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Steric Effects in the Singlet–Triplet Transitions of Methyl- and Chlorobiphenyls[1]

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Abstract: A potential energy diagram has been constructed which explains semiquantitatively the effects of ortho and para methyl and chloro substitution on S ↔ T transitions of biphenyl. Triplet EPR spectra indicate that the ortho-substituted biphenyls maintain planar triplets. Both ortho-substituted biphenyls display maximum phosphorescence intensities at the same energy as does biphenyl itself. However, rate constants for reversible energy transfer from triplet benzophenone to the ortho-substituted biphenyls are only 1–5% as large as those for transfer to biphenyl itself. The greater twist in the ground states of the ortho-substituted biphenyls necessitates a greater change in geometry during these nonvertical energy transfers. The lower rate constants probably reflect the involvement of rotationally excited ground states.

A few years ago, it was reported that the lowest triplet state of biphenyl is planar and thus possesses a markedly different conformation from the twisted ground state.[2] This conclusion was based on the observation of a 10 kcal difference between the "0–0" bands for phosphorescence and S → T absorption of biphenyl and on the efficiency with which biphenyl quenches triplet ketones. Subsequent spectroscopic[3-5] and theoretical[6] investigations have also concluded that triplet biphenyl is planar.

Ortho substituents increase the barrier to planarity in the ground state of biphenyl[7] and ought to similarly destabilize the planar conformation of the triplet state. The original report noted that several ortho-substituted biphenyls were worse quenchers than biphenyl itself,[2] but it could not be determined whether the triplets had become nonplanar. Lewis and Kasha's classic paper on phosphorescence[8] indicated that 2,2'-dihalobiphenyls phosphoresce at appreciably higher energies than biphenyl itself; they suggested nonplanar triplets. In contrast, Marchetti and Kearns have reported that ortho bromo and iodo substituents *lower* the 0–0 phosphorescence energy of biphenyl.[9] Since so little is known about steric effects in excited states and since interest in the consequences of geometric differences between ground and excited states remains high, it seemed worthwhile to determine how large a substituent can be in the ortho position without forcing triplet biphenyl out of planarity and how much rates of nonvertical energy transfer[10] vary with geometric differences between ground and excited state. This paper reports our investigations of the spectroscopic and triplet quenching behavior of the methyl- and chlorobiphenyls.

Results

Quenching of Triplet Benzophenone. The efficiencies with

which naphthalene, biphenyl, and 2-, 3-, and 4-chlorobiphenyl quench the photoreduction of benzophenone in benzene containing 0.5 M isopropyl alcohol[11] were determined. In a given run, degassed solutions containing a fixed concentration of ketone and varying concentrations of quencher were irradiated in parallel at 25 °C with the 365-nm region of a mercury arc. Disappearance of ketone was monitored by UV analysis. After irradiation, each tube was opened and poured into a vial which was kept tightly stoppered in the dark overnight. This preanalysis procedure was employed since the absorbance of samples immediately after irradiation was high and decreased slowly to steady values, a phenomenon which is probably related to the formation of thermally unstable radical-coupling products.[13,14] Stern–Volmer plots of Φ^0/Φ vs. quencher concentration were linear and yielded the slopes (K_q) listed in Table I. Naphthalene, biphenyl, 2-chlorobiphenyl, 2-methylbiphenyl, and 4-methylbiphenyl were also used to quench the phosphorescence of benzophenone in degassed benzene solution, for which K_q values are also listed in Table I.

