The Kinetic Acidity of Oligofluorobenzenes Correlated with Their Gas Phase Deprotonation Energies

Manfred Schlosser* and Elena Marzi[a]

Abstract: The relative reactivities of fluorobenzene, all di-, tri-, and tetrafluorobenzenes and pentafluorobenzene toward *sec*-butyllithium have been assessed in tetrahydrofuran at −100 °C. At this temperature no subsequent transmetalation reactions take place but those compromise the outcome of the competition experiments if the latter are conducted at −75 °C. The rates determined at −100 °C reflect the basicity differences between the naked (oligo)fluorophenyl anions to the extent of 10 %.

Keywords: (trans)metalation · gas-phase acidity · kinetics · linear free energy relationship · organometallic reactions

Introduction

The translation of structure into properties will remain an everlasting objective of chemistry. An even greater challenge is to quantify such connections. The most prominent examples in this fundamental area are linear free energy relationships between equilibria and rates.

The permutational hydrogen/metal interconversion is formally just a subcategory of acid/base reactions. However, as polar organometallic reagents can only survive in apolar, paraffinic or ethereal media, any heterolytic carbon–metal dissociation is unrealistic. As a consequence, the mechanistic details of their chemical transformations are of unprecedented complexity.[1]

The aim of our continuing endeavors is to make absolute and relative rates of metalation (i.e., hydrogen/metal permutation) reactions predictable. Key reference data are in this context the experimental or computational gas-phase acidities of the *CH* acids from which the organometallic reagents or the metalation products are derived. When measuring the relative rates with which the metalation of oligochlorobenzenes by *sec*-butyllithium proceeds in tetrahydrofuran at −100 °C, we discovered an unexpected parallelism. The differences between the free energies of activation exhibited a linear relationship with the gas-phase deprotonation energies of the chloroarenes undergoing metalation, the correlation coefficient being 0.12 (Figure 1).[2] Simplified this means, the transition state of the reaction is endowed with 12 % of carbanion character.

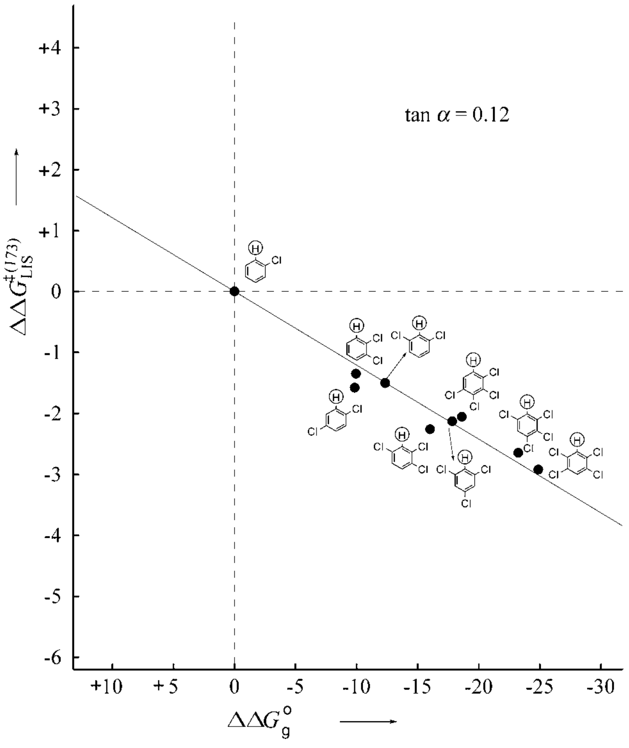

Figure 1. Deprotonation of mono-, di-, tri-, tetra-, and pentachlorobenzene(s): relative free activation energies of metalation $\Delta\Delta G^{\ddagger(173)}_{\mathrm{LIS}}$ by *sec*-butyllithium in tetrahydrofuran at −100 °C versus differential equilibrium acidities $\Delta\Delta G^{o}_{g}$ in the gas phase.

