*J. Org. Chem.* **1996,** *61,* 3145−3150

# Equilibrium Ion Pair Acidities of Polyhalogenated Benzenes in THF. Extrapolation to Benzene[1]

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*Received September 7, 1995*⊗

The equilibrium cesium ion pair acidities of six polyfluorobenzenes at 25 °C and six polychlorobenzenes at −20 °C were determined in THF. For fluorinated benzenes the additive (negative) effects of fluorine on p*K* (partial equilibrium factors) are o = 5.2, m = 3.0, and p = 1.4. From these the cesium ion pair p*K* (per H) of benzene is extrapolated to be 44.8 at 25 °C. For chlorobenzenes the additive contributions for *o*-, *m*-, and *p*-chlorine are 4.2, 2.7, and 2.1, respectively. The corresponding p*K* of benzene is 47.0 at −20 °C. Aggregation studies show that in the concentration range $10^{-3}$–$10^{-4}$ M the cesium salt of 1,2,4,5-tetrachlorobenzene and the cesium and lithium salts of 1,2,4,5-tetrafluorobenzene are monomeric. The p*K* of benzene on the Li scale is extrapolated to be 39.5.

## Introduction

Fluorobenzene has long been known to be metalated by alkyllithiums at the ortho position.[2] Chlorobenzene itself can be metalated in THF at low temperature (−105 °C) and used synthetically.[3] Kinetic studies of fluorobenzene with potassium amide in liquid ammonia led to approximate rates relative to benzene of ortho, $10^6$, meta, $10^3$, and para, $10^2$.[4,5] Polyfluorinated benzenes were shown to undergo facile tritium exchange with methanolic sodium methoxide.[6] The results could be expressed as a contribution per fluorine to the logarithm of the relative rates (partial rate factors) as $f_o = 5.3$, $f_m = 2.1$, and $f_p = 1.1$. These reactivities agree rather well with the relative tritium exchange rates of the different hydrogens in fluorobenzene, relative to benzene, toward lithium cyclohexylamide (LiCHA) in cyclohexylamine (CHA); log $k_{rel}$ = o, 5.5; m, 1.9; p, 1.0.[7] Preliminary equilibrium ion pair acidities of polyfluorobenzenes with cesium cyclohexylamide gave comparable results for effects of individual fluorines.[8] The strong ortho-directing effect of fluorine has also recently attracted the attention of theoreticians.[9]

(Pentafluorophenyl)lithium[10] and (pentachlorophenyl)lithium[11] have been prepared as reasonably stable reagents at low temperature. Other polyhalophenyl metal derivatives have also been used extensively in organic synthesis.[12] Our earlier equilibrium studies in cyclohexylamine were of limited scope and are best considered to be preliminary. Our recent development of ion pair acidity scales in THF, a much more common solvent for synthesis use, prompted a reexamination and extension of the earlier work on the halobenzenes with our newer and better techniques. In the present study we report the equilibrium ion pair acidities of a number of polyfluoro- and polychlorobenzenes with cesium as the gegenion and more limited studies of the corresponding lithium compounds. The results permit conclusions regarding the aggregation states of these compounds, a type of study not done in the earlier work.

## Results and Discussion

Ion pair acidities are defined in terms of the proton transfer equilibrium of eq 1, which is used to determine the corresponding ion pair p*K* values. In eq 1 IndH is

$$\mathrm{ArH} + \mathrm{M^+Ind^-} \rightleftarrows \mathrm{Ar^-M^+} + \mathrm{IndH} \qquad (1)$$

$$\mathrm{p}K_{\mathrm{RH}} = \mathrm{p}K_{\mathrm{IndH}} + \Delta \mathrm{p}K \qquad (2)$$

an indicator on the previously established cesium[13] or lithium[14] scale, depending on $M^+$.[15] The p*K* of the indicators are referenced to p*K* = 22.90 of fluorene at 25 °C. The indicator salts have visible spectra, but the aryl anions do not; thus, measurements were done by the "single indicator technique", in which a known amount of substrate is added to a mixture of indicator and its salt and the resulting decrease in absorbance is associated with conversion of indicator salt to the invisible aryl salt. This technique makes high demands on purity of solvents and reagents but has been shown to give reproducible results of high precision in our laboratory.[16] With the halogenated benzenes, however, the equilibrating solutions were generally unstable. After the initial

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⊗ Abstract published in *Advance ACS Abstracts,* April 15, 1996.