Quenching constants increase with decreasing ketone concentration for biphenyl and its 3-chloro and 4-methyl derivatives, but not for the ortho-substituted derivatives. Such concentration dependence indicates reversible energy transfer.[2,15,16] Figures 1 and 2 display the dependence of K_q^{-1} on ketone concentration and Table II lists actual $k_t\tau_B$ values (1/interpret). With k_t known to equal 5×10^9 M^{-1} s^{-1} for naphthalene,[17] τ_B values for triplet benzophenone and therefore k_q values for the biphenyls could be calculated.

$$K_q = \frac{k_t\tau_B}{1 + k_{-t}[B]\tau_Q} \qquad (1)$$

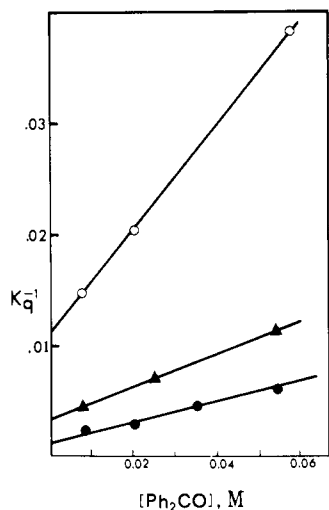$$^3B^* + Q_0 \underset{k_{-t}}{\overset{k_t}{\rightleftharpoons}} B_0 + {}^3Q^* \qquad (2)$$
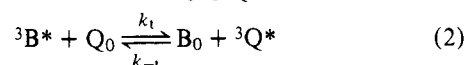
Figure 1. Dependence of Stern-Volmer quenching slopes on benzophenone concentration for photoreduction in 0.5 M isopropyl alcohol: (O) biphenyl; (▲) *m*-chlorobiphenyl; (●) *p*-chlorobiphenyl.
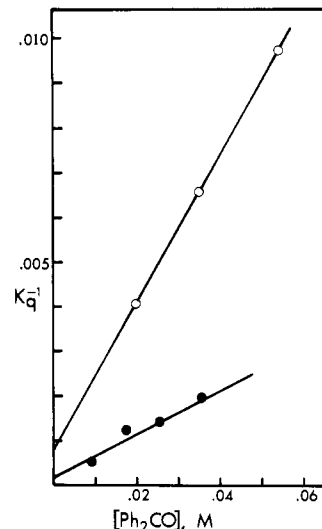

Figure 2. Dependence of Stern-Volmer quenching slopes on benzophenone concentration for phosphorescence in degassed benzene: (O) biphenyl; (●) *p*-methylbiphenyl.

Table I. Quenching of Triplet Benzophenone by Biphenyls in Benzene

Quencher	Ketone concn, M	$K_q{}^a$	$K_q{}^b$
Naphthalene	0.054	4330 ± 105	40 000 ± 4 000
Biphenyl	0.054	26 (24)[c]	103
	0.35		153 ± 15
	0.021	49 ± 1.0	250
o-Chlorobiphenyl	0.053	1.1	11.8
	0.035		13.9 ± 0.2
	0.020		11.5 ± 0.3
	0.0075		11.7
m-Chlorobiphenyl	0.054	89	
	0.025	144	
	0.0083	219	
p-Chlorobiphenyl	0.054	169 ± 3	
	0.035	217 ± 3	
	0.020	345	
	0.0074	500	
o-Methylbiphenyl	0.052		96
	0.013		95
p-Methylbiphenyl	0.035		520
	0.025		716
	0.017		833

[a] Quenching of photoreduction by 0.5 M 2-propanol. [b] Quenching of phosphorescence in pure benzene. [c] Quenching of phosphorescence in the presence of 0.5 M 2-propanol.

Absorption spectra of the biphenyls in heptane solution are quite similar. All three chlorobiphenyls, like biphenyl itself, display an intense, structureless band, with λ_{max} near 250 mm, corresponding to the $^1A \rightarrow {}^1L_a$ transition of benzene. Table III lists the λ_{max} values and molar extinction coefficients. Meta substituents produce only slight changes.

