An *ab Initio* Study of Some Phenyl- and (Halophenyl)alkali Compounds

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Ab initio calculations are presented for alkali metal derivatives of fluoro- and chlorobenzenes for comparison with previously determined experimental substitutent effects. Calculated substituent effects for one alkali metal are linearly related to those of another. (Difluorophenyl)lithiums show additivity of substituent effects calculated from (monofluorophenyl)lithiums but dichloro derivatives do not, an effect attributed to the higher polarizability of chlorine. *meta*- and *para*-fluoro substituents show excellent agreement with experiment. *ortho*-fluoro and chlorine substituents do not. These differences are rationalized.

In the accompanying paper[1] we presented relative ion pair acidity equilibria for several fluorinated and chlorinated benzenes. The results were interpreted in terms of additive contributions from individual halogens and led to the corresponding ion pair p*K* of benzene itself. Ion pair equibria are expected to be less sensitive to solvent than equilibria involving free ions and may therefore be more readily modeled by computations of gas phase reactions. In this paper we present such computations for phenyl, fluorophenyl, and chlorophenyl derivatives of the alkali metals and compare the results to the experimental solution equilibria.

Computational Details

All computations made use of the GAUSSIAN92[2] or GAMESS[3] with the 6-31+G* basis set.[4−8] This standard basis was used as well for lithium and sodium. For potassium the diffuse function and polarization exponents were set to 0.078 and 0.1, respectively. For the heavier alkali metals, K, Rb, and Cs, the effective core potentials (ECP) of Hay and Wadt,[9] (341/311/1) for K and (341/321/1) for Rb and Cs, were augmented with a set of six d orbitals ($d = 1.0$). For cesium the ECP of Ross, Powers, Atashroo, Ermler, LaJohn and Christiansen,[10] hereafter referred to as Ross, was also used. Stationary points were characterized by frequency analysis; the minima have zero imaginary frequencies. C_s symmetry was assumed with the symmetry plane that of the benzene ring. Energies are summarized in Table 1.

Results and Discussion

The calculations included the anions derived by deprotonation of the benzenoid compounds. The calculated gas phase acidity of benzene, 414.5 kcal mol^{-1}, agrees only qualitatively with the experimental value of 401.7 kcal mol^{-1},[11] in part because of the effect of temperature. Saunders reports a deprotonation energy of benzene at the 6-31+G* level of 406.9 kcal mol^{-1} when corrected to 298 K and with inclusion of zero-point energy (ZPE) differences.[12] He also found differences from experiment of about 8 kcal mol^{-1} for a number of acids at this computational level. Relative values are generally in much better agreement. Gas phase deprotonation energies have recently been reported for chlorobenzene.[13] Values relative to benzene are ortho, −13.5, meta, −11.5, and para, −12.0 kcal mol^{-1}, all ±2. The higher acidity of para relative to meta is unexpected but could result from experimental error. The calculated values are of the same magnitude, −13.5, −9.8, and −8.4 kcal mol^{-1}, respectively. The para position is calculated to be less acidic than the meta, but the differences are within the reported experimental errors. An experimental value has been reported for a gas phase acidity of fluorobenzene, 387.2 kcal mol^{-1},[14] 13.5 kcal mol^{-1} lower than that of benzene by the same method (high-temperature mass spectrometry) at the same temperature.[15] It seems clear that this value must pertain to the ortho position. For comparison, Wenthold and Squires[13] report that fluorobenzene is slightly more acidic than chlorobenzene. Our calculation gives the result that the ortho position of fluorobenzene is less acidic than that of chlorobenzene, −12.1 vs −13.5 kcal mol^{-1} compared to benzene. The calculations may be affected by a basis set superposition effect (BSSE) in which the carbanion lone pair derives some additional stabilization by the many basis functions on the ortho chlorine compared to the smaller fluorine; the basis sets used are still relatively small but were necessitated by the rather large compounds studied. Such an effect should be much lower for meta and para and for the ion pair systems.

