# Photochemistry of Bromobiphenyls: Steric Effects and Electron Transfer

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Evidence is presented that photolytic fission of the C–Br bonds of bromobiphenyls is preceded by electron transfer. The enhanced rate of photodecomposition of 2-bromobiphenyls is shown to result from the release of steric strain in the excited state.

THE photochemistry of aryl halides is under active investigation, not least because of the importance of some of these compounds as environmental pollutants.[1] Aryl chlorides, which have been studied most extensively, afford mainly products explicable in terms of intermediate aryl radicals [2] probably derived from the triplet excited state of the halide. However, it seems unlikely that simple homolytic C–Cl fission [equation (i)] occurs,

$$^3Ar–X \longrightarrow Ar\cdot + X\cdot \qquad (i)$$
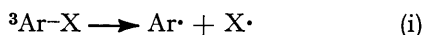
since there is usually a large energy defect between the triplet excitation energy and typical C–Cl bond dissociation energies.[3] The possibility of electron transfer has therefore been invoked [3,4] [equation (ii)]. Triplet

$$D + {}^3ArCl \longrightarrow D^{\cdot+} + Ar\cdot + Cl^- \qquad (ii)$$
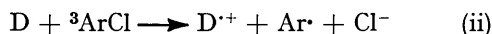
energies are largely independent of the identity of the halogen (Table 1) so that the energy defect decreases in the order chloride > bromide > iodide.

		Triplet energies		
Substituent	B.D.E.[b]	Phenyl	Naphthyl	Biphenylyl
H	440	350 [c]	255 [e]	275 [e]
Cl	365	d	250 [f]	275 [g]
Br	305		250 [f]	280 [g]
I	255		245 [f]	275 [g]

[a] All energies in kJ mol⁻¹. [b] S. W. Benson, ' The Foundations of Chemical Kinetics,' McGraw-Hill, New York, 1960, p. 670. [c] G. N. Lewis and M. Kasha, *J. Amer. Chem. Soc.*, 1944, **66**, 2100. [d] Monomeric halogenobenzenes reported nonphosphorescent (E. C. Lim and S. K. Chakrabarti, *Mol. Phys.*, 1967, **13**, 293). [e] J. G. Calvert and J. N. Pitts, ' Photochemistry,' Wiley, New York, 1966, p. 297. [f] Average value for α- and β-isomers from ref. e and L. G. Thompson and S. E. Webber, *J. Phys. Chem.*, 1972, **76**, 221. [g] Data are for 4-substituted compounds (ref. 13); other isomers appear similar.

In the case of aryl iodides, where the preparative aspects of the photochemistry have been thoroughly studied,[5] fragmentation may well occur by the simple fission corresponding to (i). Much less is known about

the photochemistry of aryl bromides,[6] though the subject promises to increase in importance with the growing use of polybromobiphenyls as plasticisers and flame retardants.[7] It is with the photoreactivity of some simple bromobiphenyls that this report is concerned.

RESULTS AND DISCUSSION

Direct Photolysis.—Direct irradiation of a series of bromobiphenyls in cyclohexane at *ca.* 300 nm results in reductive debromination as the major reaction (Table 2).

Substrate	Concn. (M)	ϕ_r [b]	% Conversion
2-Bromo	7.85×10^{-2}	0.046 (11.5)	16
3-Bromo	2.13×10^{-2}	0.004 (1.0)	5
4-Bromo	1.65×10^{-2}	0.015 (3.8)	25
2,5-Dibromo	7.31×10^{-2}	0.041 (10.3)	16
2,2'-Dibromo	3.95×10^{-2}	0.034 (8.4)	23
4,4'-Dibromo	2.23×10^{-2}	0.022 (5.4)	27

Examination of the involatile residue shows dimerisation to quaterphenyls to be occurring also. The products are thus analogous to those found in other aryl halide systems [1–5] and explicable in terms of intermediate aryl radicals. The reactions appear to proceed from triplet excited states, as might be expected for heavy-atom compounds, in that rates are retarded by a factor of two in air-saturated as compared with degassed solutions, while quenching, albeit inefficient,[8] is observed in the presence of typical triplet quenchers.