Para substituents produce red shifts (Cl, 690 cm^{-1}, 2.0 kcal; CH$_3$, 745 cm,$^{-1}$ 2.1 kcal). Ortho substituents produce blue shifts (Cl, 1120 cm^{-1}, 3.2 kcal; CH$_3$, 2180 cm^{-1}, 6.2 kcal). The latter effect is, of course, well-documented for ortho-substituted biphenyls.[7]

Phosphorescence spectra were recorded at 77 K in heptane and in 5:1 methylcyclohexane:isopentane (MCIP). Figure 3 compares the spectrum of biphenyl itself with those of some chloro derivatives. Table III lists 0-0 band energies for all biphenyls studied. Meta substituents decrease transition energies
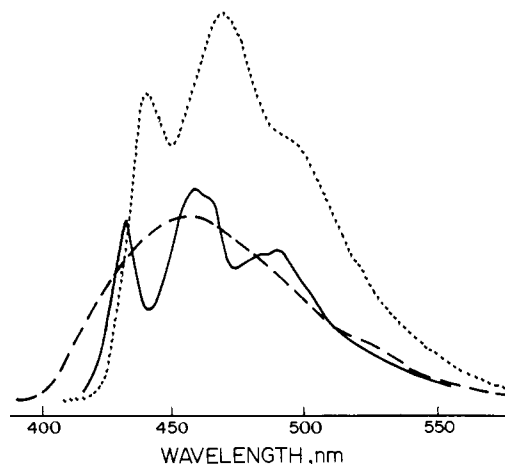

Figure 3. Phosphorescence spectra in MCIP at 77 K for biphenyl (—), *p*-chlorobiphenyl (· · ·), and *o*-chlorobiphenyl (- - -). Relative intensities as shown.

slightly and para substituents more so. Ortho substituents produce structureless spectra with onsets but not maxima shifted to higher energy.

Triplet EPR spectra of all the substituted biphenyls were measured in ethanol glasses at 77 K. Both $\Delta M = 1$ and $\Delta M = 2$ transitions are readily measurable. Table III lists the zero-field parameters for the methylbiphenyls.[18] The three chlorobiphenyls gave spectra identical with that of biphenyl and with the same long decay time.[19] Since the phosphorescence decays of the chlorobiphenyls are considerably faster than that of biphenyl, we fear that the EPR signals may be dominated by traces of biphenyl either originally present or produced photolytically.[20]

Discussion

We would like to construct potential energy diagrams for ground and triplet state biphenyls which explain (1) the nearly identical EPR spectra for all the methylbiphenyls; (2) the effects of ortho and para substituents on the energies of both $S_0 \rightarrow S_1^*$ absorption and $T^* \rightarrow S_0$ emission; and (3) the opposite effects of ortho and para substituents on the rate constants for triplet energy transfer from benzophenone to biphenyl.

Planarity of Triplet. In triplets with minimal spin-orbit coupling, the value of the zero-field parameter D depends on

Table II. Kinetic Parameters for Biphenyl Quenching of Triplet Benzophenone

Quencher	Monitor	$k_{-t}\tau_Q$, M^{-1}	$k_t\tau_B$, M^{-1}	$1/\tau_B$, 10^5 s^{-1}	k_t, 10^8 M^{-1} s^{-1}
Naphthalene	Reduction		4 400	11.4	50
	Emission		40 000	1.2	50
Biphenyl	Reduction	58	80	11.4	0.9 (2.5)[a]
	Emission	435	1 330	1.2	1.6
o-Chlorobiphenyl	Reduction		1.1	11.4	0.013
	Emission	0	12.4	1.2	0.015
m-Chlorobiphenyl	Reduction	46	290	11.4	3.3
p-Chlorobiphenyl	Reduction	62	770	11.4	8.8
p-Methylbiphenyl	Emission	190	5 000	1.2	6.2
o-Methylbiphenyl	Emission		96	1.2	0.12