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Table 1. Energies, -E, in a.u. for Various Species at 6-31+g*; K(ψ), Rb and Cs were Treated by the Pseudopotential Approximation

M	M^+	$C_6H_5M^a$	o-FC_6H_4M	m-FC_6H_4M	p-FC_6H_4M	2,6-$F_2C_6H_3M$
H		230.71109	329.56660			428.42115
anion		230.05058	328.92519	328.91797	328.91376	427.79926
Li	7.23555	237.54208	336.41187	336.40193	336.40012	435.28065
Na	161.65929	391.92735	490.79872	490.78795	490.78563	589.66895
K	598.99613	829.22363	928.09739	928.08552	928.08253	
K(y)	27.70571	257.93279		356.7947	356.79171	455.67913
Rb	23.44376	253.65969	352.53393	352.52188	352.51873	451.40672
Cs(HW)[a]	19.47931	249.68408	348.55878	348.54663	348.5433	447.43203
Cs(R)[b]	19.73221	249.94814	348.82178	348.81006	348.80701	

M	o-ClC_6H_4M	m-ClC_6H_4M	p-ClC_6H_4M
H	689.61016		
anion	688.97116	688.96534	688.96298
Li	696.45569	696.44630	696.44503
Cs(HW)[a]	708.60375	708.59172	708.58956
Cs(R)[b]	708.86732	708.85495	708.85295

	Dihalophenylmetals, $X_2C_6H_3M$					
M, X	2,5	2,3	3,4	2,6	2,4	3,5
H, F	428.41964	428.41456	428.41456	428.42115	428.42115	428.42115
H, Cl	1148.5077	1148.5030	1148.5030	1148.5075	1148.5075	1148.5075
Li, F	435.26920	435.26439	435.25218	435.28065	435.26888	435.26081
Li, Cl	1155.3576	1155.3509	1155.3422	1155.3659	1155.3561	1155.3485
Cs, F			447.39795	447.43203		
anion, F	427.78999	427.78488	−427.77292	427.79926	427.78738	427.78422
anion, Cl	1147.8831	1147.8747	1147.8684	1147.8885	1147.8804	1147.8773

[a] Hay−Wadt ECP, ref 9. [b] Ross ECP, ref 10.

For comparison with the experimental results in solution, we calculated fluorobenzene metalated at all three positions by all of the alkali metals and chlorobenzene metalated by lithium and cesium. Normal all-electron calculations were done for the lithium and sodium compounds. The para isomers are straightforward because of the symmetry axis through the carbon−metal bond and the substituent. The meta isomer does not have such symmetry, but the perturbation at the carbanion center is minimal. For example, the two Li−C−C_{ortho} angles are 122.58° and 122.52°. In the optimized structure of (o-fluorophenyl)lithium, the lithium is bent toward fluorine with r(Li−F) = 1.919 Å and a corresponding Li−C−C bond angle of 85.67°. This displacement of Li^+ toward the fluorine lone pairs is not unreasonable for an unsolvated gas phase species but would not be a reasonable model for a solution structure in which solvent is expected to compete more effectively for coordination to lithium than a fluorine substituent. Accordingly, the lithium was constrained to make an idealized angle of 120° with the adjacent carbon bearing the fluorine. Optimization yields a species that has an energy 4.1 kcal mol^{-1} above that of the fully optimized geometry. The C−F bond distance in the constrained species is significantly shorter (1.364 Å) than the corresponding distance in the fully optimized structure (1.421Å). Thus, the fully optimized structure appears to be on the way toward benzyne plus LiF. Only the corresponding constrained structure was considered for the o-chloro isomer.

The calculations provide values for the isodesmic equation (1), which can be expressed in an equivalent

$$Ar-H + M^+ = Ar^-M^+ + H^+ \qquad (1)$$

form as an ion pair acidity relative to benzene, eq 2. The energies for reaction 2 provide the desired substituent effects and are summarized in Table 2.

Table 2. Halogen Substituent Effects on Metalation Energies (−ΔE, kcal mol^{-1})

	fluorine			chlorine		
M	ortho	meta	para	ortho	meta	para
H	0	0	0	0	0	0
anion	12.12	7.45	4.81	13.50	9.85	8.36
Li	8.96	2.72	1.59	9.13	3.23	2.44
Na	9.90	3.19	1.74			
K	11.45	4.00	2.13			
K(ψ)	11.38	4.02	2.14			
Rb	11.75	4.19	2.21			
Cs(HW)[a]	12.04	4.41	2.32	12.92	5.37	4.01
Cs(R)[b]	11.38	4.03	2.11	12.62	4.87	3.60

[a,b] See footnotes to Table 1.