Isomers containing *ortho*-bromine atoms are photolysed significantly more efficiently than the others, and this suggests a steric acceleration such as was sought unsuccessfully in the iodobiphenyl series,[9] and recently observed in a series of tetrachlorobiphenyls.[10] We now present evidence to show that this acceleration is indeed a steric phenomenon.

Wagner [11] has inferred experimentally that the triplet

[1] O. Hutzinger, S. Safe, and V. Zitko, ' The Chemistry of PCB's,' CRC Press, Cleveland, 1974; L. Fishbein, *J. Chromatog.*, 1972, **68**, 345; see also citations in ref. 2.

[2] R. J. Majer and J. P. Simmons, *Adv. Photochem.*, 1964, **2**, 137; J. T. Pinhey and R. D. G. Rigby, *Tetrahedron Letters*, 1969, 1267.

[3] L. O. Ruzo, N. J. Bunce, and S. Safe, *Canad. J. Chem.*, 1975, **53**, 688.

[4] M. Ohashi, K. Tsujimoto, and K. Seki, *J.C.S. Chem. Comm.*, 1973, 384; B. Stevens, *Adv. Photochem.*, 1971, **8**, 161.

[5] R. K. Sharma and N. Kharasch, *Angew. Chem. Internat. Edn.*, 1968, **7**, 36.

[6] T. Matsuura and K. Omura, *Bull. Chem. Soc. Japan*, 1966, **39**, 944; M. G. Kuz'min, Y. A. Mikleev, and L. N. Guseva, *Doklady Akad. Nauk S.S.R.*, 1967, **176**, 368; C. Párkány and Y. J. Lee, *Tetrahedron Letters*, 1974, 115.

[7] *E.g.* Technical Bulletins, Michigan Chemical Corp., Chicago.

[8] L. O. Ruzo and N. J. Bunce, *Tetrahedron Letters*, 1975, 511.

[9] N. Kharasch and T. G. Alston, unpublished observations, cited in ref. 5.

[10] L. O. Ruzo, M. J. Zakik, and R. D. Schuetz, *J. Amer. Chem. Soc.*, 1974, **96**, 3809.

[11] P. J. Wagner, *J. Amer. Chem. Soc.*, 1967, **89**, 2820.

excited state of biphenyl is planar, unlike the ground state which, in solution, is believed to be twisted about the inter-ring bond. This is consistent with the simple MO picture of biphenyl where the inter-ring π-bond order is greater in the excited than the ground state,[12] so that there should be more destabilization of the excited state upon twisting. The greater reactivity of *ortho*-substituted bromobiphenyls could thus be explained in terms of relief of steric strain upon ejection of the bromine substituent, allowing a planar biphenylyl radical to be attained. Four experimental facts support this concept, as follows. (i) Photolysis of 2,5-dibromo-biphenyl affords almost exclusively 3-bromobiphenyl, *i.e.* only the *ortho*-bromine atom is lost. (ii) The decomposition of 2,2'-dibromobiphenyl is accelerated less than that of 2-bromobiphenyl, even though the former is more severely hindered (see u.v. data in Table 3 and the arguments below). However, loss of a single bromine atom from the dibromo-compound leaves a monobromo-biphenylyl radical which is still subject to steric constraint. (iii) The i.r. C–Br stretching bands of the bromobiphenyls (Table 3) show that the C–Br bond in

TABLE 3

Spectroscopic properties of brominated biphenyls

	U.v.[a]			I.r.[b]	Mass spectrum[c] Intensity $(M-Br)^{+}/$
Compound	λ_{max}/nm	ε_{max}	$\varepsilon_{300\ nm}$	ν_{C-Br}/cm^{-1}	M^{+}
2-Bromo	236sh	4 500	2	456	0.93
3-Bromo	254	18 100	71	445	0.74
4-Bromo	256	21 500	86	472	0.64
2,2'-Dibromo	228sh	3 400	0.4	448	2.62
4,4'-Dibromo	265	24 000	140	495	0.22
2,5-Dibromo	238sh	4 700	22	439, 449	

[a] Ethanolic solution; Cary 118C spectrophotometer. [b] Beckman IR 12 instrument. [c] Varian-MAT CH 7 spectrometer operated at 70 eV ionizing voltage.