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[a] Prof. Dr. M. Schlosser, Dr. E. Marzi
Institute for Chemical Sciences and Engineering
Ecole Polytechnique Fédérale (EPFL, BCh)
1015 Lausanne (Switzerland)
Fax: (+41) 21-6939365
E-mail: manfred.schlosser@epfl.ch

DOI: 10.1002/chem.200401094

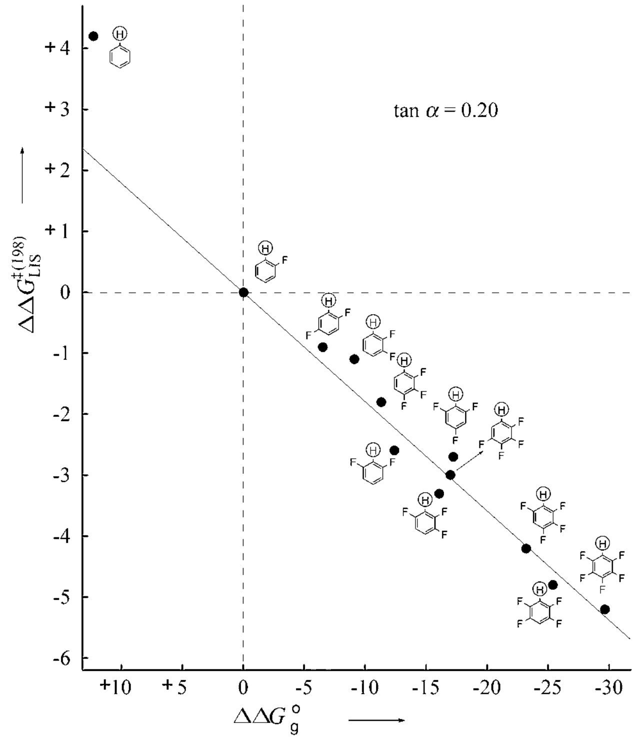
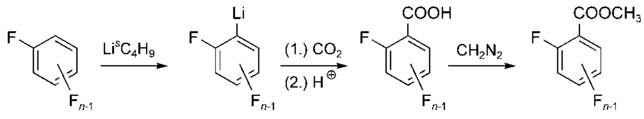


Figure 2. Deprotonation of mono-, di-, tri-, tetra-, and pentafluorobenzene(s): relative free activation energies of metalation $\Delta\Delta G^{\ddagger(198)}_{\mathrm{LIS}}$ by *sec*-butyllithium in tetrahydrofuran at −75 °C versus differential equilibrium acidities $\Delta\Delta G^{\circ}_{\mathrm{g}}$ in the gas phase.

When analyzing retrospectively similar data previously collected in the fluoroarene series[3] at −75 °C, we again came across a linear free energy relationship. However, this time the differences in the activation energies averaged one fifth of the relative gas-phase acidities. In other words, the carbanion character of the pertinent transition state appeared to have grown to 20 % (Figure 2).

Results and Discussion

To find out whether the marked selectivity difference in the chloro and fluoro series was caused by an element or temperature effect, we repeated the competition experiments with the (oligo)fluorobenzenes in tetrahydrofuran at −100 °C, that is under exactly the same reaction conditions as previously applied to the (oligo)chlorobenzenes. As in the related earlier work,[2,3] the relative rates were assessed by competition experiments. Two substrates exhibiting comparable reactivity were mixed and treated conjointly with an insufficient amount of *sec*-butyllithium. After 45 min at −100 °C, the mixture was poured on an excess of freshly crushed dry ice. After having determined the concentration of the unconsumed (oligo)fluorobenzenes in the organic layer, the carboxylates were extracted into the aqueous phase. After neutralization, the fluorinated benzoic acids were converted with diazomethane into the corresponding methyl esters (Scheme 1), which were quantified again by gas chromatography.



Scheme 1.

Once again a linear relationship between the differential free activation energies $\Delta\Delta G^{\ddagger}_{\mathrm{LIS}}$ and the corresponding relative deprotonation energies $\Delta\Delta G^{\circ}_{\mathrm{g}}$ in the gas phase was observed. However, this time the sensitivity slope and, as a corollary, the carbanion character of the haloarene at the transition state amounted to only 0.10 (Figure 3) and thus came close to the number derived for the chloro family.