$$Ph^-M^+ + ArH = PhH + Ar^-M^+ \qquad (2)$$

Potassium was calculated both in a full all-electron computation and by explicit consideration of the valence electrons only using the effective core potential (ECP) of Hay and Wadt.[9] The energy of eq 1 is essentially the same by the two methods, −303.45 and −303.72 (ECP) kcal mol^{-1}. The substituent effects summarized in Table 2 are also quite similar by the two methods. This comparison provides a useful justification for the use of the ECP approximation in this type of application.[16] For rubidium, the ECP of Hay and Wadt was used but for cesium two methods were compared. The use of the Hay−Wadt ECP for cesium, Cs(HW) leads to a bond length for CsH that is too long, 2.75 Å compared to the experimental value of 2.494 Å. The ECP of Ross, Cs(R),[10] gives a better CsH bond length, 2.60 Å and comparable to that of a similar calculation by Lambert et al.,[17] 2.59 Å. The two methods give substantially different values for eq 1, −317.72 (Hay-Wadt) vs −310.72

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(16) For an authoritative review of pseudopotentials, see: *Pseudopotential Calculations of Transition Metal Compounds—Scope and Limitations*; Frenking, G., Antes, I., Böhme, M., Dapprich, S., Ehlers, A. W., Jonas, V., Neuhaus, A., Otto, M., Stegmann, R., Veldkamp, A., Vyboishchikov, S. F., Eds.; VCH: New York, 1995; Vol. 7.

Table 3. Multiple Substituent Effects, Dihalophenyls, kcal mol^{-1}

	anion				Li				Cs	
	F		Cl		F		Cl		F	
substr	calcd	found	calcd	found	calcd	found	calcd	found	calcd	found
2,5	19.57	19.37	23.35	22.53	11.68	11.65	12.36	11.88		
2,3	19.57	19.35	23.35	20.22	11.68	11.82	12.36	10.60		
3,4	12.26	11.84	18.21	16.27	4.31	4.14	5.67	5.16	6.71	6.51
2,6	24.24	24.24	27.00	26.03	17.92	17.89	18.62	17.21	24.05	23.76
2,4	16.93	16.79	21.86	20.99	10.55	10.51	11.57	11.03		
3,5	14.90	14.80	19.70	19.02	5.44	5.44	6.46	6.28		

Table 4. Calculated and Experimental Substituent Effects on the p*K* of Benzene

subst	expl[a]	Cs(H)	Cs(Er)
o-F	−5.2	−8.82	−8.34
m-F	−3.0	−3.23	−2.95
p-F	−1.4	−1.70	−1.54
o-Cl	−3.6	−9.47	−9.25
m-Cl	−2.4	−3.94	−3.57
p-Cl	−1.9	−2.94	−2.64

[a] From ref 1. The experimental results for Cl were scaled by 0.849 to convert from −20 to 25 °C.

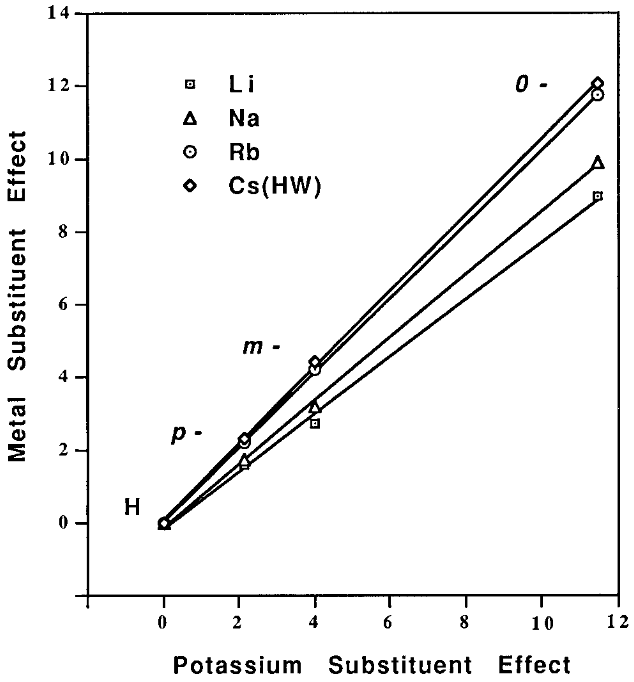

Figure 1. Substituent effects for Li, Na, Rb, and Cs (with Hay−Wadt ECP) compared with effects for potassium. Slopes are Li, 0.787; Na, 0.869; Rb, 1.025; and Cs, 1.048.