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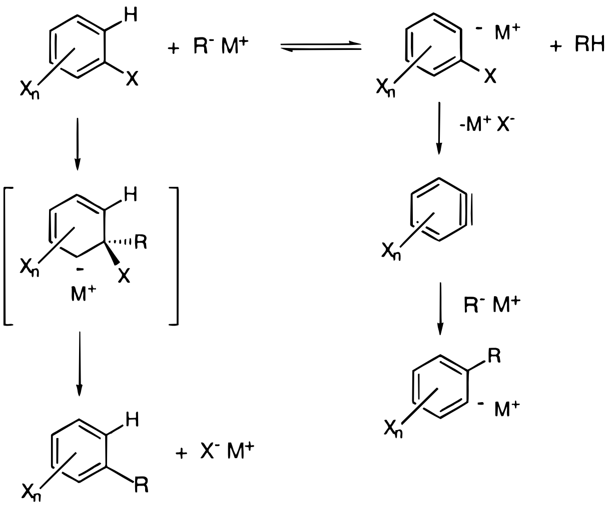
**Scheme 1**

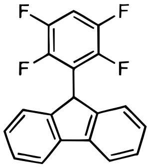


decrease in absorbance on adding the substrate, the absorbance decreased more or less rapidly, indicative of further reactions.

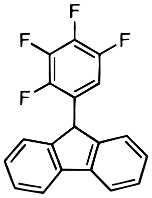
One possible such reaction is elimination of the ortho halogen to give a benzyne which then reacts further. (*o*-Fluorophenyl)lithium and -sodium are known to be highly unstable in THF at temperatures above −50 °C.[17] This reaction appears to be slower with the polyfluorobenzenes. For example, on adding 1,2,4,5-tetrafluorobenzene to its cesium indicator salt, the absorbance fell rapidly to its equilibrium value and then decayed slowly, over a period of hours, apparently by benzyne formation (Scheme 1).

Nucleophilic aromatic substitution is also facile for polyhalobenzenes, particularly for leaving fluoride and with fluorines in the ortho and meta positions.[18] This reaction possibility is also shown in Scheme 1.

For pentafluorobenzene, after the initial mixing the absorption by the indicator anion vanished in a few seconds and new peaks formed immediately, making the single indicator measurements impossible. In a preparative scale reaction, pentafluorobenzene was added to a solution of fluorenylithium in THF. The yellow color changed immediately to red. After the mixture was quenched with benzoic acid, a mixture of isomeric products with the structure $C_{19}H_{10}F_4$ was isolated and assigned by GC-MS, $^1H$ and $^{19}F$ NMR, and comparison with authentic materials prepared independently to be a 85:15 mixture of the isomers 9-(2,3,5,6-tetrafluorophenyl)-, **1**, and 9-(2,3,4,5-tetrafluorophenyl)fluorene, **2**. Product



**1**



**2**

**1** undoubtedly arises from the nucleophilic addition of fluorenyllithium to the 3-position of pentafluorobenzene; this position specificity (para to H, ortho and meta to the Fs) is common in such reactions.[18] Product **2** probably arises from addition of fluorenyllithium to the tetrafluorobenzyne formed by ortho LiF elimination from (pentafluorophenyl)lithium. As a further test the reaction of fluorenyllithium with hexafluorobenzene was checked in THF at room temperature and found to occur rapidly to generate 9-(pentafluorophenyl)fluorene. The nucleophilic reactions of indicators make the measurements of 1,2,3,4- and 1,2,3,5-tetrafluorobenzenes less reliable because in these substrates there is one fluorine atom surrounded by two other fluorines, making such positions especially susceptible to nucleophilic attack. Such reaction is still more facile with pentafluorobenzene because the 3-position now also bears two meta fluorines.

**Table 1. Transmetalation Equilibria of Fluorinated Benzenes**[a]

| ArH | InH[b] | Δp*K*[c] |
|---|---|---|
| 1,2,4,5-tetrafluoro | BDDA | 0.76 ± 0.04 |
| 1,2,4,5-tetrafluoro | DP3 | 0.56 ± 0.06 |
| 1,2,3,5-tetrafluoro | BDPM | −0.04 ± 0.15 |
| 1,2,3,5-tetrafluoro | BDDA | 1.96 ± 0.07 |
| 1,2,3,4-tetrafluoro | TPM | 0.90 ± 0.16 |
| 1,2,4-trifluoro | TPM | 0.39 ± 0.04 |
| 1,2,4-trifluoro | p-BB | −0.13 ± 0.05 |
| 1,3,5-trifluoro | TpTM | 0.03 ± 0.04 |
| 1,3,5-trifluoro | DPM | −0.20 ± 0.03 |
| 1,3-difluoro | DoTM | 0.16 ± 0.11 |
| 1,3-difluoro | DPM | 0.83 ± 0.16 |