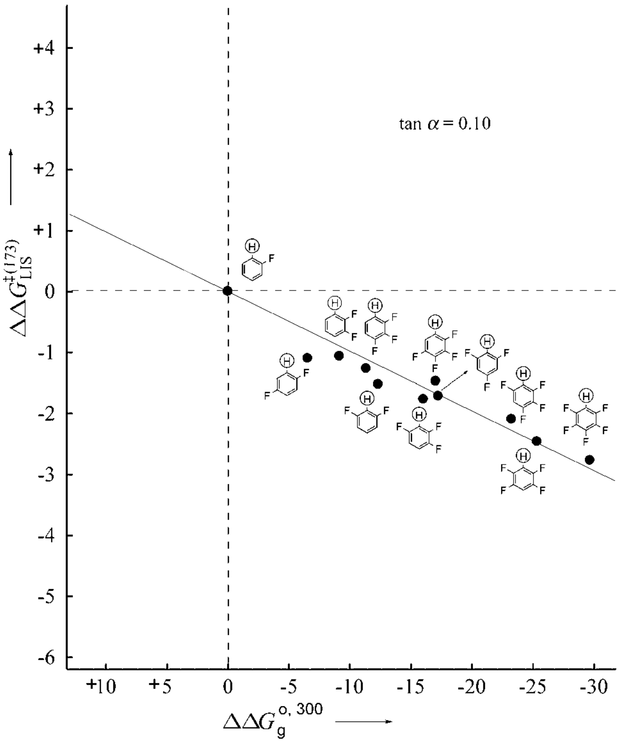


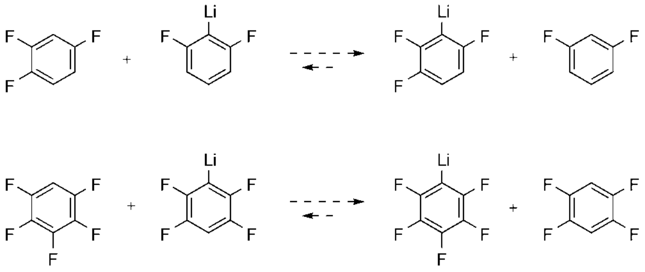
Figure 3. Deprotonation of mono-, di-, tri-, tetra-, and pentafluorobenzene(s): relative free activation energies of metalation $\Delta\Delta G^{\ddagger(173)}_{\mathrm{LIS}}$ by *sec*-butyllithium in tetrahydrofuran at −100 °C versus differential equilibrium acidities $\Delta\Delta G^{\circ}_{\mathrm{g}}$ in the gas phase.

How can we rationalize this conspicuous temperature dependence? Common wisdom would expect a decrease in reactivity and an increase in selectivity when the reaction temperature is lowered. It is true, exceptions are documented. This holds in particular for organometallic chemistry where aggregation and ionization phenomena may override standard behavior.[1] The sodium-promoted polymerization of styrene represents the most striking example. Upon cooling, the process becomes faster and faster as progressively the proportion of the thousandfold more reactive solvent-separated ion pairs grows at the expense of the relatively inert contact species.[4,5]

It would be unrealistic to assume ionization of simple alkyllithium compounds in ethereal solvents. In contrast, a temperature effect on the population of coexisting aggregation states is conceivable. The composition of the prevalent ground state species of *sec*-butyllithium or isopropyllithium in tetrahydrofuran is unknown. According to the work of Bartlett et al.,[6] the reagent conserves its tetrameric structure when stoichiometric amounts of dimethyl ether, diethyl etherm, or tetrahydrofuran are added to its solution in heptanes at −25 °C. Therefore, it might be tetrameric or at least dimeric in neat tetrahydrofuran at −75 °C. Lower temperatures favor deaggregation;[1] it forms a 9:1 monomer/dimer mixture at −108 °C and a 4:1 mixture at −96 °C.[7] If really two different organometallic species were to promote the metalation reaction at the different temperatures, differences in the discrimination between substrates would become intelligible.

To test this hypothesis, we replaced *sec*-butyllithium by *tert*-butyllithium which is monomeric[7] in tetrahydrofuran even at −75 °C. Although this time there was no ambiguity about the nature of the kinetically competent reagent species, the outcome of the competition experiments still proved temperature-dependent. The substrate pairs 1,2,3-trifluorobenzene/1,4-difluorobenzene, 1,3,5-trifluorobenzene/1,3-difluorobenzene, and 1,2,4-trifluorobenzene/1,3-difluorobenzene produced higher rate ratios at −75 °C than at −100 °C (3.4, 3.2, and 3.3 versus 2.1, 2.0, and 2.2, respectively).