[a] Reference 2.
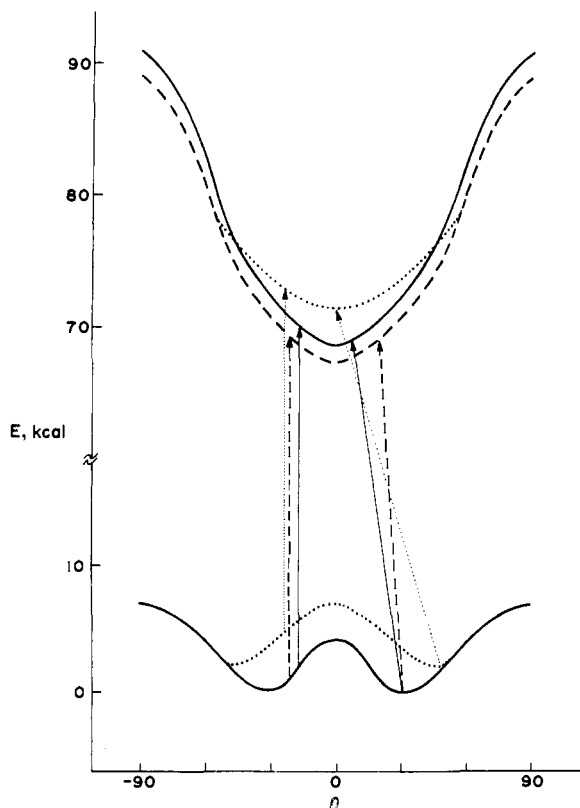
Figure 4. Potential energy diagram for twisting about the central bond of triplet (upper curves) and ground state (lower curves) biphenyl (—), p-chlorobiphenyl (- - -), and o-chlorobiphenyl (· · ·). Arrows explained in text.

Table III. Spectroscopy of Substituted Biphenyls

Substitution	λ_{max}, nm[a]	0–0 Phos, kcal[b]	D, cm^{-1c}	E, cm^{-1c}
None	248 (16 700)	65.6	0.1089	0.0035
2-Cl	241 (8000)	d		
3-Cl	248 (16 000)	64.8		
4-Cl	252 (19 200)	64.2		
2-CH$_3$	235[e]	d	0.1067	0.0070
3-CH$_3$	249[e]	64.7	0.1077	0.0042
4-CH$_3$	253[e]	64.5	0.1067	0.0036
2,2'-(CH$_3$)$_2$	227[e]	d	0.1068	0.0060
			0.1211	0.0085
3,3'-(CH$_3$)$_2$	250[e]	64.7	0.1067	0.0034
			0.1067	0.0070
4,4'-(CH$_3$)$_2$	256[e]	63.5	0.1062	0.0037

[a] In heptane, molar extinction coefficients in parentheses. [b] 0–0 phosphorescence band energy, in MCIP. [c] Zero-field parameters, ref 18. [d] Broad, see Figure 3. [e] Reference 7.

the strength of the spin–spin interaction and thus provides a very sensitive probe of the relative coplanarity of the two rings in biphenyl.[3] The nearly identical D values for biphenyl, all three methylbiphenyls, and all three dimethylbiphenyls indicate that single ortho substituents as small as methyl do not prevent the triplet from attaining planarity. Since a chloro substituent is no more demanding sterically than a methyl[21] (see Table III), we presume that triplet o-chlorobiphenyl is also planar. We have already discussed the slight variations in the zf parameters and the different triplets corresponding to the Z and E conformers of the 2,2'- and 3,3'-dimenthylbiphenyls.[18] We repeat here only our observation that one triplet (conformer) of 2,2'-dimethylbiphenyl remains planar, while the other (presumably the Z conformer) is twisted.

Energetics. The magnitude of fluorine hyperfine interactions on the triplet EPR spectra of fluorobiphenyls indicates that the free spin density is located primarily at the ortho and para carbons.[22] Para methyl or chloro substitution results in a stabilization of 1.0–1.3 kcal/mol. Ortho substitution would pre-

sumably have a comparable effect except for severe nonbonded interactions. The triplets probably maintain planarity by undergoing changes in bond lengths and angles as suggested by Westheimer for planar ground states.[23] The actual phosphorescence spectra of the ortho-substituted biphenyls are interesting in that the maximum intensity typically occurs just about where it does for biphenyl, but at 1–2 kcal higher energy than for the corresponding para-substituted compound. As shown in Figure 3, the onset of emission occurs at considerably higher energy in the ortho-substituted biphenyl than in biphenyl itself. This latter effect was not noted by Marchetti and Kearns[9] but must be related to Lewis and Kasha's report[8] of higher energy phosphorescence from 2,2'-dihalobiphenyls.