o-bromobiphenyls in the ground electronic state is not unusually weak. The stretching frequencies parallel the calculated (zero order HMO, planar model) C–Br π-bond orders; thus the *ortho* rate increase suggests a steric effect in the excited state rather than an intrinsic weakness of *ortho* C–Br bonds. (iv) Similar phosphorescence spectra are observed [13] for all three monobromobiphenyl isomers, although E_{T} for the *ortho*-isomer may be a little higher. Phosphorescence lifetimes are markedly different, that of the *ortho*-compound being appreciably shorter. A similar reduction in the triplet state lifetime as estimated by the quenching method has been observed in *ortho*-substituted isomers in the tetra-chlorobiphenyl series.[10] This accords with Wagner's [11] observations on the allowedness of $S_0 \longleftrightarrow T_1$ transitions in biphenyl where the two states have different equilibrium geometries. For 2-bromobiphenyl, if both S_0 and T_1 are twisted, the $T_1 \longrightarrow S_0$ transition becomes more allowed and the T_1 lifetime is reduced. A corollary

is that if the excited state of 2-bromobiphenyl were equally as long lived as its isomers', the expected enhancement of the efficiency of photodecomposition would be even greater than that reported in Table 2.

The angle of twisting in the *ortho*-substituted biphenyls was determined by using a simplification of Suzuki's method.[14] Zero-order HMO calculations were carried out making the following assumptions: (i) that the calculated gap (ΔE) between the highest occupied and lowest vacant MOs of the ground state biphenyl was proportional to the spectroscopic transition energy; (ii) that the same HMO parameters [15] were applicable for the Br substituents regardless of location; (iii) that the inter-ring bond integral varied as $\cos^2\theta$, where θ is the angle between the planes of the rings. Unlike Suzuki, we took no account of any lengthening of the inter-ring bond upon twisting.

Based on literature spectroscopic data [14] for crystalline ($\theta = 0°$),[16] solution (θ unknown), and vapour ($\theta = 43°$),[17] plots of ΔE vs. $\nu_{max.}$ and ΔE vs. θ indicate an interplanar angle of 20° for biphenyl in solution (see Table 4); the

TABLE 4

Calculated transition energies for biphenyl derivatives assuming various geometries

Interplanar angle (°)	ΔE[a]	Interplanar angle (°)	ΔE[a]
Biphenyl		2,2'-Dibromobiphenyl	
0	1.460	0	1.450
10	1.473	20	1.500
20	1.515	30	1.565
30	1.580	45	1.695
45	1.712	60	1.830
2-Bromobiphenyl		90	1.946
0	1.452	3-Bromobiphenyl	
20	1.507	0	1.458
30	1.573	20	1.512
45	1.703	4-Bromobiphenyl	
60	1.840	0	1.447
90	1.946	20	1.502
		4,4'-Dibromobiphenyl	
		0	1.437

[a] In β units.

test results are thus in satisfactory agreement with those of Suzuki.

A calibration plot of $\nu_{max.}$ vs. ΔE for some reference compounds was then made. The choice of reference compounds in studies of this kind is always a problem, and is compounded in biphenyl systems by the fact that it cannot be assumed that the non-*ortho*-substituted compounds are necessarily planar. We chose bromo-benzene, biphenyl (20°), and 4,4'-dibromobiphenyl as reference models. The last compound was assumed to be planar in view of the documented [18] influence of conjugating substituents in negating small steric effects in the biphenyl series. Data points for 3- and 4-bromo-biphenyl, calculated both for the planar situation and for

[12] H. H. Jaffé and M. Orchin, ' Theory and Interpretation of Ultraviolet Spectra,' Wiley, New York, 1964, ch. 12.
[13] C. M. O'Donnell, K. F. Harbaugh, R. P. Fisher, and J. D. Winefordner, *Analyt. Chem.*, 1973, **45**, 609.
[14] H. Suzuki, ' Electronic Absorption Spectra and Geometry of Organic Molecules,' Academic Press, New York, 1967, ch. 12.