[a] p*K* measurements corrected to a per H basis. [b] Abbreviations and p*K* values for InH:[13,29] BDDA, 9-biphenylyl-10,10-dimethyldihydroanthracene, 27.78; DP3, 1,3-diphenylpropene, 27.85; BDPM, biphenylyldiphenylmethane, 30.07; TPM, triphenylmethane, 31.26; p-BB, *p*-benzylbiphenyl, 31.70; TpTM, tri-*p*-tolylmethane, 33.10; DoTM, di-*o*-tolylmethane, 34.22; DPM, diphenylmethane, 33.25. [c] $\Delta pK = pK_{ArH} - pK_{InH}$.

**Fluorinated Benzenes.** With the exception of pentafluorobenzene, it was possible to measure the p*K*s of a series of fluorinated benzenes at 25 °C with the single indicator technique using cesium as the counterion. The polyfluorinated benzenes used were 1,2,4,5-, 1,2,3,5-, and 1,2,3,4-tetrafluoro, 1,2,4- and 1,3,5-trifluoro, and 1,3-difluoro. The results for the transmetalation equilibria are summarized in Table 1, and the derived p*K* values are summarized in Table 2. The p*K* of pentafluorobenzene was extrapolated according to “partial p*K* factors” derived assuming that the effects of the individual fluorines are additive. This assumption gives rise to the following six equations in four unknowns:

$$pK(1245\text{-}F_4) = pK_o - 2o - 2m$$

$$pK(1234\text{-}F_4) = pK_o - o - 2m - p$$

$$pK(1235\text{-}F_4) = pK_o - 2o - m - p$$

$$pK(124\text{-}F_3) = pK_o - 2o - m$$

$$pK(135\text{-}F_3) = pK_o - 2o - p$$

$$pK(13\text{-}F_2) = pK_o - 2o$$

Table 2 also shows how well the best fit values,[19] $o = 5.2 \pm 0.3$, $m = 3.0 \pm 0.1$, $p = 1.4 \pm 0.2$, and $pK_o = 44.8 \pm 0.6$, reproduce the experimental results. The uncer-

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**Table 2. Summary of p*K*s of Fluorinated Benzenes in THF at 25 °C**

| fluorinated benzene | p*K*(expt) | p*K*(calcd)[a] |
|---|---|---|
| pentafluoro | | 27.0 |
| 1,2,4,5-tetrafluoro | 28.4 ± 0.1 | 28.4 |
| 1,2,3,5-tetrafluoro | 29.9 ± 0.1 | 30.0 |
| 1,2,3,4-tetrafluoro | 32.2 ± 0.2 | 32.2 |
| 1,2,4-trifluoro | 31.6 ± 0.1 | 31.4 |
| 1,3,5-trifluoro | 33.1 ± 0.1 | 33.0 |
| 1,3-difluoro | 34.3 ± 0.2 | 34.4 |

[a] Assuming an additive effect of each fluorine using the values $o = 5.2$, $m = 3.0$, $p = 1.4$, and $pK_o = 44.8$.

**Table 3. Comparison of Partial Fluorine Factors**

| position | log $k_T$ NaOMe/MeOH[a] | log $k_T$ LiCHA/CHA[b] | p*K* CsCHA/CHA[c] | p*K* THF/Cs[d] |
|---|---|---|---|---|
| o | 5.25 ± 0.32 | 4.5 | 5.7 | 5.2 ± 0.3 |
| m | 2.07 ± 0.16 | 1.9 | 2.3 | 3.0 ± 0.1 |
| p | 1.13 ± 0.26 | 1.0 | 1.1 | 1.4 ± 0.2 |

[a] Reference 6. [b] Reference 7. Deuterium rates gave 5.8, 2.0, and 1.1, respectively. [c] Reference 8. [d] This work.

tainties are given as the standard deviations. The errors for $pK_o$ and for the parameter *o* are relatively high because of the important role of a single compound, 1,2,3,4-tetrafluorobenzene, in distinguishing between these parameters. Nevertheless, the position parameters fall off in an expected inductive manner, and, indeed, the values agree remarkably well with those derived from other kinetic and equilibrium measurements as compared in Table 3.

The parameter $pK_o$ in this analysis refers to the cesium ion pair p*K* of benzene. The derived value of 44.8 (per hydrogen; the molecular p*K* is therefore 44.0) is not unreasonable and is probably the most accurate value for benzene currently available. From the general correspondence of the cesium ion pair values with ionic p*K* values in DMSO even for localized carbanions, the DMSO p*K* of benzene is probably not much different.[20] The aqueous p*K* may be somewhat lower because of the additional stabilizing effect of hydrogen bonding.