Rotational Potential Energy. Figure 4 estimates the effects of para and ortho chloro substitution on the potential energy of biphenyl as a function of the dihedral angle between its rings. It is assumed that para substitution has a negligible effect on the ground state, but lowers the excited state potential by 1.3 kcal at $\theta = 0°$ and 2.3 kcal at $\theta = 90°$. The latter figure is the difference in triplet energies of benzene and chlorobenzene.[24] We assume ground state dihedral angles of 30° for biphenyl itself and 48° for o-chlorobiphenyl.[25] We have arbitrarily assumed that the ortho chlorine destabilizes the planar ground state by 3 kcal. The fact that the maximum phosphorescence intensity of o-chlorobiphenyl occurs at the same energy as that of biphenyl indicates that the ortho chlorine destabilizes the planar triplet by almost the same amount as it destabilizes the planar ground state. Since the central phenyl–phenyl bond is shorter in the excited state,[6-9] steric destabilization must be greater in the triplet than in the ground state. However, the greater steric effect is apparently offset by the substituent's inductive stabilization.

The broadness and higher energy onsets of the ortho-substituted compounds' phosphorescence both result from the

rather flat excited state surface near $\theta = 0°$. There must be significant population of excited states twisted by as much as $20°$. These emit into the slope of a ground state potential well.

Finally, the well-known large increases in absorption transition energies caused by ortho substituents[7] are due to the large increases in ground state twisting and to the steep slopes of the excited state surfaces at large twist angles. Previous treatments of steric effects on absorption spectra[7] have not explicitly considered large differences in geometry between ground and excited states.

Energy Transfer. We have already shown that triplet energy transfer from benzophenone to biphenyl itself is exothermic by only 1 kcal and therefore is readily reversible.[16] The value of k_t is considerably below the diffusion-controlled limit common to most exothermic electronic energy transfer processes, presumably because biphenyl must change geometry during energy transfer in order for the process to be exothermic.[2] We are not sure why our two current k_t measurements for biphenyl vary by a factor of 2. Fortunately, the discrepancy does not affect our conclusions, which are semiquantitative in nature.

The lower triplet energies of the meta- and para-substituted biphenyls are evident in the larger, though still not diffusion-controlled, k_t values. These substituted biphenyls need not twist as much in order for energy transfer to be exothermic. The geometric changes required during this "nonvertical" energy transfer have been discussed previously from two viewpoints. Twisting may be coupled with excitation transfer,[8] in which case the acceptor starts in its preferred ground state geometry and the process requires some thermal activation in order for the acceptor to change geometry. This process is represented on the right of Figure 4 by the slanted arrows which separate each ground state minimum from the nearest excited state surface 69 kcal (the donor triplet energy) higher in energy. According to this picture, only some $10°$ of twisting is required for p-chlorobiphenyl compared to over $20°$ for biphenyl itself, thus the higher k_t for the former.

An alternative hot-band analogy has been presented[26] in which only vertical energy transfer occurs to rotationally excited ground states. The arrows on the left of Figure 4 represent this process. With biphenyl some 1.5 kcal of rotational energy is required as compared to less than 1.0 kcal for p-chlorobiphenyl. The fourfold difference in k_t values corresponds to an 0.8 kcal energy difference and is certainly consistent with the hot-band explanation.

An ortho chlorine lowers k_t some two orders of magnitude. If the energies in Figure 4 are exact, the o-chlorobiphenyl must twist a full $48°$ for energy transfer to remain thermoneutral. Even twisting to $\theta = 0°$ may leave energy transfer slightly endothermic, in which case part of the decrease in k_t involves a Boltzmann factor. However, inasmuch as twisting occurs during energy transfer, if a $10°$ ground state twist lowers k_t by $\frac{1}{6}$ (from 5×10^9 M^{-1} s^{-1}) and a $20-30°$ twist another $\frac{1}{7}$, the necessity for a full $48°$ twist may well lower k_t the full amount observed.