(Ross) kcal mol^{-1}. They also give significantly different substituent effects.

The calculated substituent effects in Table 2 lead to a number of systematics and correlations. The effects for each metal plotted against that for potassium give a series of straight lines with slopes increasing from Li to Cs(HW) (Figure 1). Potassium was chosen as the reference because both all-electron and ECP effects agree well. Cs(R) has effects virtually identical with those for K, and its slope of unity does not give this monotonic progression. The changing slopes are what one would expect for the classical electrostatic interaction of the C−F bond dipole with the increasing C−M dipole at the carbanion center. The effects at any one position give good straight line correlations with the reciprocal of the ionic radius of the metal. A glance at Table 2 shows that the free anion does not follow this correlation. The meta and para effects are relatively greater than the metal effects compared to the ortho effect. The difference perhaps is associated with the different rates of falloff with distance of charge−dipole and dipole−dipole interactions. Alternatively, the effectively enhanced stabilization of all of the (*o*-fluorophenyl)metals relative to the free ion may be indicative of electrostatic interaction between cation and fluorine lone pairs. Although the Cs(R) ECP gives a different correlation from Cs(HW), the differences are actually small and the use of Cs(R) should be satisfactory for most purposes.

In the previous work the assumed additivity of substituent effects was given a limited experimental test in the sense that the experimental points exceeded the number of parameters to be determined but only by a small number. Additional tests of such additivity were made computationally. The energies for difluoro- and dichlorophenyl anions, lithiums, and some cesiums are summarized in Table 1. The substituent effects are summarized in Table 3 in which the “calculated” effects, those obtained by summing the substituent effects of individual halogens, are compared with those “found” by complete calculation. The fluorine derivatives show generally excellent agreement with additivity. For phenyl anions the average deviation is 0.2 kcal mol^{-1}; for the (fluorophenyl)lithiums the effects are smaller in magnitude and the average deviation, 0.07 kcal mol^{-1}, is correspondingly also smaller. The effects for only two (difluorophenyl)cesiums were calculated, but they also show good agreement. Additivity, however, is far poorer for chlorine. The results in Table 3 show that each chlorine in the dichlorophenyl anions and lithiums is less stabilizing than chlorine in the monochloro analogues. This probably results from a mutual polarization that reduces the net inductive effect of each chlorine in polychloro compounds. Such polarization is less important for the less polarizable fluorines. This effect shows up particularly for the *o*-dichloro compounds; the added strain in such systems may also indicate the need for calculation beyond Hartree−Fock; that is, correlation corrections may be required in these cases.

The calculations are compared to experiment in Table 4. In the previous paper[1] the partial equilibrium p*K* constants for the fluorine substituents were deduced from experimental cesium ion pair p*K* values to be *o*-, 5.2, *m*-, 3.0, and *p*, 1.4. The meta and para values agree well with the energies in Table 2, expressed as p*K* values to be 3.25 and 1.71 (2.96 and 1.55 for Cs(R) ECP), respectively. For the arylcesium compounds with fluorine distant from the carbanionic center, the gas phase computation is an effective quantitative model for the solution thermodynamics. For the ortho substituent, however, the experimental value of 5.2 p*K* units is much

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less than the calculated value of 8.85 (8.37 for Cs(R)) p*K* units. For this case it seems likely that the ortho substituent interferes with the solvation of the cesium cation causing a reduced effect in solution. The environment around cesium for (*m*- and *p*-fluorophenyl)cesium is similar to that of the reference compound phenylcesium, but any ortho substituent could well have an effect of reducing access to cesium by solvent. The difference is about 4.5 kcal mol^{-1}. The experimental substituent effects for chlorine are all significantly lower than those calculated. Part of the difference for *o*-Cl is probably also a steric hindrance to solvation, but the differences for the meta and para positions probably result from the limitation for the more polarizable chlorine of evaluating individual substituent effects from results for polychlorinated systems. That is, as indicated by the calculations discussed above the summation of substituent effects for fluorine is a much better approximation than that for chlorine.

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Supporting Information Available: Cartesian coordinates for the results of the computations, (13 pages). This material is contained in libraries on microfiche, immediately follows this article in the microfilm version of the journal, can be ordered from the ACS; see any current masthead page for ordering information.

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