Some measurements were possible on the Li scale in THF.[21] The p*K* of pentafluorobenzene could not be determined accurately; it could only be estimated as 21–23. More accurate measurements were possible for 1,2,4,5-tetrafluorobenzene using benzo[*b*]fluorene and dibenzo[*bh*]fluorene as indicators. These transmetalation reactions are relatively fast (5–10 min), and the subsequent decrease in the absorbance of the indicator anion shows a first-order decay (the fluoroarene is in a large excess over the indicator anion). This result indicates that decomposition through the benzyne mechanism is much slower than transmetalation. After several hours, new absorption peaks appear probably because of the formation of benzynes and reaction with the indicator anion, but these changes are slow and do not interfere with the p*K* measurements The p*K* of 1,2,4,5-tetrafluorobenzene was found to be 23.15 ± 0.02 against benzo[*b*]fluorene and 23.08 ± 0.02 against dibenzo[*bh*]fluorene. The average value, 23.1, is 5.3 p*K* units lower than that of the corresponding cesium salt undoubtedly because the aryllithiums are contact ion pairs (CIP) determined relative to solvent separated ion pair (SSIP) indicators. This type of result appears to be common for localized anions.[22] No other Li p*K*s of fluorinated benzenes could be determined since they have higher p*K*s and the Li scale is limited; for less acidic indicators, the lithium equilibria are established too slowly. Assuming that the partial equilibrium factors found in the cesium scale can be applied to the aryllithiums, the calculated p*K* of pentafluorobenzene is 21.5 and that for benzene is p*K* = 39.5, a per-hydrogen value corresponding to monomeric phenyllithium. Since it is known that in THF phenylithium exists as a dimer,[23] the experimental lithium p*K* of benzene is expected to be still lower.

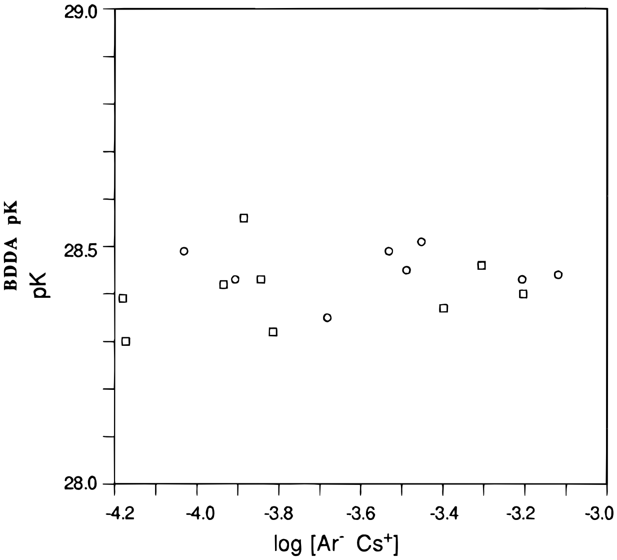

**Figure 1.** Observed p*K* of 1,2,4,5-tetrafluorophenylcesium as a function of concentration with two indicators: (○) BDDA; (□) DP3.

For most of the cesium results, the side reactions were relatively slow and the resulting p*K* values are considered to be reasonably reliable even though the single indicator technique was used. For example, in the measurement of 1,2,4,5-tetrafluorobenzene against 9-biphenylyl-10,10-dimethyldihydroanthracene (BDDA), equilibrium was established rapidly after the initial mixing of indicator and substrate solutions; that is, the absorbance of the indicator fell sharply to reach the equilibrium point. Thereafter, the absorbance of the indicator decayed slowly over a period of several hours, probably because of the formation of benzynes. This relative stability permitted further studies of the state of aggregation of this carbanion salt. Equilibrium p*K* measurements of both the Cs and Li salts could be made over the concentration range $10^{-3}$–$10^{-4}$ M. The results, summarized in Figures 1 and 2, show no change in $\Delta pK$ with concentration and that, therefore, both the Li and Cs salts exist as monomers in THF at these concentrations. It seems likely by analogy that the other fluoroaryl systems studied are likewise monomeric in our measurements. Figures 1 and 2 also demonstrate that the assigned uncertainties in the p*K* values of ±0.1 are not unreasonable for the relatively stable salts.