According to Figure 4, hot-band energy transfer to the o-chlorobiphenyl requires some 3 kcal of rotational energy, 1.5 kcal more than for biphenyl itself. The relative k_t values for the two acceptors indicate that an extra 3.0 kcal is required by the o-chlorobiphenyl. The 1.5 kcal discrepancy probably reflects slight inaccuracies in the figure.

If the hot band and concurrent twist models for nonvertical energy transfer are really distinct, they can be considered to be competitive processes. The hot-band model *must* contribute, since ground states must be in rotational equilibrium. Accordingly, any contribution from an energy transfer mode involving concurrent twisting should appear as a k_t value larger than the one predicted from the left-hand side of Figure 4. We

certainly see no evidence for such extra reactivity, but far more results and better potential energy diagrams are required before the original concept of nonvertical energy transfer[10] need be replaced completely by the hot-band model.

Our studies on the methylbiphenyls were not as thorough as for the chlorobiphenyls. An ortho methyl decreases the rate of energy transfer, but not by as much as an ortho chlorine. Since energy transfer is so close to thermoneutral, slight differences in ground state geometries and in triplet energies can produce large differences in k_t values.

We should point out that the measured rate constant for self-quenching of benzophenone[27] is too small to explain the variations in Figures 1 and 2. The slopes yield values of $k_{-t}\tau_Q$. Since the triplet lifetimes of the biphenyls under our experimental conditions are unknown, we cannot compare various k_{-t} values. In the case of o-chlorobiphenyl, however, there is no evidence for any reverse energy transfer. We presume that the biphenyl undergoes rapid loss of chlorine[20] from its triplet but have not looked for products.

Conclusions. With the help of phosphorescence and triplet EPR spectra it is possible to construct potential energy diagrams which explain the large effects of ortho substituents on rates of energy transfer to biphenyl despite the small effects on triplet energy and geometry. In particular, the effects of single ortho substituents are due to a more twisted ground state, not to a nonplanar triplet as previously assumed. Since energy transfer rates seem to be very sensitive to the degree of twisting required in the acceptor biphenyl, further more extensive studies could add unique information about steric effects in energy transfer, the extent of which is seemingly quite variable,[28] and further refine our understanding of nonvertical energy transfer.

Experimental Section

Materials. Benzene was a commercial thiophene-free product which was further purified by washing with sulfuric acid and distillation from phosphorus pentoxide. Isopropyl alcohol was reagent grade distilled from sodium. Naphthalene, biphenyl, 2-chlorobiphenyl, 4-chlorobiphenyl, and 4-methylbiphenyl were all reagent grade materials recrystallized three times from ethanol, and dried in a vacuum desiccator. 2-Methylbiphenyl (K & K) was purified by preparative gas chromatography. 3-Methylbiphenyl (K & K) was vacuum distilled, passed through alumina, and frozen out of ethanol three times. The three dimethylbiphenyls were provided by Professor Gary Griffin.[29] Benzophenone was Eastman reagent grade recrystallized from petroleum ether–hexane.

Quenching of Photoreduction. Benzene solutions were prepared containing 0.5 M isopropyl alcohol, a given concentration of benzophenone, and various concentrations of naphthalene or a biphenyl. Duplicate 3-ml aliquots of each solution were placed in identical 13 × 100 mm Pyrex tubes which were then degassed to 0.01 Torr in three or four freeze–pump–thaw cycles and sealed. All tubes except two in a given run were irradiated in parallel on a "Merry-go-round" apparatus.[30] A set of Corning No. 7-83 filters isolated the 365-mm region of a Hanovia 450-W medium-pressure mercury arc. After photolysis each tube was broken open and the contents were poured into 1-dram bottles which were kept tightly capped in the dark for 24 h. The absorbance of each sample, including the unirradiated ones, was then measured at 340, 350, 360, and 370 mm on a Gilford Model 200 spectrometer. Percentage conversions were then calculated from the average absorbances of duplicate samples, which generally varied less than 2%. The 0.0075 M ketone samples were analyzed directly in 10-mm cells, 0.02 and 0.035 M samples were diluted one-to-five before analysis in 10-mm cells, and the 0.05 M samples were analyzed directly in 10-mm cells containing matched 9-mm quartz fillers.