At this point we began to suspect that we were confronted with artifacts as far as the numbers collected at −75 °C were concerned. When we carried out the earlier study,[3] we did of course not fail to probe the constancy of the determined relative rates as a function of the reaction time. We had exposed 1,2-difluorobenzene to the action of 2-fluorophenyllithium during 0.5, 2, and 6 h and found virtually no changes due to transmetalation. The reaction between the 1,4-isomer and 2-fluorophenyllithium was also found to be negligibly slow (< 5 % after 2 h). As we realized now, we had looked at the wrong end of the acidity scale. When mixtures of 1,2,4-trifluorobenzene and 2,6-difluorophenyllithium and of pentafluorobenzene and 2,3,5,6-tetrafluorophenyllithium were kept 2 h at −75 °C, 36 % and 58 % of the initially present aryllithium was detected to be converted into the transmetalation products 2,3,6-trifluorophenyllithium and pentafluorophenyllithium, respectively (Scheme 2). Even if these proportions are still far away from the acid–base equilibria, the observed drift towards the least basic components seriously distorts the true kinetic ratios and makes the results worthless. On the other hand, the data at −100 °C are not at all compromised by side reactions or subsequent transformations. The ratios assessed by competition experiments at −100 °C proved to be absolutely time-invariant.



Scheme 2.

A last comment refers to the kinetic acidity of benzene. As it was found to be totally inert toward *sec*-butyllithium at −100 °C, there was no way to juxtapose it with fluorobenzene or congeners in this respect. But also its relative rate monitored at −75 °C[3] has to be considered with utmost caution. The pertinent kinetic measurements encompass several arenic substrates exhibiting diverging reactivities throughout. This means an accumulation of potentially large errors was inevitable and this makes the result doubtful. For example, if the relative benzene reactivity does not fit into a given rate/basicity correlation this may just have to be imputed to this experimental uncertainty. Alternatively, the discrepancy may be resolved by renouncing the straight line, the crucial criterium of any linear free energy relationship, as an overidealization, holding at best within the boundaries of a narrow structural segment, and to replace it by a parabolic curvature which should more accurately mirror rate/stability comparisons when the transition state of a series of analogous reactions moves from reactant-like to product-like or, in the present case, to intermediate-like.

Anyhow, the lasting uncertainties about the benzene relative rates would invalidate any attempt to base far-reaching conclusions on such findings. To provide reliable information on the reactivity of benzene toward simple alkyllithium compounds, one has to resort to more sophisticated methods such as the isotope dilution technique.[8]

Experimental Section

Generalities: Abbreviations and laboratory routines have been explained in previous publications from this laboratory.[9–12] The stationary phases of the gas chromatography columns used in the present work are encoded as BGB-2.5 (= 2.5 % of diphenylpolysiloxane and 97.5 % of dimethylpolysiloxane), Bentone (= 50 % of dimethyloctadecylammonium bentonite and 50 % of didecylphthalate), DB-1701 (= 14 % of cyanopropylphenylpolysiloxane + 86 % of dimethylpolysiloxane); DB-FFAP (= polyethylene glycol) and DB-WAX (= acid modified polyethylene glycol).

Starting materials and authentic compounds for comparison: Fluorobenzene, and di-, tri-, and tetrafluorobenzenes and pentafluorobenzene are all commercial (Apollo Scient., Stockport, UK-SK62QR). 2-Fluorobenzoic acid[13] (m.p. 122–124 °C), 2,3-,[14] 2,4-,[15] and 2,6-difluorobenzoic acids (m.p. 159–161 °C, 132–134 °C and 158–160 °C, respectively),[16] 2,3,4-,[17] 2,3,6-,[18] and 2,4,6-trifluorobenzoic acid (m.p. 115–117 °C, 126–127 °C and 141–142 °C, respectively),[19] 2,3,4,5-,[20] 2,3,4,6-,[21] and 2,3,5,6-tetrafluorobenzoic acid (m.p. 87–89 °C, 101–103 °C and 151–153 °C, respectively),[22] and pentafluorobenzoic acid[23] (m.p. 105–106 °C) are well documented in the literature as are their methyl esters. 2-Chloro-1,3-trifluorobenzene,[24] 2-chloro-1,4-difluorobenzene,[25] 2-chloro-1,3,4-trifluorobenzene,[26] 3-chloro-1,2,4,5-tetrafluorobenzene,[27] and chloropentafluorobenzene[28] are also known compounds.