**Chlorinated Benzenes.** We also studied six polychlorobenzenes, pentachlorobenzene, 1,2,4,5-, 1,2,3,4-, and 1,2,3,5-tetrachloro- and 1,3,5- and 1,2,4-trichlorobenzenes. In these measurements it was assumed that the

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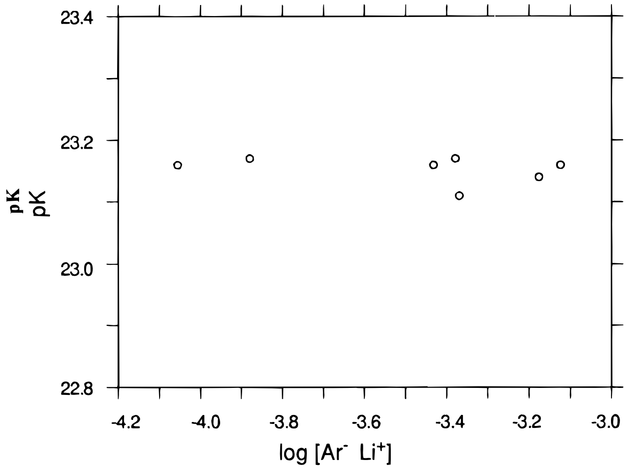

**Figure 2.** Observed p*K* of (1,2,4,5-tetrafluorophenyl)lithium as a function of concentration.

transmetalation equilibria are nearly instantaneous, but it was found at room temperature that (polychlorophenyl)cesium salts decompose relatively rapidly. Measurements were therefore done at −20 °C where decomposition is much slower. The reliability of the measurements depends on the substrate. For example, 1,2,4,5-tetrachlorobenzene and 1,2,4- and 1,3,5-trichlorobenzenes gave reliable measurements. After their equilibration with a given indicator, the absorbance of indicator decayed only slowly with time.

As in the fluorine case, measurements with pentachlorobenzene were difficult. After the initial mixing the indicator absorbance fell off rapidly and the decay did not follow pseudo-first-order kinetics as one would expect for a benzyne mechanism with the neutral indicator in large excess. Thus, for this case the extrapolation back to zero time to determine the concentration of indicator anion at equilibrium is only approximate. The indicator anion probably reacts with neutral pentachlorobenzene displacing the *p*-Cl as in the corresponding case of pentafluorobenzene discussed above. It was found that (triphenylmethyl)cesium reacts rapidly with hexachlorobenzene, but the product of the reaction was not isolated and characterized. The same observation holds for the isomeric 1,2,3,5- and 1,2,3,4-tetrachlorobenzenes. The transmetalation equilibria of the chlorinated benzenes and their p*K* values are summarized in Tables 4 and 5. The p*K* values of the indicators at 25 °C were extrapolated to −20 °C using previously determined Δ*H*° values,[24] again using fluorene as a standard with an assigned p*K* of 22.90. The Li p*K*s are expected to be about 5 p*K* units lower than the Cs p*K*s, as in the fluorine cases; however, this could not be tested directly.

The aggregation properties of (1,2,4,5-tetrachlorophenyl)cesium were studied by measuring the concentration dependence of its p*K* against (triphenylmethyl)cesium. The results summarized in Figure 3 show that the $pK_{Cs/THF}$ value of 1,2,4,5-tetrachlorobenzene at −20 °C essentially does not change within a $(0.9-7.0) \times 10^{-4}$ M concentration range. Thus, all of the (halophenyl)cesium salts measured in this study are monomeric in the concentration region $10^{-3}-10^{-4}$ M.

**Table 4. Transmetalation Equilibria of Chlorinated Benzenes**[a]

| ArH | InH[b] | Δp*K*[c] |
|---|---|---|
| pentachloro | 9-PX | 0.3 ± 0.2 |
| pentachloro | BDPM | 0.1 ± 0.1 |
| 1,2,4,5-tetrachloro | BDPM | 1.1 ± 0.1 |
| 1,2,4,5-tetrachloro | TPM | 0.0 ± 0.1 |
| 1,2,3,5-tetrachloro | TPM | 0.9 ± 0.1 |
| 1,2,3,4-tetrachloro | TpTM | 0.9 ± 0.2 |
| 1,2,3,4-tetrachloro | TPM | 1.1 ± 0.2 |
| 1,2,4-trichloro | TpTM | 1.1 ± 0.1 |
| 1,2,4-trichloro | DoTM | 0.0 ± 0.1 |
| 1,3,5-trichloro | TpTM | 1.4 ± 0.1 |
| 1,3,5-trichloro | DoTM | 0.1 ± 0.1 |

[a] p*K* measurements corrected to a per hydrogen basis. [b] Abbreviations and p*K* values at −20 °C for InH: 9-PX, 9-phenylxanthene, 30.39; BDPM, biphenylyldiphenylmethane, 31.66; TPM, triphenylmethane, 32.91; TpTM, tri-*p*-tolylmethane, 35.01; DoTM, di-*o*-tolylmethane, 36.22. These p*K* values were obtained using the p*K*s at 25 °C in ref 13 with the ΔH° values in ref 25 and are referenced to the p*K* of fluorene at −20 °C = 22.90 (per hydrogen). [c] $\Delta pK = pK_{ArH} - pK_{InH}$.

