(27) Freeman, P. K.; Ramnath, N. *J. Org. Chem.* **1991**, *56*, 3646–3651.

(28) Bunce, N. J.; LaMarre, J.; Vaish, S. P. *Photochem. Photobiol.* **1984**, *39*, 531–535.

(29) Magata, N.; Okada, T.; Kanada, Y.; Shioyama, H. *Tetrahedron* **1988**, *110*, 6143.

(30) Weller, A. Z. *Phys. Chem. Neue Folge* **1982**, *130*, 129.

Table IX. λ_{max} of Charge-Transfer Complex of Betaine for Solvent Polarity Measurement

solvent	λ_{max} (nm)	E_T
CH₃OH	518	55.2
CH₃OD	522	54.8
CD₃OD	522	54.8
90% aq CH₃OH	512	55.8
80% aq CH₃OH	508	56.3
EPA[a]	602	47.5
{97.5% Et₂O	720	39.7
2.5% EtOH		

[a] Mixture of ethanol, isopentane, and diethyl ether in a 2:5:5 (v/v) ratio.

against the respective concentrations of the quenchers.

Sensitization of Cis → Trans Isomerization of cis-1,3-Pentadiene[14] by 4-Bromobiphenyl. Solutions of cis-1,3-pentadiene were made in 0.0113 M 4-bromobiphenyl in acetonitrile (Table II). Two sets of degassed solutions of these mixtures were irradiated for 60 min at 300 nm. The amount of the trans isomer formed was determined by GLC analysis on a Varian 3700 gas chromatograph equipped with an FID using a series combination of a 10% SE-30 on Chrombsorb P (80/100) AW/DMCS and a 7% Carbowax 20 M on Chrombsorb P (80/100) AW/DMCS column. The column was programmed for 35 to 200 °C at a rate of 25 °C/min increase after 12 min at the initial temperature. The injection port temperature was 250 °C and detector temperature was 300 °C. The quantum yield of cis → trans isomerization was determined from the amount of trans isomer formed. Corrections for back reactions of the isomers were made according to the method of Lamola and Hammond[10] as described in the determination of ϕ_{isc} of 4-bromobiphenyl.

Effect of Light Intensity on ϕ_{prod} of 4-Bromobiphenyl in Acetonitrile. The intensity of incident light was varied by varying the number of lamps in the reactor where the normal number of lamps are eight. Variation was achieved with eight lamps and only one lamp. Further reduction was achieved by using a cylindrical metal shield for one lamp. The quantum yield of product formation reported is the average of two samples. The intensity of light and quantum yield of product formation were determined by using three solutions of azoxybenzene actinometer.

Phosphorescence and Lifetime Measurements of 4-Bromobiphenyl. The phosphorescence spectrum and lifetime

of the triplet state of 4-bromobiphenyl were obtained at 77 K using an Aminco-Bowman Spectrometer with a rotating cam. The exponential decay of emission intensity at 480 nm was monitored on an oscilloscope and a PC was used as a time-averaging computer. The average of 256 sweeps of signal repetitions was recorded for a total of approximately 250 data points.

Determination of ϕ_{ISC} of 4-Bromobiphenyl.[10] A solution of 0.186 M (126.7 mg) of trans-1,3-pentadiene and 0.0100 M (23.6 mg) of 4-bromobiphenyl and 0.0899 M (153.0 mg) of dodecane (internal standard) was prepared in a 10-mL volumetric flask. Several samples of this solution (1 mL each) were degassed, and two sets each of the degassed solutions were irradiated at 300 nm for 0.5, 1, 12, and 24 h. The cis/trans ratios obtained at 0.5 and 24 h were actually used to calculate the ϕ_{isc} and are as follows: (i) at 0.5 h trans/cis = 11.2/1.0 and (ii) at 24 h trans/cis = 4.2/1.0 (photostationary state). The quantum yield of intersystem crossing was then calculated according to the method described by Hammond and Lamola.[10]

Solvent Polarity Measurement (E_T Scale). E_T values were measured for CH₃OD, CD₃OD, 90% aqueous CH₃OH, 80% aqueous CH₃OH, EPA, and 97.5% Et₂O/2.5% EtOH using 2,6-diphenyl-4-(2,4,6-triphenyl-N-pyridinio)phenolate, which was prepared according to Dimroth.[16a] The polarity of solvents were determined according to Dimroth's method that involves measuring the λ_{max} of the charge-transfer complex of the betaine in the solvent under consideration. E_T is calculated using the following equation:

$$E_T = \frac{2.859 \times 10^4}{\lambda_{max} \text{ (nm)}}$$

Table IX shows the λ_{max} obtained in various solvents and the calculated E_T values.

Solvatochromic Parameters. The solvatochromic parameters for the solvents with no literature values were measured according to the literature and cited references therein: α_1,[18] β_1,[19] π_1^*,[20] δ_H.[21] Reviews[22] give a full list of references for linear solvation energy relationships and the methods of calculation.