Table 1. Reaction between oligofluorobenzenes and *sec*-butyllithium in tetrahydrofuran at −100 °C: relative rates k_A/k_B calculated from the amounts (in mmol) of the substrates A and B present before and after the reaction.[a]

A[b]	B[b]	$[A]_0$[c]	$[B]_0$[c]	$[A]_t$[c]	$[B]_t$[c]	$[A]_p$[d]	$[B]_p$[d]	k_A/k_B[e]
1,3-Cl$_2$	F$_1$	5.00	5.04	0.66	4.17	0.89	4.39	10.7
1,2-	1,3-Cl$_2$	5.06	5.01	2.16	3.20	2.25	3.36	1.9
1,3-	1,3-Cl$_2$	5.05	5.00	0.87	3.94	1.20	4.14	7.4
1,4-	1,3-Cl$_2$	5.05	5.02	1.84	3.17	2.21	3.28	2.2
1,3-	1,2-	5.01	4.99	1.61	3.39	1.80	3.38	2.9
1,4-	1,2-	4.95	4.97	2.35	2.33	2.43	2.47	1.0
1,3-	1,4-	5.03	4.96	1.39	3.45	1.47	3.77	3.5
1,2,3-	1,2-	5.01	4.99	1.83	2.89	2.12	3.18	1.8
1,2,4-	1,2-	5.02	5.01	0.91	4.04	1.06	4.10	7.9
1,3,5-	1,2-	4.95	5.00	1.46	4.19	1.49	4.15	6.9
1,3-	1,2,3-	4.94	5.02	1.84	3.08	1.97	3.13	2.0
1,3-	1,2,3,4-	5.02	5.01	2.32	2.54	2.51	2.74	1.1
1,2,4-	1,3-	5.04	4.98	2.15	2.97	2.32	2.87	2.0
1,3,5-	1,3-	5.06	5.00	2.13	2.93	2.21	2.68	1.6
1,2,3-	1,4-	4.95	4.94	1.77	2.70	1.96	2.84	1.7
1,2,4-	1,4-	5.00	5.03	0.68	3.87	0.74	4.20	7.6
1,3,5-	1,4-	5.00	4.98	1.24	4.07	1.40	4.30	6.9
1,2,4-	1,2,3-	5.00	4.99	1.15	3.79	1.39	3.85	5.3
1,3,5-	1,2,3-	5.02	5.04	1.57	3.99	1.77	3.93	5.0
1,2,4-	1,3,5-	4.97	4.95	2.36	2.67	2.44	2.28	1.2
1,2,3,4-	1,2-	4.99	5.02	1.43	3.61	1.49	3.61	3.8
1,2,3,4-	1,2,3-	5.03	4.97	1.13	2.82	1.88	3.10	2.1
1,2,4-	1,2,3,4-	4.99	5.02	1.41	3.71	1.30	3.70	4.2
1,2,3,5-	1,2,4-	4.96	5.01	1.62	3.25	1.94	3.52	2.6
1,2,4,5-	1,2,4-	5.04	5.03	0.93	4.01	0.95	4.16	7.5
1,3,5-	1,2,3,4-	5.06	5.02	1.35	3.76	1.51	3.89	4.6
1,2,3,5-	1,3,5-	5.02	5.04	1.48	3.37	1.34	3.24	3.0
1,2,4,5-	1,3,5-	4.99	4.99	0.95	4.11	1.14	4.14	8.5
1,2,3,5-	1,2,3,4-	4.99	5.01	1.14	4.01	1.13	4.09	7.3
1,2,4,5-	1,2,3,5-	5.04	5.07	1.66	3.31	1.57	3.49	2.6
F$_5$	1,2,3,5-	5.00	5.00	0.93	3.90	1.16	4.02	6.8
F$_5$	1,2,4,5-	5.06	5.01	1.91	3.56	1.64	3.52	2.9