**Table 5. p*K* of Polychlorinated Benzenes in THF at −20 °C**

| polyhalobenzene | p*K*(expt) | p*K*(calcd)[a] |
|---|---|---|
| pentachlorobenzene | 31.1 ± 0.5 | 31.0 |
| 1,2,4,5-tetrachlorobenzene | 32.9 ± 0.1 | 33.1 |
| 1,2,3,5-tetrachlorobenzene | 33.8 ± 0.2 | 33.7 |
| 1,2,3,4-tetrachlorobenzene | 35.2 ± 0.7 | 35.2 |
| 1,2,4-trichlorobenzene | 36.1 ± 0.1 | 35.9 |
| 1,3,5-trichlorobenzene | 36.3 ± 0.1 | 36.5 |

[a] Calculated from $pK_o = 47.0$, $o = 4.2$, $m = 2.7$, $p = 2.1$.

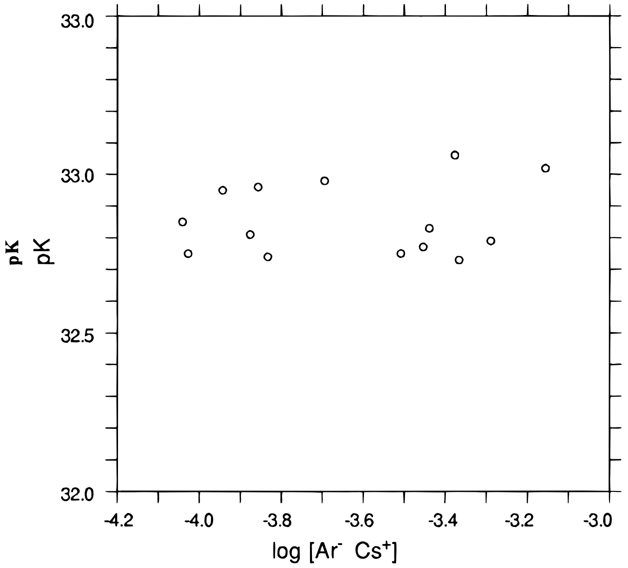

**Figure 3.** Observed p*K* of (1,2,4,5-tetrachlorophenyl)cesium as a function of concentration.

The p*K* values of the chlorinated benzenes are not generally as precise as the fluorinated benzenes, and the dissection into partial equilibrium factors gives parameters that have larger probable errors. Nevertheless, the derived least-squares values, $pK_o = 47.0 \pm 0.9$, $o = 4.2 \pm 0.4$, $m = 2.7 \pm 0.2$, and $p = 2.1 \pm 0.3$, give rise to p*K* values in excellent agreement with experiment as summarized in in Table 5. The $pK_o$ corresponds to the cesium ion pair p*K* of benzene at −20 °C relative to the p*K* of fluorene = 22.90. The fact that we were able to measure the p*K* of pentachlorobenzene and not of pentafluorobenzene is in accord with previous observations that (pentafluorophenyl)lithium is less stable than (pentachlorophenyl)lithium.[25]

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**"Halogen Dance" Reactions.** The concepts of equilibrium acidity and kinetic acidity have been applied extensively in rationalizing the mechanisms of organic reactions. As an example, the present equilibrium acidity data for polychlorobenzenes are applied to the mechanism of the "halogen dance" reaction. In the 1970s, there were extensive studies on such reactions by Bunnett and other investigators.[26] The base-catalyzed halogen dance comprises a set of isomerization, disproportionation, and degenerate rearrangement reactions that occur when certain oligohalobenzenes are exposed to appropriate bases in given solvents.[27,28] Mach and Bunnett[28] did a detailed study of the chlorine dance on chlorinated benzenes and derived a mechanism involving initial proton transfer to form an aryl anion which displaces on chlorine to form a new aryl anion followed by protonation. The present results permit a more quantitative rationalization of their results.