[15] A. Streitweiser, ' Molecular Orbital Theory for Organic Chemists,' Wiley, New York, 1961, p. 135.
[16] A. Hargreaves and S. H. Rizvi, *Acta Cryst.*, 1962, **15**, 365.
[17] O. Bastiansen, *Acta Chem. Scand.*, 1949, **3**, 409.
[18] D. W. Sherwood and M. Calvin, *J. Amer. Chem. Soc.*, 1942, **64**, 1350.

$\theta = 20°$ are also placed on the graph (see Figure), and the deviation from the curve of the planar values argues strongly for the inability of a single bromo-substituent to overcome the steric effect in biphenyl. From the experimental (Table 3) absorption maxima of 2-bromophenyl and 2,2'-dibromobiphenyl, ΔE was obtained. Plots of ΔE vs. θ for each compound afforded θ, the angle at which ΔE corresponded to the spectroscopic transition energy (Table 4). For 2-bromobiphenyl and 2,2'-dibromobiphenyl, the calculated interplanar angles were thus 38 and 48°, respectively. For the 2,2'-dibromo-compound the value is to be compared with 64° (scale models)[19] and 68—85° (dipole moment studies in benzene);[20] it is smaller than the 75° observed by electron diffraction,[21] but this is to be expected by
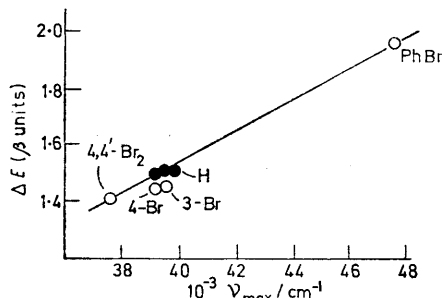
Calculated energy gap (ΔE) vs. spectroscopic transition energy for bromobiphenyls and reference compounds; open circles, planar model; closed circles, 20° interplanar angle

analogy with biphenyl, where the interplanar angle is smaller in solution than in the vapour phase.

Triethylamine-assisted Photolyses.—The effect of triethylamine is to enhance both the rate of photodecomposition of the bromobiphenyls and the proportion of the photoreduction product (Table 5). Photolyses of aryl

TABLE 5

Direct vs. triethylamine-assisted photolyses of bromobiphenyls [a]

Substrate	Concn. (M)	% Light abs. at 300 nm	ϕ_r [b]	% Conversion	% ArH [c]
Direct photolysis					
2-Bromo	0.176	55	0.056 (14.0)	50	44
3-Bromo	0.172	>99	0.004 (1.0)	4	41
4-Bromo	0.168	>99	0.010 (2.5)	9	44
2,2'-Dibromo	0.172	15	0.027 (6.8)	25	50
With Et₃N (2.9M)					
2-Bromo	0.176	55	0.104 (26.0)	93	95
3-Bromo	0.172	>99	0.008 (2.0)	8	86
4-Bromo	0.168	>99	0.011 (2.8)	10	98
2,2'-Dibromo	0.172	15	0.060 (15.0)	56	74

[a,b] See Table 2. [c] Chemical yield of photoreduction product.
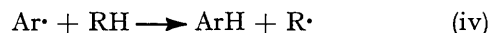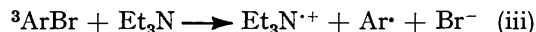
halides in the presence of bases have generally been considered to proceed by way of electron transfer.[4,6,22] The present results parallel those of our previous study of the chloronaphthalenes[2] and permit a similar explan-

ation. In the presence of triethylamine, reaction (iii) leads to an aryl radical which subsequently abstracts

$$^3\text{ArBr} + \text{Et}_3\text{N} \longrightarrow \text{Et}_3\text{N}^{\cdot+} + \text{Ar}\cdot + \text{Br}^- \quad \text{(iii)}$$

$$\text{Ar}\cdot + \text{RH} \longrightarrow \text{ArH} + \text{R}\cdot \quad \text{(iv)}$$

hydrogen. At these concentrations, the aryl radical apparently abstracts hydrogen rather than substitute another aromatic nucleus. Consequently, the quaterphenyls that are formed on direct photolysis must arise by another route, and taken together with the insufficiency of the triplet excitation energy to cause bond rupture, this suggests the pathway of equation (v),

$$\text{Ar'H} + {}^3\text{ArBr} \longrightarrow \text{Ar'H}^{\cdot+} + \text{Ar}\cdot + \text{Br}^- \quad \text{(v)}$$

where Ar'H may be a second molecule of the bromobiphenyl or a product aromatic compound. Some of the resulting radical cations may now attack other aryl residues in a kind of Friedel–Crafts substitution, thus affording quaterphenyls in this system. Support for this proposal comes from the work of Ronlán *et al.*,[23] who prepared quaterphenyls by anodic oxidation of biphenyls.