[a] $[A]_p$ and $[B]_p$ obtained by subtracting the amount of A- and B-derived methyl benzoate (determined by gas chromatography; see text) from the initial quantities $[A]_o$ and $[B]_o$, ideally identical with $[A]_t$ and $[B]_t$. [b] 1,3-Cl$_2$ = 1,3-dichlorobenzene; F$_1$ = fluorobenzene; F$_5$ = pentafluorobenzene; 1,2 = 1,2-difluorobenzene; 1,2,3- = 1,2,3-trifluorobenzene; and so on. [c] $[A]_o$, $[B]_o$ and $[A]_t$, $[B]_t$ are the amounts before and after the reaction with *sec*-butyllithium. [d] $[A]_p$ and $[B]_p$ are calculated by subtracting the amount of products (methyl benzoates) formed after consecutive treatment of the substrate pairs A and B with *sec*-butyllithium, carbon dioxide, acid and diazomethane from the initial amounts $[A]_o$ and $[B]_o$. [e] Average error found by repetitive experiments: 3–10 %.

Transmetalation experiments: 1,3-Difluorobenzene (1.0 mL, 1.1 g, 10 mmol) was mixed with a solution of *sec*-butyllithium (10 mmol) in tetrahydrofuran (14 mL) and hexanes (6 mL) cooled in a dry ice/methanol bath. After 15 min at −75 °C, 1,2,4-trifluorobenzene (1.0 mL, 1.3 g, 10 mmol) and chlorobenzene (5.1 mL, 5.6 g, 5.0 mmol) were added. Samples (ca. 1 mL) were withdrawn after 2, 5, 15, 45, and 180 min and were treated with 1,1,2-trichloro-1,2,2-trifluoroethane (2.4 mL, 3.7 g, 2.0 mmol) and then analyzed by gas chromatography (60 m, BGB-2.5, 30 min 60 °C, 10 min 200 °C [20 °C min−1]) using 2-chloro-1,3-difluorobenzene and 2-chloro-1,3,4-trifluorobenzene as authentic reference compounds and chlorobenzene as an internal standard for quantification of the peak areas. An analogous experiment was carried out starting from 1,2,4,5-tetrafluorobenzene which was allowed to react with pentafluorobenzene.

Competition experiments: Pairs of substrates A and B (ca. 5 mmol each) and the "internal standard" cumene (reference compound for quantification; ca. 1 mmol) were dissolved in tetrahydrofuran (10 mL) and cooled to −100 °C. This mixture was analyzed by gas chromatography (2 m, 10 % Bentone, 50 °C (15 min)→140 °C (40 min; heating rate 10 °C min^{-1}); 60 m BGB-2.5, 60 °C (30 min)→200 °C (20 min; heating rate 30 °C min^{-1})). *sec*-Butyllithium (5.0 mmol) in cyclopentane (3.5 mL) was added. After 45 min at −100 °C, the mixture was poured on freshly crushed dry ice. Once the excess of carbon dioxide had been slowly evaporated, a 1.0 M aqueous solution (10 mL) of sodium hydroxide and, as a second "internal standard", benzoic acid (1.0 mmol) were added. The unconsumed substrates A and B together with the cumene standard were extracted with diethyl ether (3 × 10 mL) and their concentrations were determined by gas chromatography (conditions: see above). The aqueous phase was acidified to pH 1 and extracted also with diethyl ether (3 × 10 mL). The combined organic layers were treated with ethereal diazomethane until the yellow color persisted. The relative concentrations of the methyl esters were again probed by gas chromatography (30 m, DB-1701, 70 °C; 30 m, DB-FFAP, 75 °C; 30 m, DB-WAX, 90 °C).

The relative rates k_A/k_B (see Table 1) were calculated by inserting the concentrations of the substrates A and B, before and after the reaction with *sec*-butyllithium ($[A]_0$, $[B]_0$ and $[A]_t$, $[B]_t$, respectively), into the familiar logarithmic expression.[29,30]

The yields of the A- and B-derived products (fluorinated methyl benzoates) were also determined by gas chromatographic comparison of their peak areas with that of a suitable standard (methyl benzoate) corrected by independently established calibration factors. These data were merely used to check on the internal consistency of the results collected, the detected quantities of acids (or their methyl esters) ideally equalizing the difference between initially present and afterwards unconsumed substrates ($[A]_p = [A]_0 - [A]_t$; $[B]_p = [B]_0 - [B]_t$).