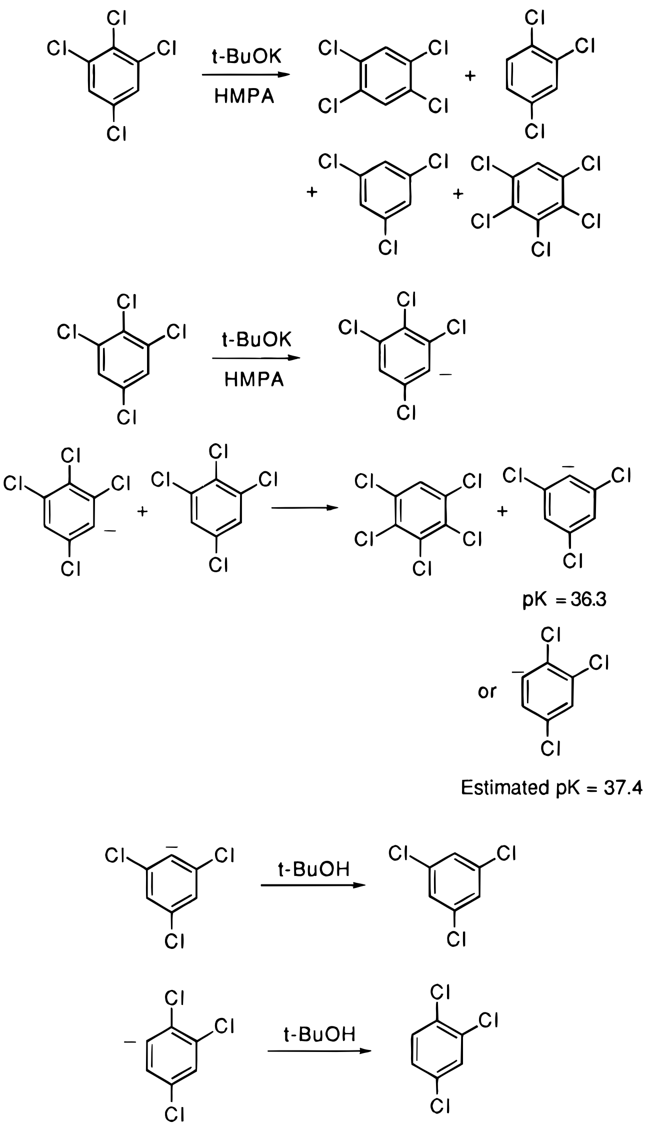
For example, treatment of 1,2,3,5-tetrachlorobenzene with potassium *tert*-butoxide in hexamethylphosphoric triamide (HMPA) gives rapid disproportionation to penta- and trichlorobenzenes as well as interconversion to 1,2,4,5-tetrachlorobenzene. More 1,3,5-trichlorobenzene is produced than its 1,2,4-isomer, and 1,2,3-trichlorobenzene is not formed. These results are summarized in Scheme 2.

In order for the disproportionation to succeed, the initial aromatic must be sufficiently acidic to be deprotonated. If the aryl anion produced by chlorine exchange is too basic, the chlorine transfer does not occur. Our results now permit a more quantitative discussion. A p*K* of less than about 34 on the present THF scale appears to be the limit for initiation of the reaction. Pentachlorobenzene with a p*K* of 31.0 disproportionates rapidly to hexachlorobenzene and two of the tetrachlorobenzenes. 1,2,3,4-Tetrachlorobenzene with a p*K* of 35 does not undergo the chlorine dance, nor do the trichlorobenzenes with their higher p*K*s. As shown in Scheme 2, the use of partial equilibrium factors shows that transfer of the 2-chlorine from 1,2,3,5-tetrachlorobenzene results in a more stable aryl anion than transfer of the 1-chlorine; hence, more 1,3,5-trichlorobenzene is formed than 1,2,4-isomer. Transfer of the 5-chlorine would produce an aryl anion corresponding to a p*K* of 39.5, a value so high that virtually no 1,2,3-trichlorobenzene is produced. Similarly, 1,2,3,5-tetrachlorobenzene and its 1,2,4,5-isomer have comparable acidities and both are formed in disproportionation of pentachlorobenzene. 1,2,3,4-Tetrachlorobenzene is much less acidic, and none was detected.