Just as in the direct photolyses, the *ortho*-substituted compounds are the most reactive in the presence of amine. Once again, calculations on a planar model of bromobiphenylyl radical anions give no expectation of an abnormally weak *ortho* C–Br bond, so that a steric effect must again be operating. Consistent with this, the inter-ring π-bond order is higher in the radical anion than in the neutral molecule, as it is in the excited as compared with the ground state (Table 6). Thus the

TABLE 6

Selected calculated bond orders in bromobiphenyls [a]

	2-Bromo	3-Bromo	4-Bromo	2,2'-Dibromo	4,4'-Dibromo
C–C Bond orders					
Ground state	0.338	0.337	0.338	0.338	0.338
Excited state	0.594	0.593	0.591	0.594	0.589
Radical cation	0.467	0.464	0.463	0.467	0.461
Radical anion	0.465	0.466	0.466	0.465	0.466
C–Br bond orders					
Ground state	0.111	0.109	0.110	0.111	0.110
Excited state	0.139	0.116	0.151	0.133	0.147
Radical cation	0.150	0.119	0.172	0.144	0.168
Radical anion	0.100	0.106	0.079	0.100	0.079

[a] Assuming planar model.

finding that an electron-transfer mechanism is operating and hence that bromine is lost from the radical anion in no way vitiates the steric arguments developed above; indeed it can be seen that the C–Br π-bond orders in the radical anion are such as to suggest that *para*-substituted bromobiphenyls would be the most reactive. A similar inter-ring bond order change is also apparent in comparing the neutral molecule with the radical cation, and it is interesting that the mass spectra of *o*-bromobiphenyls show a greater extent of bromine ejection than

[19] G. H. Beaven and D. M. Hall, *J. Chem. Soc.*, 1956, 4637.
[20] A. C. Littlejohn and J. W. Smith, *J. Chem. Soc.*, 1954, 2552.
[21] O. Bastiansen, *Acta Chem. Scand.*, 1950, **4**, 926.
[22] J. A. Barltrop and R. J. Owers, *Chem. Comm.*, 1970, 1462; J. A. Baltrop, *Pure Appl. Chem.*, 1973, **33**, 179.
[23] A. Ronlán, K. Bechgaard, and V. D. Parker, *Acta Chem. Scand.*, 1973, **27**, 2375.

the *meta-* or *para-*isomers. Such an effect has been observed previously in the chloro-analogues.[24]

EXPERIMENTAL

Photolytic and analytical procedures have been described in detail elsewhere.[2] The photolyses were carried out in duplicate, and reported values are averages, based upon at least duplicate analyses of each reaction mixture. The biphenyl derivatives were commercial products, purified by appropriate combinations of recrystallisation, distillation, and chromatography until free of impurities (g.l.c.), except for 2,5-dibromobiphenyl. This was prepared by diazotising 2,5-dibromoaniline with pentyl nitrite in the presence of an excess of benzene,[25] and obtained in 49% yield as an *oil* after column chromatography and distillation (Found: M^+, 311.8972. $C_{12}H_8{}^{79}Br{}^{81}Br$ requires M, 311.8972).

Spectroscopic properties of the compounds studied are given in Table 3; photolysis products and quantum yields are reported in Tables 2 and 5. HMO parameters were in all cases those recommended by Streitweiser;[15] selected results are presented in Tables 4 and 6 and in the Figure.

[24] S. Safe and O. Hutzinger, *J.C.S. Chem. Comm.*, 1971, 446; *J.C.S. Perkin I*, 1972, 686.
[25] J. I. G. Cadogan, *J. Chem. Soc.*, 1962, 4257.