As follows from Table 1 and Figure 4, the above measurements by competition kinetics are redundant. More rate ratios were collected than necessary for the extraction of all relative reactivities. This allows one to check on the reliability of the numbers and, at the same time, to make them more compatible with each other by averaging them. Figure 5 illustrates how we proceeded. Each of eight congeners was juxtaposed to three congeners having one fluorine atom more or less (e. g., fluorobenzene to 1,2-, 1,3-, and 1,4-difluorobenzene, or 1,2,4,5-tetrafluorobenzene to 1,2,3-, 1,2,4-, and 1,3,5-trifluorobenzene). This gives six possible combinations for which relative rate data can be made available. The experimentally determined numbers were now modified until a single and internally consistent set of three k_{rel} values was obtained. In general, the harmonization of the experimental data required only minor modifications. Whenever the changes exceeded 25 %, this is indicated (see Figure 5). Such strong deviations are mostly associated with 1,2-difluorobenzene, 1,2,3-trifluorobenzene, and 1,2,3,4-tetrafluorobenzene. There are several possible explanations for this. Such substrates are far less reactive than those having the deprotonation site flanked by two fluorine atoms. Competition experiments involving two such classes of substrates can be realized only with difficulty if at all. Therefore, the assessment of relative rates has often to rely on indirect comparisons which entail a summing up of errors. For example, the reactivity of pentafluorobenzene relative to 1,2,3,4-tetrafluorobenzene

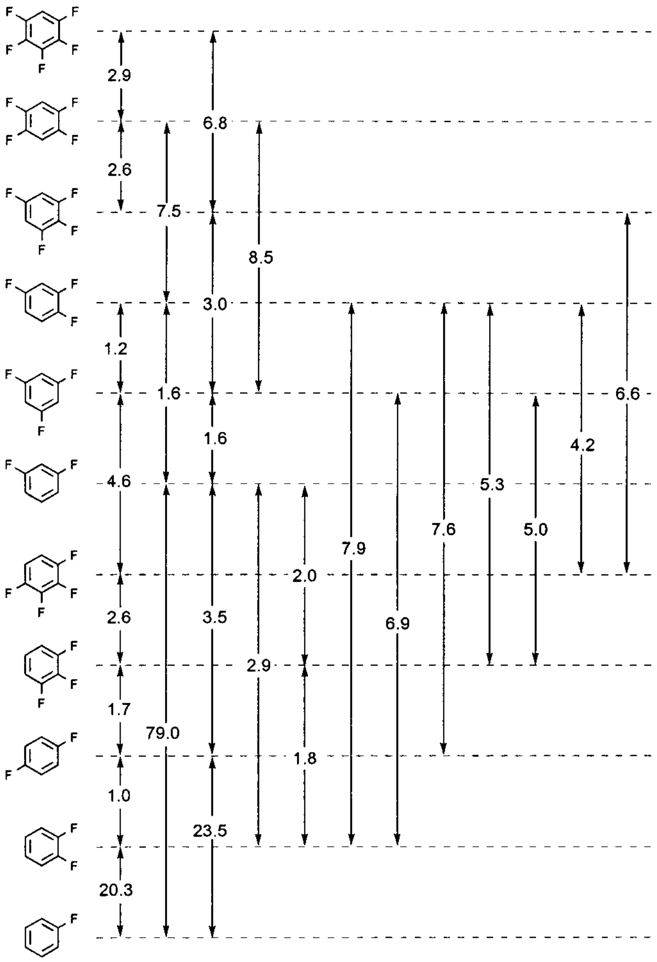


Figure 4. Reaction between oligofluorobenzenes and *sec*-butyllithium in tetrahydrofuran at −100 °C: schematized overview of the tested combinations of substrates A and B and the resulting relative rates k_A/k_B.

Table 2. Reaction of oligofluorobenzenes with *sec*-butyllithium in tetrahydrofuran at −100 °C: rates relative to fluorobenzene.