Quenching of Benzophenone Phosphorescence. Solutions were prepared in the same way, except most did not contain isopropyl alcohol. The room-temperature phosphorescence of the samples was measured in an Aminco-Bowman spectrophotofluorometer with an IP-21 photomultiplier. The sample compartment was modified to hold the 13-mm diameter tubes so as to produce minimum variations in emission with positioning of the tubes. Excitation was at 375 mm;

emission intensities were measured at 450 and 480 mm with readings being taken directly off the microphotometer. Tubes were then opened and aerated; the residual signal was measured and subtracted from that of the unopened tube. Emission spectra recorded on a Houston X-Y recorder were identical with those reported for benzophenone in other solvents.[31]

EPR spectra of the biphenyls were obtained in both ethanol and methylcyclohexane glasses at 77 °K on a Varian E-4 EPR spectrometer. The light from a 1 kW high-pressure mercury-xenon arc, filtered only through water, was focused directly onto the cavity.

Phosphorescence spectra of the biphenyls were obtained at 77 °K on the Aminco with the phosphoroscope attachment. Excitation was at 254 mm. Biphenyl concentrations were approximately 10^{-2} M. Absorption spectra were obtained on a Cary 14.

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Selectivity and Reactivity of Hot Homolytic Aromatic Substitution by Recoil Chlorine Atoms

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Abstract: Hot homolytic aromatic chlorination has been studied in simple monosubstituted benzenes C_6H_5X (X = F, Cl, Br, I, NH_2, OCH_3, NO_2) using recoil chlorine atoms produced via the $^{37}Cl(n,\gamma)^{38}Cl$ reaction. In the gas phase, Cl-for-H substitution is a minor process, proceeding exclusively via hot direct replacement with little selectivity. In the liquid phase, dilution experiments reveal that two processes contribute to hydrogen substitution: a one-step reaction being first order with respect to the concentration of the aromatic substrate and a multistep process involving at least two substrate molecules. In either case the Cl atoms exhibit slight electrophilic features. Application of the Hammett correlation reveals a higher selectivity ($\rho^+ = -1.43$) for the multistep than for the one step process ($\rho^+ = -0.56$). Both chlorination reactions seem to proceed via complex formation. In the case of Cl-for-X substitution, thermoneutral or exothermic processes (X = Cl, Br, I, NO_2) can be attributed to thermal σ-complex formation, while endothermic processes (X = F, OCH_3, NH_2) are typically low yield, direct hot replacement reactions being first order with respect to the substrate concentration.

Introduction

In contrast to photolytically or radiolytically produced thermal halogen atoms, hot recoil halogen generated via nuclear reactions can undergo one-step substitution. The reactions of hot tritium and halogen recoil atoms with simple aliphatic and aromatic compounds have been studied extensively in recent years (for review cf. ref 1 and 2). Even though the major process is hydrogen abstraction, substitution of hydrogen and halogen atoms is also observed. The radiochemical yields of such substitution processes are often small but the nuclear

recoil technique so far provides the only possibility to study endothermic one-step substitution of halogen atoms. We were interested in hot homolytic aromatic substitution. Although a number of studies have been carried out in aromatic systems both with recoil tritium and recoil chlorine (for a recent review, cf. ref 2), the mechanistic question of how aromatic substitution by recoil atoms proceeds remains unanswered. Of particular interest is the question of selectivity and reactivity. Early work on aromatic recoil tritiation by Ache et al.[3] and on aromatic recoil bromination by willard and collaborators[4] revealed a rather unselective behavior. Among the recoil