## Conclusion

We reported here cesium and lithium ion pair equilibrium acidities of several polychlorinated and polyfluorinated benzenes in THF. These measurements permit the derivation of the additive contributions of ortho, meta, and para halides to the stability of the aryl carbanions. These contributions are in accord with a stabilization of carbanions by a through-space inductive effect. This approach allows the extrapolation to the p*K* of benzene, 44.8 at 25 °C and 47.0 at −20 °C on the cesium ion pair scale in THF. More limited measurements on lithium salts give a p*K* of benzene of 39.5 on the lithium scale. Several (polyhalophenyl)cesium and -lithium salts were established to be monomeric in dilute solution ($10^{-3}$−$10^{-4}$ M). Finally, the high *equilibrium* acidity effect of ortho halogens points out that prior coordination of lithium bases to halogen is not required to induce metalation at the ortho position.[9a] The present results agree remarkably well with the preliminary results communicated earlier for cyclohexylamine solutions.[8]

**Scheme 2**



## Experimental Section

The hydrocarbon indicators used in this study were available from previous studies.[13,29] They were purified by sublimation or distillation prior to use. Proton NMR spectra were determined on FT 400 and 500 MHz instruments of the UC Berkeley NMR Facility. Chemical shifts are reported in ppm relative to tetramethylsilane. Tetrahydrofuran was purified by distillation over $LiAlH_4$ and then stirred over Na−K alloy until the characteristic blue color appeared. Finally, it was stored in a quartz flask over freshly activated 3A molecular sieves for a prolonged period to reduce the water content to less than $10^{-5}$ M.[20] Reducing the water content in THF to this

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level is crucial for the success of the single indicator measurements. All of the polychlorobenzenes in this work were commercial products from Aldrich. They were purified by sublimation or, for 1,2,4-trichlorobenzene, by vacuum distillation over $CaH_2$. Fluorobenzenes were purchased from Aldrich or Pierce Chemical Co. and were distilled from $CaH_2$ or purified by preparative gas chromatography.

**9-(2,3,5,6-Tetrafluorophenyl)fluorene (1).** To a solution of 3.0 g (20 mmol) of 1,2,4,5-tetrafluorobenzene in 50 mL of THF at −78 °C was added 7.6 mL of a 2.1 M hexane solution of *n*-butyllithium (16 mmol). To the resulting suspension of a white precipitate was added a solution of 2.52 g (14 mmol) of fluorenone dropwise. The solution was allowed to warm with stirring, and the reaction was quenched. The resulting carbinol is a glassy white solid (2.80 g, 61% yield): $^1H$ NMR 7.66 (d, 2H), 7.46 (d, 2H), 7.39 (dd, 2H), 7.27 (dd, 2H), 6.97 (m, 1H), 3.47 (s, 1H); $^{19}F$ NMR showed a broad peak at −138.5 ppm relative to $CFCl_3$.

A mixture of 2.7 g (8.2 mmol) of the carbinol, 10 mL of hydriodic acid (57% in water), and 50 mL of glacial acetic acid was maintained at 80 °C for 1 h. The dark black mixture was poured into cold water and extracted with ether. The ether solution was washed with aqueous sodium sulfite until the iodine color disappeared and then with saturated $NaHCO_3$. Removal of the ether and recrystallization from methanol/toluene gave white crystals: mp 152−3 °C; $^1H$ NMR 5.50 (s, 1H), 6.98 (tt, 1H), 7.29 (m, 4H), 7.44 (m, 2H), 7.83 (d, 2H, $J$ = 8.2 Hz); $^{19}F$ NMR (proton decoupled) four broad singlets at −139.40, −139.63, −140.70, −145.76 ppm relative to $CFCl_3$; UV (THF) $\lambda_{max}$ nm ($\epsilon$) 301 (5600), 290 (4700), 266 (20 000); HMRS calcd 314.0719, found 314.0720.

**9-(2,3,4,5-Tetrafluorophenyl)fluorene (2).** The same procedure was applied to 1,2,3,4-tetrafluorobenzene, and the resulting fluorenol was reduced with HI as above to give the product as white crystals from methanol: mp 95−6 °C; $^1H$ NMR 5.42 (m, 1H), 6.23 (m, 1H), 7.49 (m, 4H), 7.62 (m, 2H), 7.83 (d, 2H); $^{19}F$ NMR (proton decoupled) −139.24 (m), −144.24 (br s), −155.78 (m), −157.94 (m); HMRS calcd 314.0719, found 314.0721.

**Acidity Measurements.** In each measurement a cell with a known amount of indicator $In^-Cs^+$ and InH in THF was cooled to −20 °C in a cell holder; then a known amount of RH was added. After brief shaking, the cell was put back into the −20 °C cell holder and the absorbance of the indicator anion was recorded. The drop in the absorbance of indicator corresponds to the concentration of arene carbanion at equilibrium. The runs at 25 °C were carried out similiarly.

**Acknowledgment.** This work was supported in part by grants from the National Institutes of Health and from the National Science Foundation.

JO9516401