Substrate[a]	k^{rel}_{173} [b]	$\Delta\Delta G^{\ddagger}_{173}$ [c]
F_1	1.0×100	0.00
1,2-	2.2×101	1.06
1,3-	8.0×101	1.51
1,4-	2.4×101	1.09
1,2,3-	3.1×101	1.18
1,2,4-	1.6×102	1.75
1,3,5-	1.5×102	1.72
1,2,3,4-	4.0×101	1.27
1,2,3,5-	4.5×102	2.10
1,2,4,5-	1.3×103	2.47
F_5	3.2×103	2.78

[a] F_1 means fluorobenzene, F_5 pentafluorobenzene, 1,4- stands for 1,4-difluorobenzene, 1,2,3- for 1,2,3-trifluorobenzene, and so on. [b] Relative rates averaged according to Figure 5. [c] $\Delta\Delta G^{\ddagger}_{173} = 0.7923 \times \lg k^{\mathrm{rel}}_{173}$.

amounts to 94 or 91 if one calculates it using 1,3,5-trifluorobenzene and 1,2,4,5-tetrafluorobenzene or 1,2,4-trifluorobenzene and 1,2,4,5-tetrafluorobenzene as relay compounds (both times 81 if averaged numbers are used). In such cases the numbers are marked by an asterisk.

The reproducibility and internal consistency of the values derived is amazingly good. The biggest deviation from the averaged values was encountered with 1,2,3-trifluorobenzene and 1,2,3,4-tetrafluorobenzene.

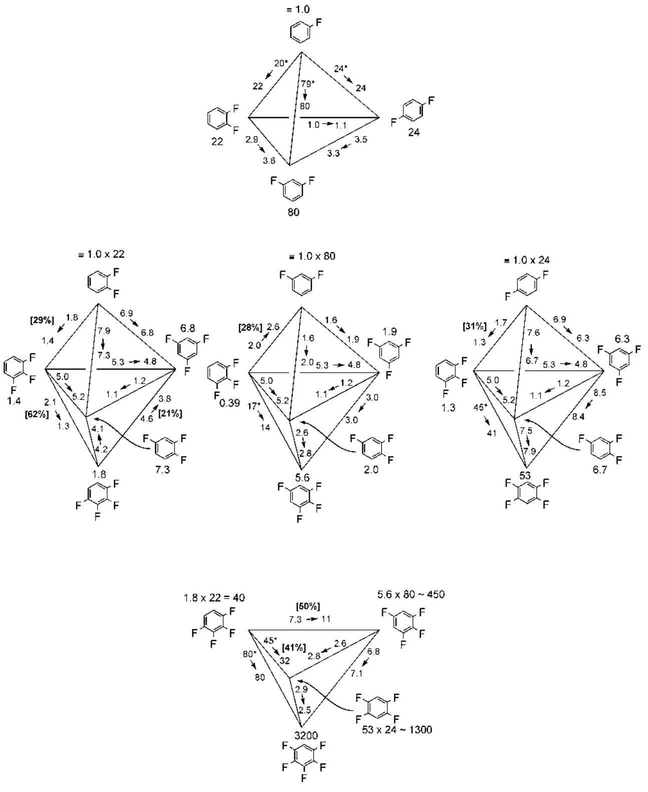


Figure 5. Averaging of relative rates by the "pyramid approach".

The reactions of these substrates are relatively slow and unclean. The vicinal proximity of halogen atoms may trigger single electron-transfer-promoted defluorination as an uncontrolled side reaction. Moreover, these compounds are particularly volatile and hence their quantitative recovery is difficult. For example, the mass balance of the 1,2,3,4-tetrafluorobenzene/1,2,3-trifluorobenzene competition experiment is poor if the $[A]_t$ and $[B]_t$ numbers are considered (totaling 3.95 rather than 5.0), but satisfactory if the $[A]_p$ and $[B]_p$ data (totaling 4.98) are used for the k_A/k_B calculation.

The relative rates used to construct Figure 3 are listed in Table 2. They cover a range of more than three powers of ten.

Acknowledgements

This work has been supported by the Schweizerische Nationalfonds zur Förderung der wissenschaftlichen Forschung, Bern (grants 20–63′584–00 and 20–100′336–02).

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Received: October 28, 2004